Thermal *cis*-to-*trans* isomerization mechanism of N-(phenylazo)-substituted nitrogen heterocycles

by

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Abstract

Triazenes, compounds containing a diazoamino moiety (–N(1)=N(2)–N(3)<), are known for their reversible *cis-trans* isomerization character and hence, have the potential to be used in photoswitchable devices and photostorage media. However, little is known about their *cis-trans* isomerization mechanism. In this thesis, kinetic studies on the thermal *cis*-to-*trans* isomerization of N-(phenylazo)-substituted nitrogen heterocycles are presented. It is shown that the isomerization rate constant increases as the size and electron-donating character of the cyclic amine increases, as the electron-withdrawing character of the *para* substituent group on the phenyl ring increases, and as the polarity of the solvent increases. All these trends are interpreted in terms of a rotational isomerization mechanism involving a dipolar transition state. In addition, photolytic cleavage of the N(2)–N(3) bond of target substrates is shown to be affected as well by the size and electronic character of the cyclic amine, the electronic character of the phenyl ring substituent, and the polarity of the solvent, with the result that the photolysis yield increases as the isomerization rate decreases.

Theoretical calculations on target substrates both in the gas phase and various solvents were also performed based on DFT-B3LYP/6-31+G* method. Overall, the *cis*-to-*trans* isomerization is predicted to take place through rotation around the N(1)=N(2) bond. Furthermore, the calculated energy barriers are found to be influenced by the size and electronic character of the cyclic amine, the electronic character of the phenyl ring substituent, and the polarity of the solvent, consistent with the effects obtained experimentally from the kinetic studies.

Acknowledgements

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I also thank Kelvin Lau, for having prepared some of the target substrates, and my friends and my lab mates (from past and present) for their friendship and assistance. All the shared time with them together made my study more enjoyable.

Last but not least, I sincerely thank my dad and mom, for all their support, encouragement and love. Without them, I could never complete my studies.

This thesis is dedicated to my dearest and beloved parents.

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List of Abbreviations, Acronyms, and Symbols

A	absorbance
A-1	acid-catalyzed unimolecular nucleophilic substitution
app.	apparent
A-S_E2	acid-catalyzed bimolecular electrophilic substitution
br	broad band (NMR)
$\Delta G^{\ddagger}$	activation free energy
δ	chemical shift
d	doublet (NMR)
DFT	density functional theory
DMF	dimethylformamide
DMSO	dimethylsulfoxide
EI	electron impact (mass spectrometry)
f_{oc}	electron density of occupied orbital
HF	Hartree Fock
HRMS	high resolution mass spectrometry
Hz	hertz
IUPAC	international union of pure and applied chemistry
J	coupling constant (NMR)
k_{obs}	observed rate constant
λ_{oc}	energy level of occupied orbital

m	*meta*
m	multiplet (NMR)
mp	melting point
MS	mass spectrometry
NMR	nuclear magnetic resonance
p	*para*
pH	negative logarithm of hydronium ion activity
ρ	Hammett reaction constant
ρ_{oc}	reactivity index
σ	Hammett substituent constant
rel.	relative
RHO	reactive hybrid orbital
s	singlet (NMR)
t	triplet (NMR); time
Tc	coalescence temperature
THF	tetrahydrofuran
UV	ultraviolet

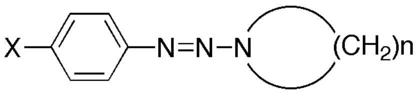
1 Introduction

Triazene and its derivatives are compounds containing the −N=N−N< (diazoamino) moiety, in all of which the three nitrogen atoms are numbered as shown in Scheme 1-1. According to the IUPAC system of nomenclature, triazenes can also be named as diazoamino compounds.[1a]

R−N(1)=N(2)−N(3)R'R"

Scheme 1-1. General structure of triazenes

Triazenes are generally classified into three types depending on the number of substituents at the terminal nitrogen atoms of the diazoamino moiety: 1-monosubstituted triazenes, 1,3-disubstituted triazenes and 1,3,3-trisubstituted triazenes.[1a] In the latter case, triazenes may be 1-substituted by a phenyl ring and 3,3-disubstituted by a cyclic amine. For instance, the compound in Scheme 1-2 with X = CH_3 and n = 4 would be named N-(*p*-methylphenylazo)pyrrolidine. In fact, N-(phenylazo)-substituted nitrogen heterocycles represented in Scheme 1-2 are the target substrates of the study presented in this thesis.



Scheme 1-2. General structure of target substrates

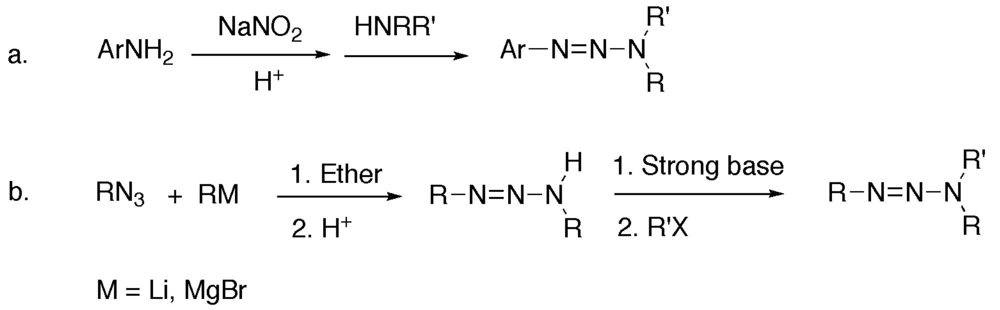
1.1 Applications of triazenes

Triazenes are of utility in many fields such as in organic synthesis and medicinal chemistry, and as laser ablation substrates. In organic synthesis, triazenes can act as excellent protecting groups for amines, due to their resistance to oxidants, reductants, alkylating reagents, and strong bases.[2,3] Triazenes can also be used to synthesize nitrogen heterocycles.[3] In medicinal chemistry, a promising application of l-aryl-3,3-dialkyl-triazenes lies on their anticancer abilities.[1b,3,4] Alkyl diazonium ions, generated by enzyme-catalyzed decomposition of triazenes, can alkylate the DNA of cancer cells, leading to their death. Thus, over the past decades, many anticancer compounds containing the triazene moiety have been synthesized and studied.[1b,3,4] Another application of triazenes, based on their photolytic character, is in laser ablation lithography, a widely used technology for microstructuring designed polymers.[5-9] Polymers which are doped with triazenes can be sensitized to achieve ablation at irradiation wavelengths where the polymers have no absorbance;[5,10] photodecomposition of triazenes leads to the release of nitrogen gas causing an instant volume and pressure increase on the polymer, resulting in its structure ablation.

Polymers doped with diazoamino compounds could have the potential as well to be used as high-density optical memory and molecular switching materials, as those doped with diazo compounds, based on light-induced photoisomerism around the nitrogen–nitrogen double bond.[11-14] Upon photoexcitation, a *trans* azo group can isomerize to its *cis* form. The reverse process can take place under thermal conditions or irradiation. *Trans-cis* isomerizations can lead to changes in absorption spectra, dipole moments, molecular orientation, refraction index, and spatial volumes.[12] By controlling the reversible isomerization process and measuring optical changes, the “WRITE” and “READ” processes in memory materials can be realized. A polymer film doped with azo compounds is homogeneous and optically isotropic, but upon linearly polarized laser beam irradiation, optical anisotropy is induced due to molecular reorientation resulting from *trans*-to-*cis* isomerization of the azo molecules in the direction perpendicular to the polarization of the laser beam.[15] This *trans*-to-*cis* isomerization and reorientation of the azo molecules will proceed until the dipole moment of all the azo molecules lies perpendicular to the direction of polarization of the laser beam, causing birefringence in the film structure. The “WRITE” process can be realized by keeping the polarized laser beam on, which induces and maintains the *trans*-to-*cis* photoisomerization. The “READ” process is realized by detecting the change in birefringence pattern, and the “ERASE” process is realized by heating or overwriting with resonant circularly polarized light, conditions under which the *cis* forms isomerize to *trans*.[12] To better exploit *cis-trans* photoisomerable materials and improve their performance, a thorough understanding of the isomerization mechanism is needed. Triazenes are known for their reversible photoisomerization character;[16-18] however, little is known about their *cis-trans* isomerization mechanism. The mechanism for thermal *cis*-to-*trans* isomerization of N-(phenylazo)-substituted nitrogen heterocycles is the focus of the studies presented in this thesis.

1.2 Synthesis of triazenes

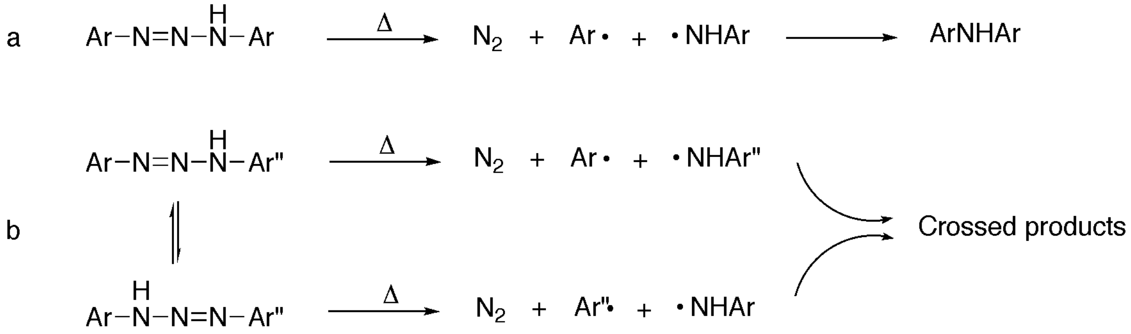
Triazenes are commonly synthesized from either anilines or alkyl azides.[3,19,20] Aryl triazenes are usually synthesized by coupling primary or secondary amines with aryl diazonium ions, which are obtained by diazotization of anilines with sodium nitrite and acids (Scheme 1-3a).[3,19,21] Alkyl diazonium ions are much more unstable than aryl diazonium ions and readily lose nitrogen to form a carbocation,[22] thus di- and trialkyltriazenes are commonly obtained from the reaction of alkyl azides with Grignard or alkyl lithium reagents (Scheme 1-3b).[3,19,20,23] As shown in Scheme 1-3, trisubstituted triazenes can be prepared from either coupling of diazonium ions with secondary amines or alkylation of disubstituted triazenes. The target compounds in this study, N-(phenylazo)-substituted nitrogen heterocycles, are usually synthesized by coupling aryl diazonium ions with the appropriate cyclic amine.[24-27]



Scheme 1-3. Synthetic methods for preparation of triazenes

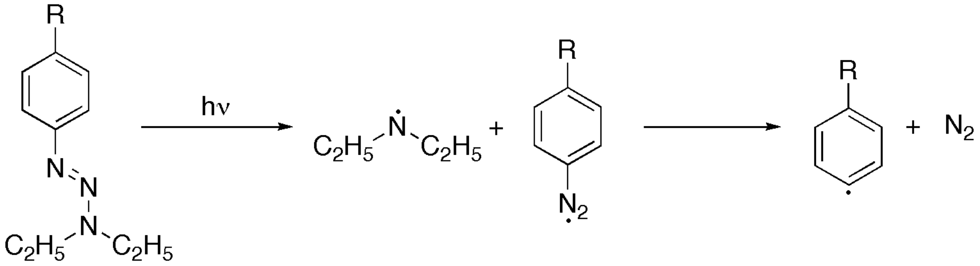
1.3 Stability of triazenes

In order to develop applications based on the use of triazenes as laser ablation substrates, switching materials, and optical storage media, knowledge of the stability of triazenes under different conditions is fundamental. Triazenes are found to be sensitive to heat, light, and acids, under which decomposition can happen easily. The thermostability of symmetrical and unsymmetrical 1,3-diphenyltriazenes in aromatic solvents was studied by Hardie and Thomson as early as 1958, showing that radicals and nitrogen are produced via a homolytic mechanism when samples are heated at around 150-160 °C. Because of tautomerization, crossed products are obtained in the case of unsymmetrical triazenes (Scheme 1-4).[28]



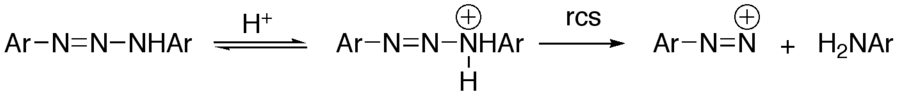
Scheme 1-4. Thermal decomposition of symmetrical and unsymmetrical diphenyltriazenes

Triazenes can also decompose and release nitrogen by UV illumination. A high energy photon from a laser may cause the bond between the diazo and amino groups of 1-aryl-3,3-diethyltriazenes to break (Scheme 1-5).[10] The quantum yield and rate constant for photolysis are strongly influenced by substitution at the phenyl ring, increasing with a decrease in the electron-withdrawing character of the substituent group in the *para* position of the phenyl ring.[10] This dependency can be explained by the substituent effect on the 1,3-dipolar resonance form of triazenes, a topic that will be discussed in Section 1.4.



Scheme 1-5. Photolysis of 1-aryl-3,3-diethyltriazenes

Protonation of N(3) of triazenes is very important to the stability of triazenes in aqueous solutions. Generally, there are two mechanisms for acid-catalyzed decomposition of triazenes in aqueous media: specific acid catalysis (A1) and general acid catalysis (A-S_E2).[27,29,30] For example, the acid-catalyzed decomposition of trialkyltriazenes in aqueous solution is proposed to follow an A1 mechanism.[31] This mechanism shows protonation at N(3) takes place in a rapid pre-equilibrium, and slow decomposition to a diazonium ion and aniline is the rate-limiting step (Scheme 1-6).



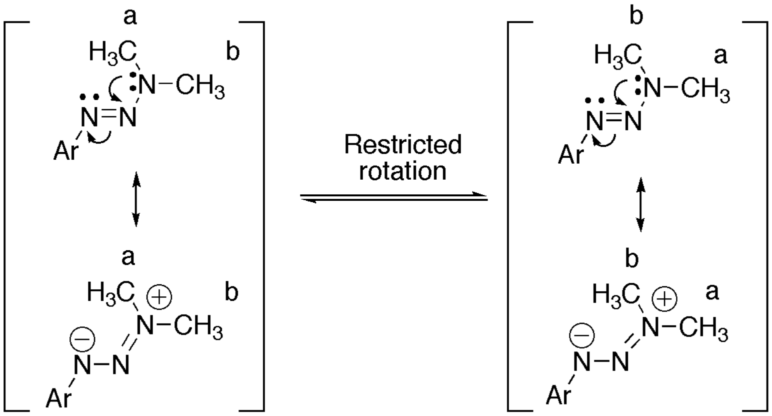
$$\text{Ar}-\text{N}=\text{N}-\text{NHAr} \xrightleftharpoons{\text{H}^+} \text{Ar}-\text{N}=\text{N}-\underset{\text{H}}{\overset{\oplus}{\text{N}}}\text{HAr} \xrightarrow{\text{rcs}} \text{Ar}-\text{N}=\overset{\oplus}{\text{N}} + \text{H}_2\text{NAr}$$

Scheme 1-6. A1 mechanism for acid-catalyzed decomposition of 1,3-diphenyltriazenes

The acid-catalyzed decomposition of N-(phenylazo)-substituted nitrogen heterocycles is proposed to involve an A-S_E2 mechanism in aqueous ethanol, the rate-limiting step of which involves simultaneous proton transfer to N(3) and N(2)–N(3) bond splitting.[27] Interestingly, the observed rate constants for decomposition decreases with increasing ring size of the heterocycle.[27] This is attributed by the authors to be due to steric hindrance for proton transfer to N(3) as the ring size increases. The observed rate constant for decomposition decreases as well when the cyclic amine ring contains an electronegative heteroatom; the presence of a heteroatom decreases the basicity of N(3), which slows down the transferring of a proton to N(3) and thus decreases the decomposition reaction rate.[27]

1.4 Restricted rotation

Rotation around the N(2)–N(3) bond of triazenes is characterized by a relatively higher energy barrier when compared to a single N–N bond. This higher rotational barrier is a result of the partial double bond character between N(2) and N(3) due to the contribution of a 1,3-dipolar resonance form (Scheme 1-7).[32-34]



Scheme 1-7. 1,3-Dipolar resonance forms of 1-aryl-3,3-dimethyltriazenes

Restricted rotation of *trans*-triazenes was first studied by low temperature ^{1}H NMR in *trans*-1-(*p*-substituted-phenyl)-3,3-dimethyltriazenes.[32,33] The signal for protons on the two

N-methyl groups is a singlet at room temperature in $CDCl_3$ and C_2D_5OD solutions, reflecting that the two N-methyl groups are identical because of a fast rotation around the N(2)–N(3) bond. Upon lowering the temperature, the signal broadened and eventually split into two distinct peaks of equal intensity at the coalescence temperature (Tc).[32,33] The rate constant k_r for restricted rotation at the coalescence temperature can be estimated by means of Eq. 1-1, in which ($\nu_A - \nu_B$) represents the chemical shift difference (in Hz) between the two splitting peaks of equal intensity.[23,32,35]

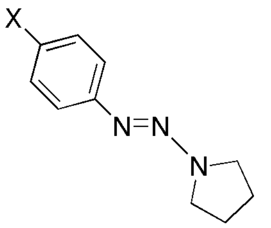
$$k_r = \frac{\pi}{\sqrt{2}}\left(\nu_A - \nu_B\right) \qquad \text{Eq. 1-1}$$

The relationship between activation free energy $\Delta G^{\ddagger}$ and rate constant k_r is given by the Eyring equation (Eq. 1-2), in which k represents the Boltzmann's constant and h represents the Plank constant.[35] Thus, the activation free energy $\Delta G^{\ddagger}$ at the coalescence temperature Tc can be obtained from Eq. 1-3.

$$k_r = \frac{kT}{h}\exp(-\Delta G^{\ddagger}/RT) \qquad \text{Eq. 1-2}$$

$$\Delta G^{\ddagger} = 4.57Tc(10.32 + \log\frac{Tc}{k_r}) \qquad \text{Eq. 1-3}$$

The restricted rotation energy barriers ($\Delta G^{\ddagger}$) for *trans*-N-(*p*-X-phenylazo)pyrrolidine (**1**) and *trans*-1-(*p*-X-phenyl)-3,3-dimethyltriazene (**2**) obtained from low temperature dynamic ^{13}C NMR experiments in $CDCl_3$ are summarized in Table 1-1.[32,33] The activation energy $\Delta G_{Tc}^{\ddagger}$ at Tc is shown to be sensitive to the type of substituent group on the phenyl ring. The restricted rotation energy barrier increases as the electron-withdrawing character of the substituent group at the phenyl ring increases. The same dependency is obtained for **2** at a constant temperature of 298 K. These trends are consistent with the origin of the restricted rotation being the partial double character between N(2) and N(3), which results from the contribution of a 1,3-dipolar resonance form hybrid to the ground state of triazenes.[32-34,36,37]



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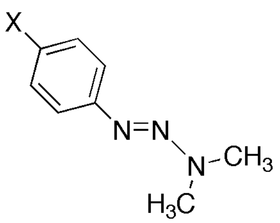


2

Table 1-1. $\Delta G^{\ddagger}$ values for restricted rotation of **1** and **2**.

	1[a]		**2**		
X	$\Delta G_{Tc}^{\ddagger}$ (kcal/mole)	Tc (K)	$\Delta G_{Tc}^{\ddagger\,b}$ (kcal/mole)	Tc[b] (K)	$\Delta G^{\ddagger}_{298}$ [c] (kcal/mole)
OCH_3	12.0	254.1			12.7 ± 0.4
CH_3	12.5	263.3	12.1	239.1	13.0 ± 0.3
H	12.7	268.3	12.7	250.5	13.7 ± 0.3
Cl	13.5	284.1	13.3	261.7	13.9 ± 0.2
CF_3			14.2	278.3	
NO_2	17.0	343.2	15.7	308.1	15.7 ± 0.2

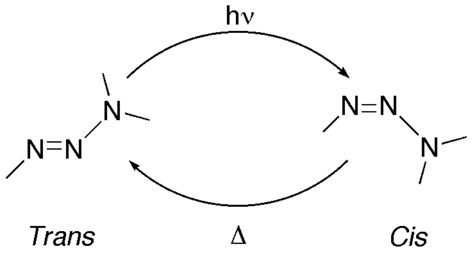
[a]Data taken from ref. 34. [b]Data taken from ref. 33. [c]Data taken from ref. 32.

Evidence for the dipolar resonance form is provided by a ^{15}N NMR study on *trans*-N-(*p*-X-phenylazo)piperidine.[38] The study shows that the chemical shifts of the three nitrogen atoms have a good linear correlation with the Hammett substituent constant (σ) values for different substituent groups on the phenyl ring. N(1) shows the largest sensitivity of chemical shift change as the substituent group changes; moreover, N(1) becomes more shielded as the electron-withdrawing character of the phenyl substituent group increases. This is consistent with the negative character of the charge of N(1) in the 1,3-dipolar resonance form of triazenes. N(2) and N(3) are more and more deshielded as the electron-withdrawing character of the phenyl substituent group increases, showing positive character for the charge on N(2) and N(3) in the 1,3-dipolar resonance form. Furthermore, an *ab initio* molecular-orbital study on *trans* $HN{=}N{-}NH_2$ and its methyl derivatives shows that the orbital containing the lone-pair electrons on N(3) is parallel to the π orbital of the N(1)=N(2) double bond, and the lone-pair electrons readily conjugate with the π system to generate a 1,3-dipolar resonance form, increasing the N(2)–N(3) bond order.[39]

Research on restricted rotation of *cis*-triazenes is very limited. Data only for symmetrical and unsymmetrical 1,3-disubstituted *cis*-triazenes are available; these have been provided by our group.[40-44] As an important part of the mechanism for thermal *cis*-to-*trans* isomerization of 1,3-diphenyltriazenes, the restricted rotation of *cis*-triazenes is discussed in Section 1.5.1.

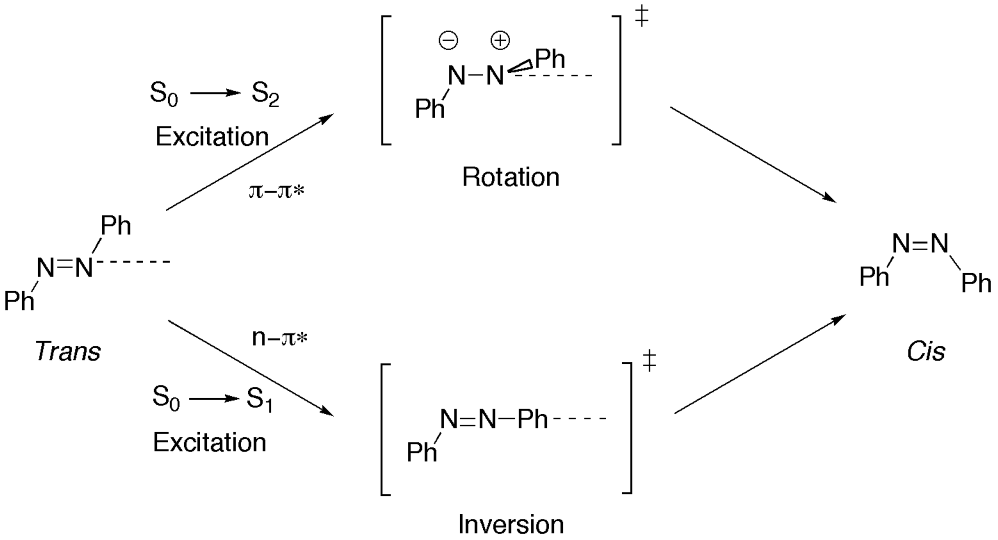
1.5 *Cis-trans* isomerization

X-ray studies show that open-chain triazenes commonly adopt the *trans* configuration in the ground state.[24,45] Upon photoexcitation, the *trans* form can easily photoisomerize to its *cis* form. As *cis*-triazenes are not stable, they spontaneously revert back to the *trans* forms (Scheme 1-8).[16-18]



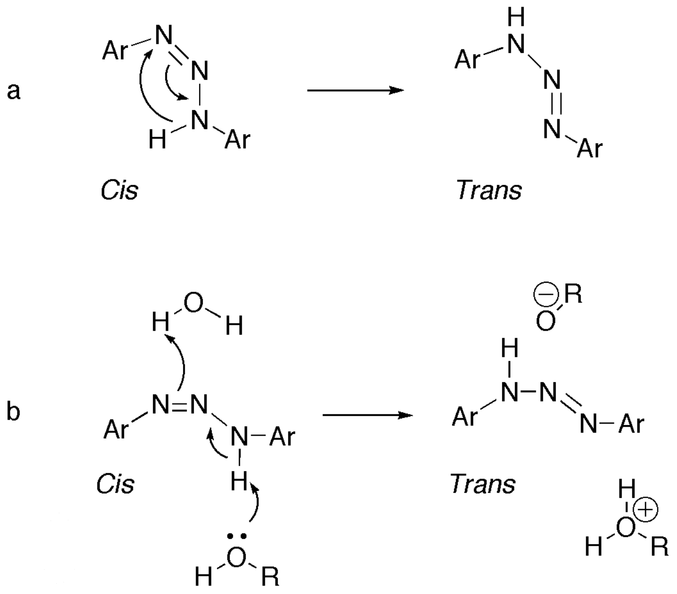
Scheme 1-8. *Cis-trans* isomerization

To the best of my knowledge, there is no study on the *trans*-to-*cis* photoisomerization mechanism of triazenes. However, it can be assumed to proceed via mechanisms similar to those of azobenzenes.[13] Upon photoexcitation of the *trans* form, an electron is excited from its ground state (S_0) orbital to an excited state orbital. Since there is no influence of oxygen or a heavy atom observed during the photoisomerization of azobenzenes, the electron is most likely to be excited to its first singlet excited state (S_1), in which the electron retains its spin under an n-π* excitation condition, or its second singlet excited state (S_2), in which the electron also retains its spin under a π-π* excitation condition.[46,47] Azo groups photoisomerize via two distinct mechanisms, following the n-π* electronic transition with an inversion of the nitrogen atom or the π-π* transition with a rotation around the bond between the two nitrogen atoms (Scheme 1-9). The nature of the electronic transition likely depends on the excitation wavelength.[47]



Scheme 1-9. Possible mechanisms for *trans*-to-*cis* photoisomerization of azobenzene

Investigations on the mechanism(s) of thermal *cis*-to-*trans* isomerization of triazenes are very limited, and these are solely based on 1,3-diphenyltriazenes.[16-18] The thermal *cis*-to-*trans* isomerization of 1,3-diphenyltriazenes was first observed in non-hydrogen bonding solvents (e.g., cyclohexane), and a 1,3-hydrogen shift mechanism as shown in Scheme 1-10a was proposed.[16] When adding alcohols (e.g., 2-propanol) to non-hydrogen bonding solvents, an acceleration of the thermal *cis*-to-*trans* isomerization was observed.[16,18] This was attributed to a solvent assisted 1,3-prototropic mechanism as shown in Scheme 1-10b. Alcohols, hydrogen bonding solvents, can act as proton donors and also as proton acceptors, resulting in an increase of the isomerization reaction rate.[16,18] Studies on the thermal *cis*-to-*trans* isomerization mechanism of 1,3-diphenyltriazenes in aqueous solutions were carried out in our group; these are described in the next Section.

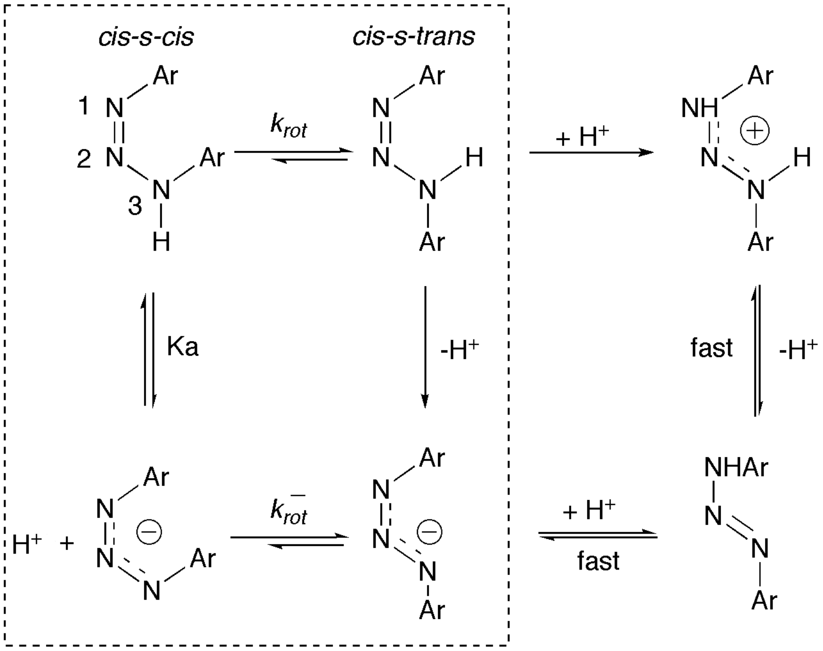


Scheme 1-10. Thermal *cis*-to-*trans* isomerization of 1,3-diphenyltriazenes by (a) 1,3-hydrogen shift; (b) solvent assisted 1,3-prototropic rearrangement.

1.5.1 Previous group studies on the thermal *cis*-to-*trans* isomerization of 1,3-diphenyltriazenes

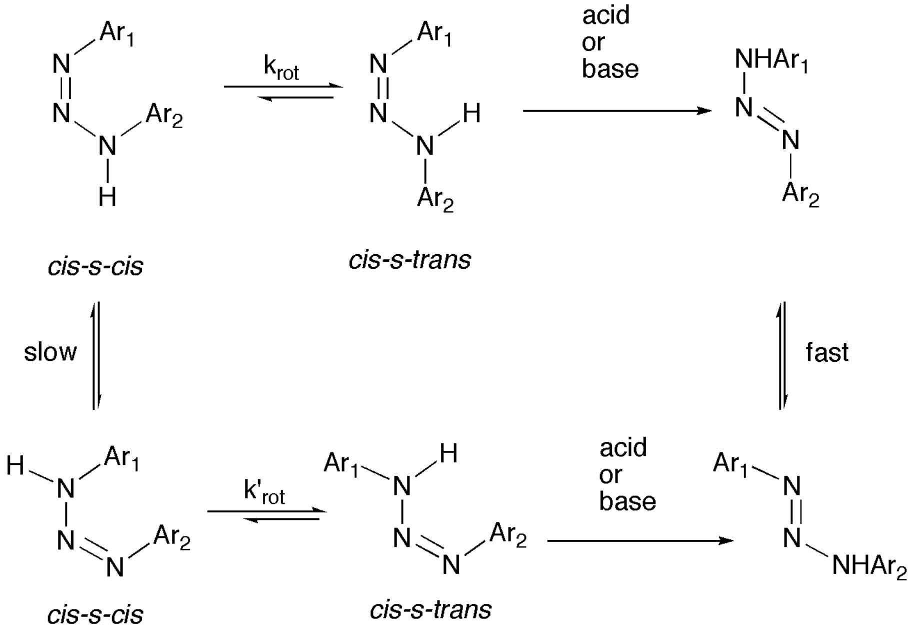
Kinetic studies were based on the use of symmetrical and unsymmetrical *meta* and *para*-substituted 1,3-diphenyltriazenes.[40-44] *Cis*-1,3-diphenyltriazenes were generated upon irradiation of the *trans* forms, and the *cis*-to-*trans* thermal isomerization of 1,3-diphenyl-triazenes was found to be catalyzed by acids and bases as a result of 1,3-prototropic rearrangements;[40,41] the proposed mechanism for symmetrical 1,3-diphenyltriazenes is shown in Scheme 1-11.

The rate-controlling step of the thermal *cis*-to-*trans* isomerization of 1,3-diphenyltriazenes depends on the pH of the solution. At pH < 10, the rate-controlling step is the 1,3-prototropic rearrangement, which is catalyzed by general acids and bases.[40,41] The acid catalysis is found to predominate as the electron-donating character of the aryl group increases, while base catalysis becomes predominant as the electron-withdrawing character of the aryl group increases.[41] At pH > 10, the rate-controlling step is the hindered or restricted rotation around the N(2)–(3) bond, which rate is independent of pH.[40,41] As shown in Scheme 1-11, only *cis-s-trans* forms isomerize to *trans* triazenes, since the 1,3-prototropic rearrangement of *cis-s-cis* forms still leads to *cis* isomers.



Scheme 1-11. Thermal *cis*-to-*trans* isomerization mechanism for symmetrical triazenes

In the case of unsymmetrical diphenyltriazenes, unlike symmetrical triazenes, photoinduced *trans*-to-*cis* photoisomerization leads to a non-equilibrium mixture of two pairs of *cis* isomers, i.e. one pair of *cis* conformers per tautomeric *trans* form.[43] Generally, thermal *cis*-to-*trans* isomerization of these two isomeric *cis* pairs follows a similar mechanism as for symmetrical triazenes (Scheme 1-12).[43] On the other hand, the two isomeric *cis* pairs isomerize independently of each other. This is attributed to hindered rotation around the N(2)–(3) single bond being faster than tautomerization of the two *cis* isomers, since 1,3-prototropic rearrangements of *cis*-s-*trans* isomers would significantly decrease the steric hindrance between the two phenyl rings.[43]



Scheme 1-12. Thermal *cis*-to-*trans* isomerization mechanism for unsymmetrical triazenes

Interestingly, the observed rate constants for restricted rotation of cyano-containing 1,3-

diphenyltriazenes are pH dependent, which is attributed to a change in the ionization state of the substrate, depicted in Scheme 1-11 (dotted box).[44] In the presence of a *p*-CN group at the ring bonded to N(3), the rotation rate constant increases as the pH increases, reflecting that deprotonation of the diazoamino group decreases the partial double bond character between N(2) and N(3).[44] This implies that the negative charge of the anionic form concentrates on the *p*-CN group rather than on the diazoamino moiety. In other cases, such as a *m*-CN group at the ring bonded to N(3) or *p*-CN group at the ring bonded to N(1), the rate constant for restricted rotation decreases as the pH increases, reflecting an increase of the partial double bond character of N(2)–N(3). This implies that the negative charge of the anionic form concentrates on the diazoamino moiety.[44]

Substituent effects on the restricted rotation of symmetrical and unsymmetrical 1,3-diphenyltriazenes have also been studied by our group. In the case of symmetrical diphenyltriazenes, the 1,3-dipolar resonance form is stabilized by an increase in the electron-withdrawing character of the aryl group bonded to N(1), while it is destabilized by the same aryl group bonded to N(3). An increase on the rotational rate constant as the electron-withdrawing character of the aryl group increases indicates that the 1,3-dipolar resonance form is more sensitive to the electronic character of the aryl group attached to N(1) than that on N(3).[41] A quantitative analysis of the rate constants for restricted rotation of symmetrical and unsymmetrical *meta* or *para*-substituted *cis*-1,3-diphenyltriazenes, by means of a multiple substituent Hammett equation, renders reaction constant (ρ) values (indicating how sensitive the reaction is to substituent effects) of -1.88 ± 0.08 and 0.70 ± 0.08 for N(1) and N(3), respectively.[44] The negative and positive signs of the ρ values for N(1) and N(3) imply that the electron density at N(1) decreases and that of N(3) increases from the ground state to the corresponding transition state, consistent with the 1,3-dipolar resonance form model (Scheme 1-7).[43] The larger absolute ρ value for N(1) indicates that the restricted rotation is more susceptible to the electronic character of the aryl group attached to N(1) than that bonded to N(3).[41,42,44]

For symmetrical diphenyltriazenes, substituent effects on the restricted rotation of *cis*-triazenes (Table 1-2)[42] are similar to those for the *trans*-triazenes given in Table 1-1, i.e., the rotational barrier increases with increasing electron-withdrawing character of the substituent.

Table 1-2. $\Delta G^{\ddagger}$ values for restricted rotation of *cis*-1,3-di(*p*-X-phenyl)triazenes

X	CH_3O	CH_3	H	Cl	CF_3
$\Delta G^{\ddagger}$ (kcal/mole)[a]	10.6 ± 0.1	11.1 ± 0.3	11.1 ± 0.8	11.7 ± 0.2	11.9 ± 0.3

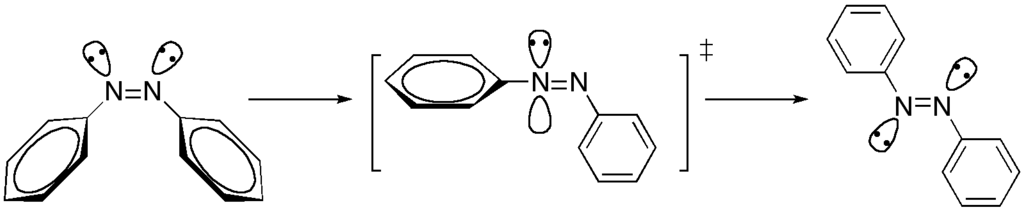
[a] Data obtained at 21°C in 30% THF-H_2O solutions.

Solvent effects on the restricted rotation of *cis*-1,3-di(*p*-X-phenyl)triazenes have also been studied. In aqueous solutions, the rate constants for restricted rotation are found to diminish with a decrease in polarity of the organic co-solvent and an increase in co-solvent concentration. This implies the molecular dipole moment increases via restricted rotation from the ground state to the transition state.[42]

1.5.2 Other possible thermal *cis*-to-*trans* isomerization mechanisms

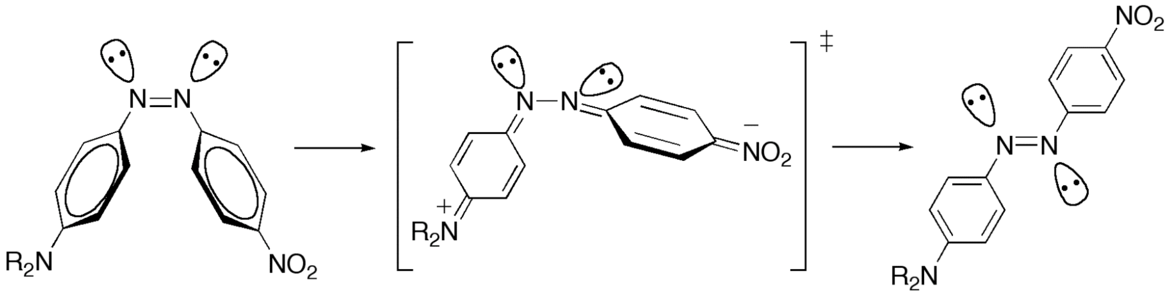
In the absence of a hydrogen attached to N(3), thermal *cis*-to-*trans* isomerization of triazenes can not proceed via a 1,3-prototropic rearrangement as in the case of 1,3-diphenyltriazenes. Possible isomerization mechanisms for trisubstituted triazenes could be similar to those for azobenzenes, for which there are two possible competing mechanisms. One possibility requires the inversion of one sp^2 hybridized nitrogen atom through an sp hybridized transition state (Scheme 1-13), whereas the other possible mechanism involves rotation around the ruptured double bond in the transition state (Scheme 1-14).[13,47,48] The energy barrier for inversion would be determined mainly by the energy change of the nonbonding orbital from sp^2 to p; the energy barrier for rotation would be determined mainly by the energy required to break the N(1)=N(2) π bond.[49]

Generally, isomerization of azobenzene and its monosubstituted derivatives proceed via an in-plane inversion mechanism similar to that for photoinduced *trans*-to-*cis* isomerization,[13,47,48] i.e., one of the nitrogen atoms rehybridizes leading to a semi-linear transition state (Scheme 1-13).



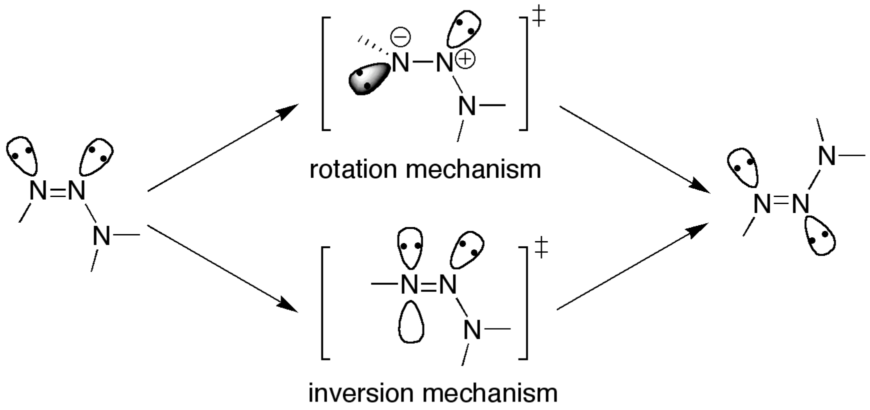
Scheme 1-13. Inversion mechanism for thermal *cis*-to-*trans* isomerization of azobenzene

In the case of the *cis*-to-*trans* isomerization of azobenzenes with “push-pull” substituents (i.e., one substituent is electron-withdrawing and the other is donating), such as 4-(dimethylamino)-4’-nitroazobenzene, experimental evidence provides support for an out-of-plane rotation mechanism, in which the nitrogen-nitrogen π bond is ruptured heterolytically and a dipolar transition state is involved (Scheme 1-14).[50,51] The isomerization rate increases rapidly with increasing polarity of the reaction medium, which reflects a large molecular polarity increase via the activation process.[50]



Scheme 1-14. Rotation mechanism for thermal *cis*-to-*trans* isomerization of a "push-pull" diazobenzene

The two above-mentioned mechanisms are illustrated in Scheme 1-15 for thermal *cis*-to-*trans* isomerization of trisubstituted triazenes. Inversion is expected to take place at N(1), since inversion of N(2) would be hindered by the amino group.[52] This effect is what is known as the "hetero effect": 1. the lone pair electrons on N(2) and N(3) repulse each other to destabilize the semi-linear transition state; 2. heteroatom N(3) could increase the s character of the lone pair electron orbital on N(2),[53] with the result that the energy gap for the rehybridization of N(2) increases (the lone pair electron orbital on N(2) would be a p orbital in the transition state).[52]

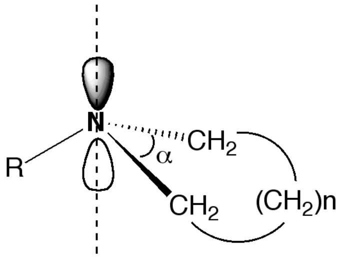


Scheme 1-15. Proposed mechanisms for thermal *cis*-to-*trans* isomerization of trisubstituted triazenes

1.6 Ring effects on electronic properties of cyclic amines

As mentioned before, the target compounds in this study are N-(phenylazo)-substituted nitrogen heterocycles. Since the ring size of cyclic amines can have a significant effect on the electron-donating character of the nitrogen atom, it is necessary to have a discussion about the ring size effects on electronic properties of cyclic amines.

Ionization potential studies show that ionization potential values for cyclic amines can reflect the basicity and electron-donating ability of the nitrogen atom.[54] As the ring size of cyclic amine increases, the ionization potential values decrease. This indicates that the lone pair electrons can be removed more easily in the case of a large ring. The C–N–C ring bond angle (α) shown in Scheme 1-16 decreases as the ring decreases in size, thus in order for efficient orbital overlap for bonding in small size cyclic amines, the two nitrogen hybrid orbitals that form the C–N bonds must increase their p-character. As a result, the remaining hybrid orbitals must increase their s-character. The increased s-character of the non-bonding orbital causes the lone pair electrons to be more tightly held as they are attracted strongly by the nucleus, which results in high ionization potential, lower basicity, and lower electron-donating ability of the cyclic amine.[54]



Scheme 1-16. General structure of cyclic amines

Theoretical analysis based on the reactive hybrid orbital (RHO) theory has been performed on the electron-donating ability of cyclic amines. The RHO concept is defined through a combination of occupied molecular orbitals to maximize the reactivity index ρ_{oc} (Eq. 1-4) for a reaction center,[55,56] the index of the amine lone-pair orbital in this case, and represents the intrinsic electron donating ability of the nitrogen atom of the cyclic amine.

$$\rho_{oc} = -f_{oc} / \lambda_{oc} \qquad \text{Eq. 1-4}$$

The parameters f_{oc} and λ_{oc} in Eq. 1-4 are the electron density and energy level of the occupied orbital, respectively.[57] As the ring size increases, the positive value of f_{oc} and the negative value of λ_{oc} are found to increase, thus the positive value of ρ_{oc} increases (Table

1-3), which implies the intrinsic electron-donating ability of the nitrogen atom increases as the ring size of the cyclic amine increases.[57]

Table 1-3. Intrinsic electron-donating ability of the nitrogen atom of cyclic amines

$(n)^a$	ρ_{oc} (RHF/6-31G*)^b	
	R = H	R = CH_3
0	2.123	2.162
1	2.333	2.340
2	2.365	2.360
3	2.372	2.364

[a]Defined in Scheme 1-16. [b]Data taken from ref. 57.

1.7 Theoretical Studies

Semi-empirical and *ab initio* methods have been used to perform geometry optimizations and calculate proton affinities and vibrational frequencies of triazenes, but no studies about the reversible *cis-trans* isomerization mechanism have been reported so far. Calculations on geometry optimization have been reported for ground-state *trans*-1-aryl-3,3-dialkyl-triazenes.[58] The N(1)=N(2) bond order of phenyl ring-substituted substrates ranges from 1.723 to 1.829 (i.e., < 2) and that for N(2)–N(3) ranges from 1.009 to 1.187 (i.e., > 1), in good agreement with the involvement of a 1,3-dipolar resonance form. It is also noticed that a decrease in the N(1)=N(2) bond order is accompanied by an increase in the N(2)–N(3) bond order. In addition, the N(2)–N(3) bond order increases as the electron-withdrawing character of the substituent group increases.[58] This is consistent with the experimental studies mentioned in Sections 1.3 and 1.4 (i.e., the restricted rotation energy barrier increases and the quantum yield of photolysis decreases as the electron-withdrawing character of the substituent group at the phenyl ring increases.)

Protonation and acid decomposition of triazenes have been simulated by theoretical calculations. Theoretical studies, on heats of formation of 1,3-diphenyltriazenes by semi empirical method[59] and proton affinities of triazene ($H{-}N(1){=}N(2){-}N(3)H_2$) by *ab initio* methods,[39,60,61] reveal that N(1) is the most favored protonation site, N(3) is slightly less favored, and N(2) is the least favored one (e.g., calculated proton affinities[60] are 227.6 kcal/mol, 196.9 kcal/mol and 218.8 kcal/mol for N(1), N(2), and N(3), respectively). The semi-empirical study also shows that protonation at N(3) is more favorable when an electron-donating group attaches on the arylamine ring since the positive charge on N(3) of the protonated molecule could be stabilized, while an electron-withdrawing group on the arylamine ring decreases the basicity of N(3).[59] The decomposition energies of protonated 1,3-diphenyltriazenes, calculated from heats of formation, show that the stability of triazenes increases as the electron-withdrawing character of the substituent group on the diazoaryl ring increases and as the electron-donating character of the substituent group on the arylamine ring increases.[59] This is attributed to the fact, as mentioned in Section 1.4, that both an electron-withdrawing group on the diazoaryl ring and an electron-donating group on the arylamine ring increase the contribution of the 1,3-dipolar resonance form, which results in an increase of the N(2)–N(3) bond order.

There are very few theoretical studies on the target compounds, N-(phenylazo)-substituted nitrogen heterocycles. Semi-empirical studies on geometry optimizations of piperidine derivatives show as a general trend that the N(1)=N(2) bond length of *para* substituted N-(phenylazo)piperidines increases as the electron-withdrawing character of the phenyl ring substituent increases, whereas the N(2)–N(3) bond length follows the opposite trend.[62] This is consistent with the substituent effects on bond lengths of *trans*-1-aryl-3,3-dialkyltriazenes mentioned above.[58] The molecular dipole moment of the piperidine derivatives (shown in Table 1-4) is found to increase significantly as the electron-withdrawing character of the substituent increases,[62] and this trend is also found in the case of *trans*-1-aryl-3,3-dimethyltriazenes.[58] This change in molecular polarity with a change in the substituent group on the phenyl ring is in good agreement with the 1,3-dipolar resonance model, i.e., the contribution of the 1,3-dipolar resonance form increases as the electron-withdrawing character of the substituent group on the phenyl ring increases, resulting in an increase in molecular dipole moment. Lastly, the vibrational frequencies and visible spectra of N-(phenylazo)-substituted nitrogen heterocycles have been predicted by HF and B3LYP methods using 6-31G* as basis set; the best agreement between experimental and calculated vibrational frequencies is obtained at the B3LYP level,[63] which is also the method used in the theoretical studies presented in Chapter 3.

Table 1-4. Calculated dipole moment for N-(*p*-X-phenylazo)piperidines by MNDO method

X	NO_2	$COCH_3$	F	Cl	H	CH_3	OCH_3	OCH_2CH_3
Dipole moment[a] (D)	7.254	3.687	3.429	3.409	1.260	1.329	1.061	0.896

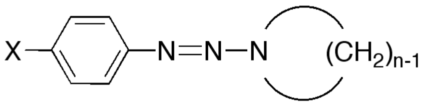
[a] Data taken from ref. 62.

1.8 Research objectives

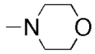
The studies presented in this thesis aimed at elucidating the mechanism for thermal *cis*-to-*trans* isomerization of N-(phenylazo)-substituted nitrogen heterocycles (Scheme 1-2). Studies focused on three aspects: (a) the effects of phenyl ring substitution, (b) the effects of cyclic amine ring size, and (c) the effects of solvents, on the rate of *cis*-to-*trans* isomerization. In addition, in order to compare with experimental results, theoretical analyses on the *cis*, *trans*, and transition state forms of target compounds, both in the gas phase and in various solvents, and reaction coordinate diagrams were carried out based on DFT-B3LYP/6-31+G* calculations.

2 Kinetic studies

As mentioned in Section 1.5, studies on the thermal *cis*-to-*trans* isomerization of triazenes are very limited and have focused solely on 1,3-diphenyltriazenes. To the best of my knowledge, there are no studies on the thermal isomerization mechanism of trisubstituted triazenes. The target compounds in this study are the N-(phenylazo)-substituted nitrogen heterocycles summarized in Chart 2-1. Conveniently, an abbreviation, X-n, is used to represent each target compound, in which X refers to the functional group on the *para* position of the phenyl ring and n represents the size of the cyclic amino moiety.



Compound	X	n
CH_3O-4	CH_3O	4
CH_3O-5	CH_3O	5
CH_3O-6	CH_3O	6
CH_3O-6-O[a]	CH_3O	6
CH_3O-7	CH_3O	7
CH_3-5	CH_3	5
Cl-4	Cl	4

[a]Cyclic amine = 

Compound	X	n
H-4	H	4
H-5	H	5
H-6	H	6
H-6-O[a]	H	6
H-7	H	7
CF_3-4	CF_3	4
CF_3-5	CF_3	5

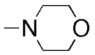
[a]Cyclic amine = 

Chart 2-1. Target compounds

2.1 Results

Cis-triazenes are generated upon photoexcitation (at 350 nm) of the corresponding *trans* forms dissolved in various organic solvents. Around the λ_{max} of the longer wavelength absorption band and right after irradiation, a decrease in absorbance can be observed as a result of *trans*-to-*cis* photoisomerization, since the *cis* isomers have lower absorptivity than the *trans* isomers in this region.[17] After photoisomerization, however, the absorbance commonly recovers in the dark to its initial value via thermal *cis*-to-*trans* isomerization, except in cases where there is significant photodecomposition (see below). The recovery traces (Figure 2-1 is representative) follow first-order kinetics, from which the observed rate constants (k_{obs}) are obtained. Resulting k_{obs} values are listed in Table 2-1 to 2-3.

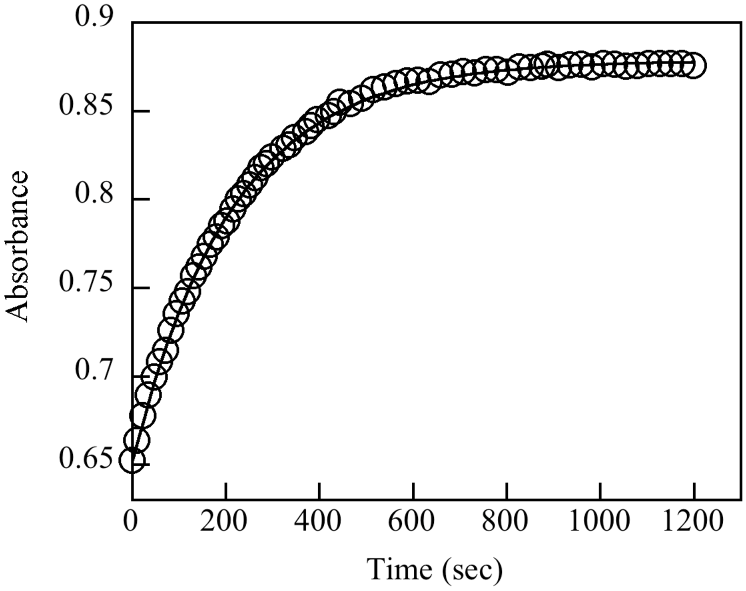


Figure 2-1. Kinetic trace recorded at 325 nm for CH_3O-5 in acetonitrile

As shown in Tables 2-1 and 2-2, k_{obs} increases as the ring size of the cyclic amine increases, regardless of the solvent, particularly in relation to values for n = 4. For example, in the case of CH_3O-n in DMF, the reaction rate constant for n = 6 is *ca*. 14,000 times as large as that for n = 4, and that for n = 7 is too fast to be accurately measured. In the case of H-n in benzene, the reaction rate constant for n = 5 is *ca*. 800 times as large as that for n = 4, and in the cases of n = 6 in polar solvents and n = 7 in both nonpolar and polar solvents, the isomerization is too fast to be measured since no absorbance change is detected (only flat traces are obtained). The same trend can also be observed in the case of

Table 2-1. First-order observed rate constants for *cis*-to-*trans* isomerization of CH_3O-n in aprotic solvents

Solvent[a]	k_{obs} (10^{-2} s^{-1})				
	CH_3O-4	CH_3O-5	CH_3O-6	CH_3O-6-O	CH_3O-7
Cyclohexane	b	b	b	b	3.19 ± 0.05
Benzene	b	0.16 ± 0.01	1.92 ± 0.04	b	7.8 ± 0.4
Acetonitrile	0.00102 ± 0.00004	0.35 ± 0.02	7.1 ± 0.1	0.49 ± 0.02	c
DMF	0.000524 ± 0.000008	0.30 ± 0.01	7.3 ± 0.1	0.652 ± 0.008	c
DMSO	0.0041 ± 0.0003	0.49 ± 0.02	13.2 ± 0.4	1.47 ± 0.04	c

[a] In solvents other than acetonitrile, solutions contain 1.3 % acetonitrile (v/v). [b] Significant substrate decomposition precluded study. [c] Reaction too fast to be accurately measured with our system ($k_{obs} > 0.15$ s^{-1}).

Table 2-2. First-order observed rate constants for *cis*-to-*trans* isomerization of H-n in various solvents

Solvent[a]	k_{obs} (10^{-2} s^{-1})			
	H-4	H-5	H-6	H-6-O[b]
Cyclohexane	c	0.59 ± 0.02	10.4 ± 0.8	2.62 ± 0.08
Benzene	0.0032 ± 0.0001	2.54 ± 0.03	d	7.2 ± 0.2
Acetonitrile	0.0279 ± 0.0008	12 ± 2	e	d
DMF	0.0314 ± 0.005	14 ± 3	e	e
DMSO	0.0611 ± 0.0001	d	e	e
Methanol	0.0258 ± 0.0008[a]	3.52 ± 0.07	e	d
Ethanol	0.0077 ± 0.0002	2.45 ± 0.04		5.5 ± 0.3
1-Propanol	0.0066 ± 0.0005	1.69 ± 0.04		4.65 ± 0.08
2-Propanol	0.0044 ± 0.0002	1.58 ± 0.03	e	4.5 ± 0.2
1-Butanol	0.0070 ± 0.0003	1.62 ± 0.03	e	4.2 ± 0.1
1-Octanol	0.0100 ± 0.0002	1.80 ± 0.06	e	6.6 ± 0.4

[a]In solvents other than acetonitrile, solutions contain 1.3 % acetonitrile (v/v). [b]For H-7 in cyclohexane and acetonitrile, no change in absorbance is detected. [c]Significant substrate decomposition precluded study. [d]Reaction too fast to be accurately measured with our system ($k_{obs} > 0.15$ s^{-1}). [e]No change in absorbance is detected.

Table 2-3. First-order observed rate constants for *cis*-to-*trans* isomerization of CH_3-5, Cl-4 and CF_3-4 in various solvents

Solvent[a]	k_{obs} (10^{-2} s^{-1})		
	CH_3-5	Cl-4	CF_3-4[b]
Cyclohexane	0.23 ± 0.02	0.027 ± 0.005	0.224 ± 0.003
Benzene	0.47 ± 0.01	0.0130 ± 0.0003	0.98 ± 0.02
Acetonitrile	2.45 ± 0.07	0.166 ± 0.006	10.3 ± 0.5
DMF	2.70 ± 0.08	0.239 ± 0.04	c
DMSO	4.3 ± 0.1	0.396 ± 0.008	d
Methanol	2.8 ± 0.2	0.072 ± 0.002	4.00 ± 0.08
Ethanol	0.55 ± 0.04		
1-Propanol	0.39 ± 0.01		
2-Propanol	0.30 ± 0.01	0.0232 ± 0.0003	1.88 ± 0.01
1-Butanol	0.34 ± 0.01		1.75 ± 0.01
1-Octanol	e	0.0223 ± 0.0001	1.67 ± 0.02

[a] In solvents other than acetonitrile, solutions contain 1.3 % acetonitrile (v/v). [b] For CF_3-5 in cyclohexane, acetonitrile, and methanol no change in absorbance is detected. [c] Reaction too fast to be accurately measured with our system ($k_{obs} > 0.15$ s^{-1}). [d] No change in absorbance is detected. [e] Significant substrate decomposition precluded study.

CF_3-n (Table 2-3), i.e., as the ring changes from n = 4 to 5, the reaction becomes too fast to be measured both in nonpolar and polar solvents. To be noticed is the fact that k_{obs} values for CH_3O-6 and H-6 are larger than those for CH_3O-6-O and H-6-O, respectively, although both sets of substrates contain a six-member ring (Table 2-1 and 2-2).

The observed rate constants shown in the previous three Tables also are found to depend on the electronic character of the *para* substituent group on the phenyl ring. Comparing k_{obs} values for substrates with n = 4 or 5, it is seen that k_{obs} increases remarkably as the electron-withdrawing character of the *para* substituent group increases. In the case of X-4 in acetonitrile, k_{obs} for X = CF_3 is *ca.* 10,000 times larger than that for X = CH_3O; in the case of X-5 in acetonitrile, k_{obs} for X = H is *ca.* 47 times larger than that for X = CH_3O, while that for X = CF_3 is too fast to be measured (both in polar and nonpolar solvents).

For any given substrate, the observed rate constant typically increases as the solvent polarity increases. This solvent effect is quite significant for a substrate with a strong electron-withdrawing group (e.g., k_{obs} for CF_3-4 in acetonitrile is *ca.* 50 times as large as that in cyclohexane). For substrates other than CH_3O-n, k_{obs} values in alcohols are typically smaller than those in polar aprotic solvents. Rate constants for CH_3O-n in alcohols could not be determined since photodecomposition is always significant (exceeding 20 %, see Table 2-4 and 2-5) and the kinetic traces are rarely first-order. Though this photolytic character is of relevance in laser ablation lithography, it is detrimental for applications involving photoswitchable devices and photostorage media.

For any given substrate in any given solvent, the percent photodecomposition can be calculated from the change in absorbance before irradiation and after isomerization is completed (see details in Section 4.2.2). The yield of the photolysis is mainly determined by the quantum yield for formation of excited states and the efficiency for photolytic bond cleavage.[64] Percent photodecomposition values are obtained in two different ways: (a) by keeping the substrate concentration constant (1.05×10^{-4} mol/L) and (b) by matching the absorbance of the solutions (to 0.50 ± 0.05) before irradiation at 350 nm. Yields shown in Table 2-4 are obtained by keeping the substrate concentration constant, and thus the absorbance values for the various samples may differ (ranging from 0.1 to 0.6). On the other hand, yields shown in Table 2-5 are obtained using solutions with matching absorbance. In the latter case, the number of photons absorbed is kept constant by fixing the irradiation time and thus, it is possible to compare the efficiency of the photolysis in the various samples. Interestingly, even when the substrate (*trans*) concentration in the solutions for the two methods is different (hence, the concentration of the photochemically generated *cis* isomers would be also different), the first-order isomerization rate constants (k_{obs}) determined for any given triazene under the two methods are essentially the same, i.e., k_{obs} is independent of substrate concentration. This indicates that the process being monitored (i.e., *cis*-to-*trans* isomerization) is a unimolecular reaction.

As shown in Table 2-4 and 2-5, the percent decomposition for substrates having the same phenyl ring substituent typically decreases as the ring size increases and as the electronegativity of the ring atoms decreases; this trend is opposite to that determined for isomerization rate constants. In the case of large rings (e.g., H-6 in polar solvents and H-7 in both nonpolar and polar solvents), there is essentially no photodecomposition. Percent decomposition values are also found to be dependent on the *para* substituent group on the phenyl ring, following a trend opposite to that determined for isomerization rate constants, i.e., percent decomposition for substrates having the same ring size decreases as the electron withdrawing character of the phenyl substituent group increases. Finally, in regards to the solvent effect, for any given substrate, the percent decomposition is observed to decrease typically as the polarity of the aprotic solvent increases. With respect to the effect of alcohols, percent yields are typically larger than those in polar aprotic solvents.

Table 2-4. Percent yield for photodecomposition of target substrates using solutions having identical substrate concentration

Solvent	Percent decomposition (%)^a							
	CH_3O-4	CH_3O-5	CH_3O-6	CH_3O-6-O	CH_3O-7	H-5	H-6	H-6-O
Cyclohexane	31	9	18	33	3	2	1	6
Benzene		10	8	23		2	0	3
Acetonitrile	6		6	6	1	0.8	<0.1	1
DMF		1	1	5	1	0.6	0.2	0.9
DMSO	11	2	2	5	0.2	0.3	0	0.5
Methanol		12	21	43				
Ethanol			20	42				
1-Propanol		32	26	46				
2-Propanol		23	25	47				
1-Butanol		29	26	49				
1-Octanol		27		67				
Water				27				

[a] Typical relative error is 10 %.

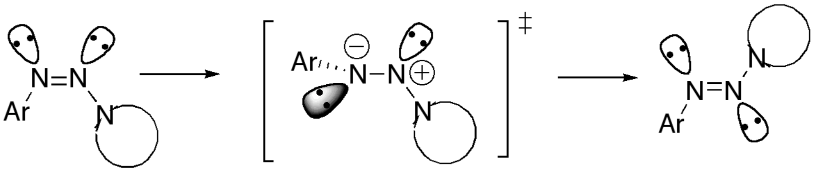
Table 2-5. Percent yield for photodecomposition of target substrates using solutions having matched absorbance

Solvent	Percent decomposition (%)[a]											
	CH_3O-4	CH_3O-5	CH_3O-6	H-4	H-5	H-6	H-6-O	H-7	CH_3-5	Cl-4	CF_3-4	CF_3-5
Cyclohexane		14	24	16	0.9	0.7	4	0	6	2	0.2	0.2
Benzene	> 30	12	12 (3)[b] (24)[c]	1	0.9	0.2	1		2	2	0.2	
Acetonitrile		5	4	0.4	0.9	< 0.1	0.5	0	0.9	0.6	0.1	1
DMF	2			0.2	0.3				1	0.3	0.2	
DMSO		4	5	2	0.5	< 0.1	0.4		0.9	0.6	0	
Methanol	45			14	0.5	0.7	1		2	9	0.1	0.1
Ethanol	45			5	1		2		3			
1-Propanol	47			6	0.3		2		4			
2-Propanol	43			5	0.5	0.2	0.7		4	1	0.3	
1-Butanol	48			10	0.7	0.2	2		5		0.4	
1-Octanol	48		63	11	4	0	11		19	4	0.4	

[a] Typical relative error is 10 %. [b] Data for CH_3O-7. [c] Data for CH_3O-6-O in toluene.

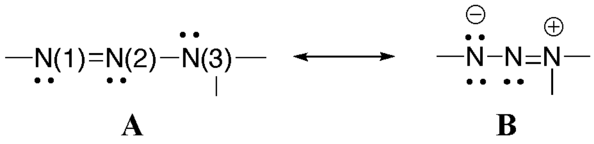
2.2 Discussion

All trends for k_{obs} values referred to in the previous Section can be interpreted in terms of an internal rotation mechanism, as described in Section 1.5.2 for “push-pull” azobenzenes,[51] in which the N=N π bond is heterolytically ruptured. As shown in Scheme 2-1, rotation around the C–N(1)=N(2)–N(3) dihedral angle through a polar transition state leads from *cis* to *trans*.



Scheme 2-1. Proposed rotation mechanism for target triazenes

The energy barrier for this polar rotation mechanism will be influenced by the ability of the phenyl ring and the cyclic amino moiety to stabilize the negative and positive charges in the polar transition state, respectively. The cyclic amino moiety and the phenyl ring will also greatly affect the contribution of the 1,3-dipolar resonance form (structure **B** in Scheme 2-2), introduced in Section 1.4, resulting from conjugation of the lone pair electrons of N(3) with the π electrons of the N(1)=N(2) bond. An increase of the contribution of the 1,3-dipolar resonance form to the ground state structure of triazenes would reduce the N(1)=N(2) bond order, resulting in a decrease of the energy barrier for rotational isomerization.



Scheme 2-2. Resonance forms of triazenes

The electron-donating character of N(3) of the target substrates, and hence the ability of N(3) to stabilize a positive charge, will depend on the size of the cyclic amine ring. As pointed out in Section 1.6, ionization potential (IP) studies[54] as well as RHO theoretical studies[57] show that the electron donating character of the nitrogen atom in cyclic amines increases as the size of the ring increases. This trend is most likely due to an increase in the s character of the nitrogen lone pair electrons orbital as the C-N-C bond angle of cyclic amines decreases.[54] The fact that k_{obs} increases in all tested solvents as the ring size of the cyclic amine increases can be attributed to the change in the electron donating character of N(3) of triazenes. Figure 2-2 shows that $\log(k_{\mathrm{obs}})$ values for CH_3O-n in acetonitrile (the only type of substrate with no less than three available data points) are proportional to the ionization potential energies and the calculated electron donating ability (ρ_{oc}) of the corresponding cyclic amine. Undoubtedly, an increase in the electron-donating character of N(3) in triazenes increases the contribution of the 1,3-dipolar resonance form to the ground state of triazenes (with the resulting decrease in the N(1)=N(2) bond order) as well as the stability of the polar transition state, leading to lower rotation energy barriers and faster rate constants. Although it is not rigorous to perform quantitative analysis based on three points, Figure 2-2 allows one to roughly estimate rate constants (and lifetimes) for isomerization of CH_3O-n. Based on the linear plot against IP (no enough data available for

ρ_{oc}), resulting k_{obs} value for n = 7 (IP = 8.41)[54] is *ca.* 11 s^{-1} (lifetime = 0.07 s). This estimated rate constant value is consistent with the experimental fact that the isomerization rate constant for CH_3O-7 is too fast (i.e., > 0.15 s^{-1}) to be accurately measured with our system.

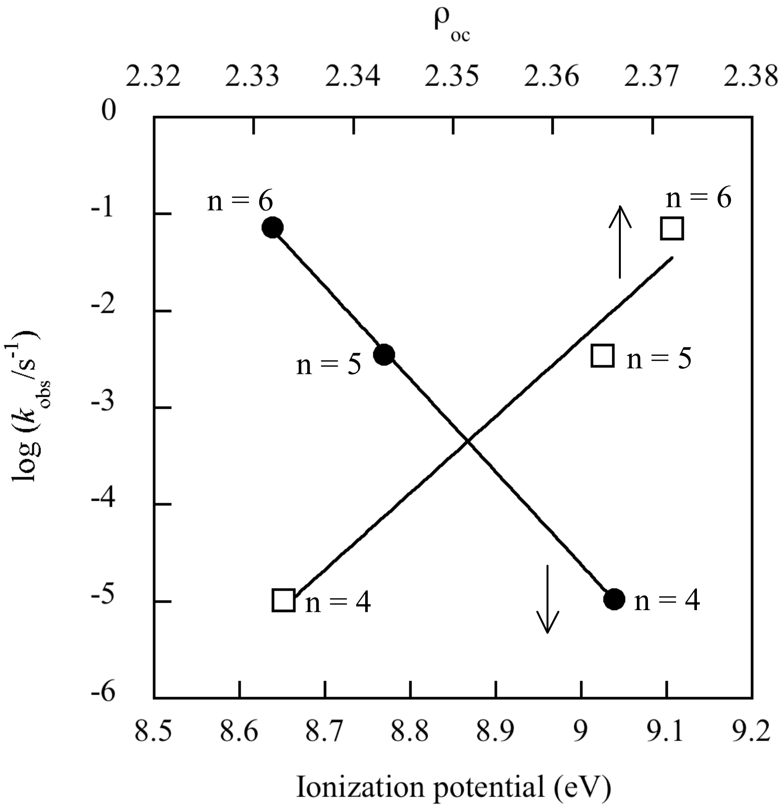


Figure 2-2. Plot of log(k_{obs}) for *cis*-to-*trans* isomerization of CH_3O-n in acetonitrile against the ionization potential (●) and calculated electron-donating character of N (ρ_{oc}, □) for cyclic amines

The slower reaction rates observed for morpholine derivatives when compared to those for piperidine derivatives can also be explained in terms of the electron-donating character of N(3). The slower rates are attributed to the decrease in the electron-donating character of N(3) in triazenes as a result of the inductive (-I) effect of the oxygen atom in morpholine. It should be pointed out here that similar ring effects are also found on the restricted rotation energy barrier for C–N amide bond in amides with cyclic amine rings. Dynamic NMR studies show that the restricted rotation energy barrier for an amide with a 5 member ring is lower than that with a 6 member ring,[65,66] which in turn is larger than that with morpholine,[65] indicating that the electron donating character of the nitrogen in the 6 member ring is larger than that in the 5 member ring and morpholine, in good agreement with the ionization potential and RHO calculation studies on cyclic amines, as well as our observed trend in isomerization rates for target triazenes.

The ability of the phenyl ring to stabilize the negative charge on N(1) is another key factor in determining the N(1)=N(2) bond order of the ground state *cis* isomer and thus the rotation energy barrier. As the electron withdrawing character of the *para* substituent on the substituted phenyl ring increases, the stability of the negative charge on N(1) would increase, leading to both an increase in the contribution of the 1,3-dipolar resonance form to the ground *cis*-structure and a stabilization of the dipolar transition state, and thus a decrease in the rotation energy barrier and an increase in the rate constant for isomerization. A quantitative analysis of this substituent effect can be carried out using the Hammett equation. This equation is only applicable to *para* and *meta* substituted aromatic compounds, since *ortho*-substituent groups may also cause steric hindrance effects.[67] The Hammett equation applicable to rate constants is written as shown in Eq. 2-1,

$$\log k_X = \log k_H + \rho\sigma \qquad \text{Eq. 2-1}$$

where k_X represents the reaction rate constant for the substituted aromatic substrate and k_H is the reaction rate constant for the unsubstituted aromatic substrate. The parameter σ is the Hammett substituent constant and measures the electronic character (electron-donating or electron-withdrawing) of the substituent group relative to H. A positive σ value refers to an electron-withdrawing group, and the more positive the σ value is, the stronger the electron-withdrawing character is. Oppositely, a negative σ value refers to an electron-donating group, and the more negative the σ value is, the stronger the electron-donating character is. The parameter ρ is called the Hammett reaction constant and measures the sensitivity of the reaction to electronic effects. A positive ρ value implies more electrons flow towards the aromatic ring in the transition state than in the ground state of starting materials. On the contrary, a negative ρ value implies fewer electrons flow to the aromatic ring in the transition state than in the ground state of starting materials. Hammett plots for rate constants for *cis*-to-*trans* isomerization of substrates X-4 and X-5 in acetonitrile are shown in Figure 2-3. The Hammett reaction constant ρ values are obtained from the slopes of the linear plots for X-4 and X-5. The positive ρ values (4.8 ± 0.3 for X-4 and 6 ± 1 for X-5) are consistent with an increase in electron density at N(1) in the transition state as rotation around the N(1)=N(2) bond takes place. Though the ρ value for X-5 is based on only three points, it is somewhat higher than that for X-4. If this difference is real, it would indicate that X-5 is more sensitive to the electronic character of the phenyl ring than X-4.

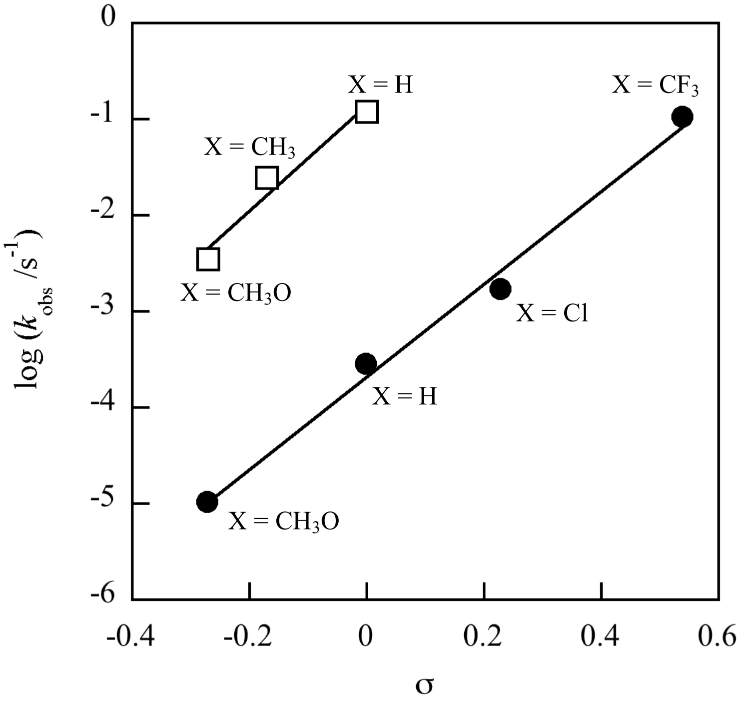
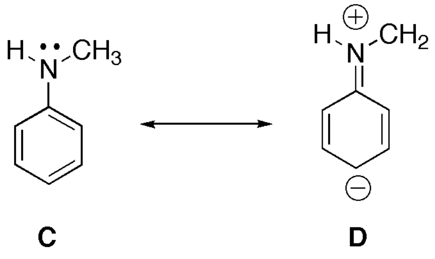


Figure 2-3. Hammett plot for first-order rate constants for *cis*-to-*trans* isomerization of X-4 (●) and X-5 (□) in acetonitrile.

Quantitative analyses have also been performed for substituent effects on thermal *cis*-to-*trans* isomerization rate constants of monosubstituted diazobenzenes[68] and 4'-X-4-diethylaminoazobenzenes[69]. Isomerization rate constants are found to increase regardless of the nature (electron-withdrawing or electron-donating) of the substituents. As a consequence, "V-shaped" Hammett plots are obtained. For 4'-X-4-diethylaminoazobenzenes, the ρ values are -3.15 (when X = electron-donating group) and 10.2 (when X = electron-withdrawing group) in DMF solutions.[69] The negative ρ value is ascribed to an inversion isomerization mechanism.[1,2] The increase in rate constant with increasing electron-donating character of the substituent group is attributed to the increasing possibility of both azo nitrogen atoms to act as sp-rehybridized sites. However, the positive ρ value cannot be unambiguously explained in terms of an inversion mechanism or a rotation mechanism.[69] In the inversion mechanism, an increase in the electron-withdrawing character of the substituent at the *para* position of the phenyl ring would increase the stability of the inversion transition state by increasing the conjugative delocalization of the lone pair electrons of nitrogen in the rehybridized transition state;[70,71] in the rotation mechanism, an increase in the electron-withdrawing character of the phenyl substituent would increase the stability of the rotation transition state by stabilizing the negative charge on N. The same argument can be used on the linear Hammett plots shown in Figure 2-3, i.e., the inversion mechanism for thermal *cis*-to-*trans* isomerization of target triazenes can not be excluded based only on this substituent effect. However, the size of the cyclic amine ring of target triazenes is another important factor influencing the isomerization rate constants. As mentioned in Section 1.6, when the size of the cyclic amine ring increases, the mesomerically electron-donating character of N(3) increases. Electron-withdrawing substituents on N(2) would strongly decrease the inversion energy barrier[52] whereas, as already discussed, electron-donating substituents are expected to decrease the rotation energy barrier by stabilizing the positive charge of the dipolar transition state. In addition, N(2) is unlikely to be the rehybridization site for an inversion mechanism due to the "hetero effect",[52] as mentioned in Section 1.5.2. Therefore, an inversion mechanism can be excluded as the isomerization mechanism for the target triazenes.

The stabilization of the polar transition state shown in Scheme 2-1, and hence the corresponding energy barrier for rotational isomerization, will be affected by the polarity of the solvent. The experimental results show that rate constants for thermal *cis*-to-*trans* isomerization are solvent dependent, i.e., rate constants increase with solvent polarity, particularly in polar aprotic solvents. This acceleration indicates an increase in molecular dipole moment from the *cis* ground-state to the transition state. As illustrated in Scheme 2-1, isomerization via a rotation mechanism undoubtedly generates a transition state more polar than the ground state *cis* isomer. The decrease in isomerization rate constant for target triazenes in alcohols relative to that in polar aprotic solvents (as shown in Table 2-2 and Table 2-3) is thought to be due to hydrogen bonding effects. Alcohols, hydrogen bond donor solvents, can stabilize the canonical form **A** (Scheme 2-2) through hydrogen bonding of the N(3) lone pair electrons, resulting in a decrease of the donating ability of N(3) and consequently, an increase in the N(1)=N(2) bond order and a decrease of the isomerization rate constant. This explanation is based on dynamic NMR studies on solvent effects on the N−Ph internal restricted rotation energy barrier in N-methylaniline.[72] The N−Ph internal restricted rotation energy barrier in hydrogen bond donor solvents is found to be much lower than that in hydrogen bond acceptor solvents (e.g., $\Delta G^{\ddagger} = 6.1$ kcal/mol in $CHCl_2F-CHF_2Cl$ mixture; $\Delta G^{\ddagger} = 7.24$ kcal/mol in dimethyl ether). Moreover, less downfield shift of the *para* ^{13}C chemical shift in hydrogen bond acceptor solvents in comparison to that in hydrogen bond donor solvents is observed. These differences are attributed to stabilization, in hydrogen bond donor solvents, of the canonical form **C** (in Scheme 2-3) via hydrogen bonding to the lone pair electrons of nitrogen, resulting in a relative low rotation energy barrier; while hydrogen bond acceptor solvents increase the double bond character of the Ph−N bond by stabilizing the canonical form **D** (in Scheme 2-3), resulting in a relative high rotation energy barrier.[72]



Scheme 2-3. Resonance structures of N-methylaniline

Upon irradiation of target triazenes, not only *trans*-to-*cis* isomerization takes place, but also photolytic cleavage of the N(2)–N(3) bond (as shown in Scheme 1-5) can occur. As mentioned at the beginning of this section, the contribution of the 1,3-dipolar resonance form of triazenes will be affected by the ability of the phenyl ring and the cyclic amino moiety to stabilize the negative charge on N(1) and positive charge on N(3), respectively. An increase of the contribution of the 1,3-dipolar resonance form to the *cis* ground state structure will decrease the N(1)=N(2) bond order, resulting in an increase of the isomerization rate constant; it will as well increase the N(2)–N(3) bond order, resulting in a decrease in the photolytic decomposition. As shown in Table 2-4 and Table 2-5, the photolytic decomposition for target triazenes is indeed influenced by the cyclic amine ring and the electronic character of the substituted phenyl ring, i.e., the percent decomposition typically decreases as the ring size of the cyclic amine increases, the electronegativity of the ring atoms decreases, and the electron withdrawing character of the *para* substituent increases. As mentioned in Section 1.3, this substituent effect is observed as well on the photolysis quantum yield of 1-phenyl-3,3-dialkyltriazenes.[10]

The photolytic decomposition is also greatly dependent on the polarity of the solvent, as shown in Table 2-4 and Table 2-5. In cyclohexane, the poorest solvent employed in this study for stabilization of dipolar forms, significant decomposition is observed with substrates having a strong electron-donating substituent (CH_3O). In polar aprotic solvents, the photolytic decomposition of substrates with electron-withdrawing groups is below 1 %. It is found as well that the photolysis quantum yield for 1-phenyl-3,3-dialkyltriazenes decreases as the polarity of the solvent increases.[58] In alcohols solutions, the photolytic decomposition for compounds with the strongest electron-donating substituent (CH_3O) used in this study exceeds 20 %, much higher than that in aprotic solvents. The much larger decomposition observed in alcohols is attributed to the same hydrogen bonding effect invoke to rationalize the trend in isomerization rate constants.[72] Alcohols can stabilize the canonical form **A** in Scheme 2-2 through hydrogen bonding of the N(3) lone pair electrons, decreasing the contribution of the 1,3-dipolar resonance and hence, decreasing the partial double bond character of the N(2)–N(3) bond. Overall, significant photolytic decomposition is found in conditions under which the 1,3-dipolar resonance form is least likely to be stabilized.

As pointed out in Section 1.4, the origin of the N(2)–N(3) restricted rotation of triazenes is its partial double bond character, resulting from the contribution of a 1,3-dipolar resonance form. Many studies have shown an increase in the rotation energy barrier of the N(2)–N(3) bond of *trans*-1-phenyl-3,3-dialkyltriazenes and *cis*-1,3-diphenyltriazenes with an increase in the electron-withdrawing character of the substituent on the phenyl ring.[33,34,42] Additionally, as mentioned in Section 1.5.1, the energy barrier for restricted rotation of *cis*-diphenyltriazenes is found to decrease as the polarity of the solvent increases.[42] Both an increase in the electron-withdrawing character of the phenyl ring substituent and in the polarity of solvent result in an increase in the contribution of the 1,3-

dipolar resonance form and hence, in the N(2)–N(3) bond order, in agreement with the results described above on the photolysis yields for target triazenes.

2.3 Conclusions

Rate constants for thermal *cis*-to-*trans* isomerization of N-(phenylazo)-substituted nitrogen heterocycles are found to increase as the size and electron-donating character of the cyclic amine increases, as the electron-withdrawing character of the *para* substituent group on the phenyl ring increases, and as the polarity of the solvent increases. All these experimental observations are in agreement with a rotational isomerization mechanism involving a dipolar transition state. On the other hand, photolytic cleavage of the N(2)–N(3) bond is found to decrease as the size and electron-donating character of the cyclic amine increases, as the electron-withdrawing character of the *para* substituent group on the phenyl ring increases, and as the polarity of the solvent increases. These opposite electronic and solvent effects on isomerization rate constants and decomposition yields are attributed to the predominant role the 1,3-dipolar resonance form of triazenes plays, i.e., an increase in the contribution of the 1,3-dipolar resonance form decreases the N(1)=N(2) bond order while increases the N(2)–N(3) bond order, resulting in a decrease in the isomerization energy barrier and an increase in the photodecomposition energy barrier.

3 Theoretical simulations

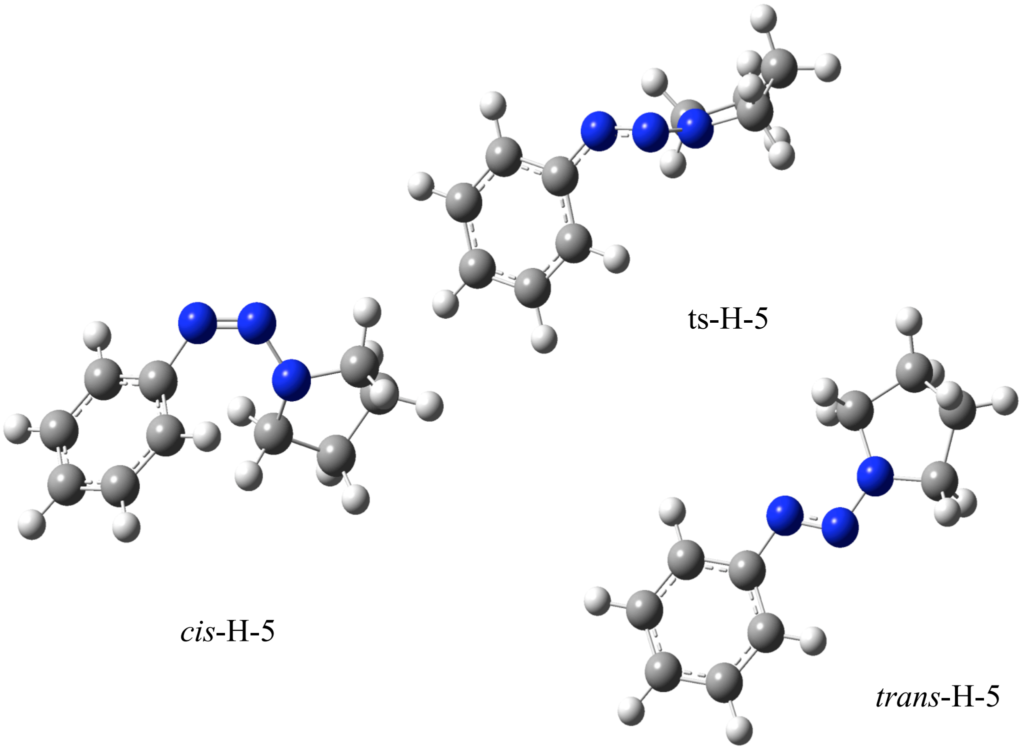
Theoretical calculations are regarded as powerful tools to predict and simulate chemical reactions as well as to obtain geometrical parameters of chemical substrates. As pointed out in Section 1.7, there is no theoretical study on the *cis*-*trans* isomerization mechanism of triazenes available so far. In order to compare with the experimental results presented in Chapter 2, geometry optimizations of the *cis* and *trans* ground-states as well as of the transition states of target triazenes were performed in both the gas phase and in various solvents. In addition, reaction coordinates for inversion and rotation isomerization pathways were generated.

3.1 Results and discussion

Firstly, ground state structures for *cis* and *trans* target triazenes are optimized in the gas phase, followed by optimization of the corresponding transition state. Shown in Figure 3-1 are the optimized structures of the *cis*, *trans*, and transition state forms of H-5. The phenyl ring in the optimized *cis* isomer is not on the same plane formed by the three nitrogen atoms due to the steric repulsion between the phenyl ring and the cyclic amine. Lacking steric repulsion, in the optimized *trans* isomer the phenyl ring is almost in the same plane of the triazeno group, in agreement with the optimized structure of *trans*-1-phenyl-3,3-penta-methylenetriazenes.[62] Selected optimized parameters for *cis* and *trans* isomers, and corresponding transition states, for CH_3O-n, H-n, CH_3-5, Cl-4 and CF_3-5 are shown in

Table 3-1 and 3-2. For any given substrate, it is noticed that the N(1)=N(2) bond length in the *cis* isomer is shorter than that in the corresponding *trans* form. On the contrary, the

N(2)–N(3) bond length in the *cis* isomer is longer than that in the corresponding *trans* form. These trends are attributed to the 1,3-dipolar resonance form having a larger contribution in the *trans* isomer than that in the *cis* form, i.e., the coplanar structure between the phenyl ring and the three nitrogen atoms in the *trans* form allows the delocalization of the negative charge on N(1) into the phenyl ring and thus a stabilization of the 1,3-dipolar resonance form. Same trends are found for the bond lengths of the *cis* isomers when compared to those for the transition state, i.e., for any given substrate, the N(1)=N(2) bond length in the transition state is longer than that in the corresponding *cis*



ts-H-5

cis-H-5

trans-H-5

Figure 3-1. Calculated structures for *cis, trans* and transition state (ts) forms of H-5

Table 3-1. Selected optimized parameters for *cis* and *trans* isomers and transition states corresponding to CH_3O-n, Cl-4, CF_3-4 and CH_3-5.

	CH_3O-4			CH_3O-5		
	Cis	TS	*Trans*	*Cis*	TS	*Trans*
N(1)=N(2) (Å)	1.257	1.265	1.266	1.257	1.271	1.273
N(2)–N(3) (Å)	1.365	1.323	1.339	1.372	1.321	1.323
C–N(1)=N(2)–N(3) (°)	-7.6	-89.5	-177.2	11.1	91.6	-179.9
Dipole (D)	3.716	5.030	1.812	3.557	5.405	2.369
	CH_3O-6			CH_3O-7		
	Cis	TS	*Trans*	*Cis*	TS	*Trans*
N(1)=N(2) (Å)	1.252	1.266	1.265	1.258	1.267	1.269
N(2)–N(3) (Å)	1.401	1.332	1.346	1.370	1.328	1.336
C–N(1)=N(2)–N(3) (°)	8.3	89.4	175. 6	-10.6	-89.0	-176.0
Dipole (D)	3.339	4.877	1.625	3.909	4.882	1.778
	CH_3O-6-O			CH_3-5		
	Cis	TS	*Trans*	*Cis*	TS	*Trans*
N(1)=N(2) (Å)	1.250	1.260	1.264	1.257	1.272	1.273
N(2)–N(3) (Å)	1.407	1.338	1.350	1.365	1.318	1.321
C–N(1)=N(2)–N(3) (°)	8.0	89.3	175.7	11.5	91.7	-179.8
Dipole (D)	2.950	3.062	0.840	3.788	5.886	2.902
	Cl-4			CF_3-4		
	Cis	TS	*Trans*	*Cis*	TS	*Trans*
N(1)=N(2) (Å)	1.258	1.272	1.269	1.257	1.272	1.273
N(2)–N(3) (Å)	1.354	1.311	1.329	1.349	1.306	1.324
C–N(1)=N(2)–N(3) (°)	8.1	89.2	177.0	8.5	89.1	177.0
Dipole (D)	3.872	7.901	4.718	4.427	9.066	5.835

Table 3-2. Selected optimized parameters for *cis* and *trans* isomers and transition states corresponding to H-n.

	H-4			H-5		
	Cis	TS	*Trans*	*Cis*	TS	*Trans*
N(1)=N(2) (Å)	1.257	1.266	1.267	1.257	1.272	1.274
N(2)–N(3) (Å)	1.357	1.319	1.333	1.363	1.318	1.319
C–N(1)=N(2)–N(3) (˚)	7.7	89.4	177.0	11. 9	91.5	-179.6
Dipole (D)	3.792	5.644	2.495	3.812	6.064	3.322
	H-6			H-6-O		
	Cis	TS	*Trans*	*Cis*	TS	*Trans*
N(1)=N(2) (Å)	1.253	1.266	1.266	1.251	1.263	1.265
N(2)–N(3) (Å)	1.382	1.329	1.341	1.388	1.333	1.344
C–N(1)=N(2)–N(3) (˚)	8.9	89.1	175.6	8.4	89.3	175.5
Dipole (D)	3.510	5.710	2.581	2.277	3.892	0.963

isomer, while the N(2)–N(3) bond length in the transition state is shorter than that in the corresponding *cis* form. In addition, the C–N(1)=N(2)–N(3) dihedral angle in the transition state is around 90˚, indicating that a rotation takes place around the N(1)=N(2) bond. For any given substrate, an increase in the dipole moment is also obtained, e.g., the dipole moment of the transition state is larger than that for the *cis* form. All these changes in geometrical parameters for the transition state relative to the *cis* isomer indicate a rotation mechanism for *cis*-to-*trans* isomerization, in which rotation around the ruptured N(1)=N(2) double bond leads to a dipolar transition state.

These theoretical calculation results are in excellent agreement with the proposed rotation mechanism for thermal *cis-trans* isomerization of target triazenes presented in Chapter 2. As mentioned in Section 1.5.2, there are two possible mechanisms for *cis-trans* isomerization of target triazenes: inversion and rotation. In order to compare the energy barrier for the inversion pathway to that of the rotation one, the corresponding reaction coordinates for H-5 in the gas phase are generated by relaxed scanning the C–N(1)=N(2) bond angle and C–N(1)=N(2)–N(3) dihedral angle; these are shown in Figure 3-2, in which all energies are given relative to the energy of the ground-state *trans* isomer. Estimated from the highest points along the reaction coordinates, the transition state for the inversion mechanism should be located at a C–N(1)=N(2) bond angle of 180° with an energy barrier of *ca.* 22.9 kcal/mol, while the transition state for the rotation mechanism should be located at a C–N(1)=N(2)–N(3) dihedral angle of 92° with an energy barrier of *ca.* 19.6 kcal/mol. In fact, the transition state structure found through the rotational reaction coordinates is consistent with the one optimized from the *cis* and *trans* isomers shown in Table 3-2. It is clear from Figure 3-2 that the energy barrier for isomerization through inversion is higher than that through rotation. On the contrary, theoretical calculations on the isomerization of diazobenzenes show that the isomerization energy barrier through rotation is higher than that through inversion.[71,73] It is noticed that the energy barrier for inversional isomerization of *p*-amino-azobenzene is around 24 kcal/mol, in which the inversion site is on the nitrogen attached to the unsubstituted phenyl.[73] This value is comparable to the inversional energy barrier for the isomerization of H-5 (22.9 kcal/mol), in which the inversion site is also on the nitrogen attached to a phenyl ring.

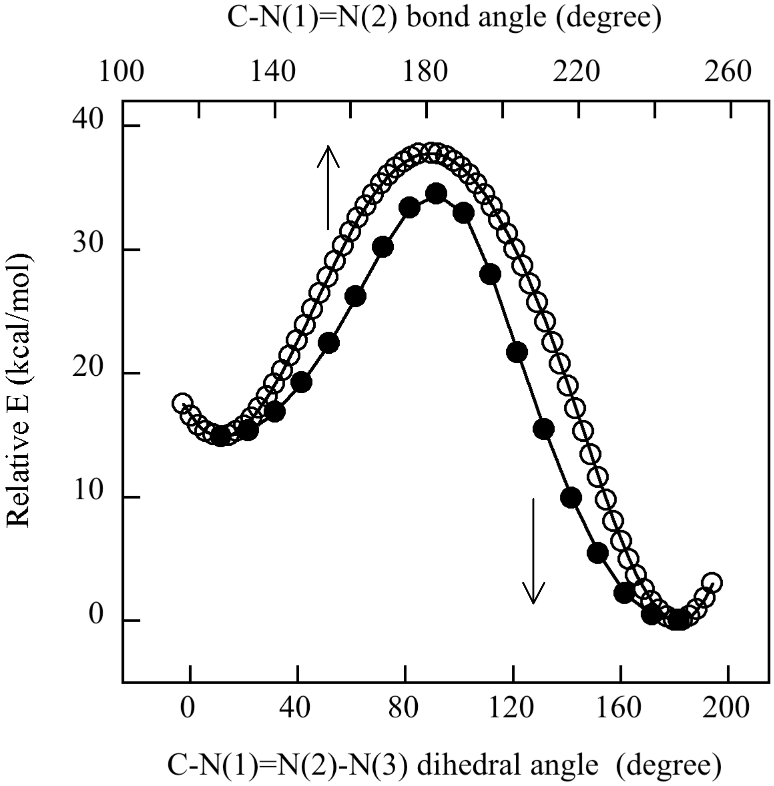


Figure 3-2. Reaction coordinates for H-5 by scanning the C–N(1)=N(2) bond angle (○) and C–N(1)=N(2)–N(3) dihedral angle (●).

A three-dimensional potential energy surface and a contour map are generated also for H-5 in gas phase by relaxed scanning of the C–N(1)=N(2) bond angle together with that of the C–N(1)=N(2)–N(3) dihedral angle. The surface is quite symmetrical and two *cis* minima with two corresponding *trans* minima are shown in Figure 3-3. In agreement with the reaction coordinates shown in Figure 3-2, the saddle point along the inversion pathway is found at a C–N(1)=N(2) bond angle of 180˚, with an energy barrier at *ca.* 22.9 kcal/mol; while that along the rotation pathway is found at a C–N(1)=N(2)–N(3) dihedral angle of

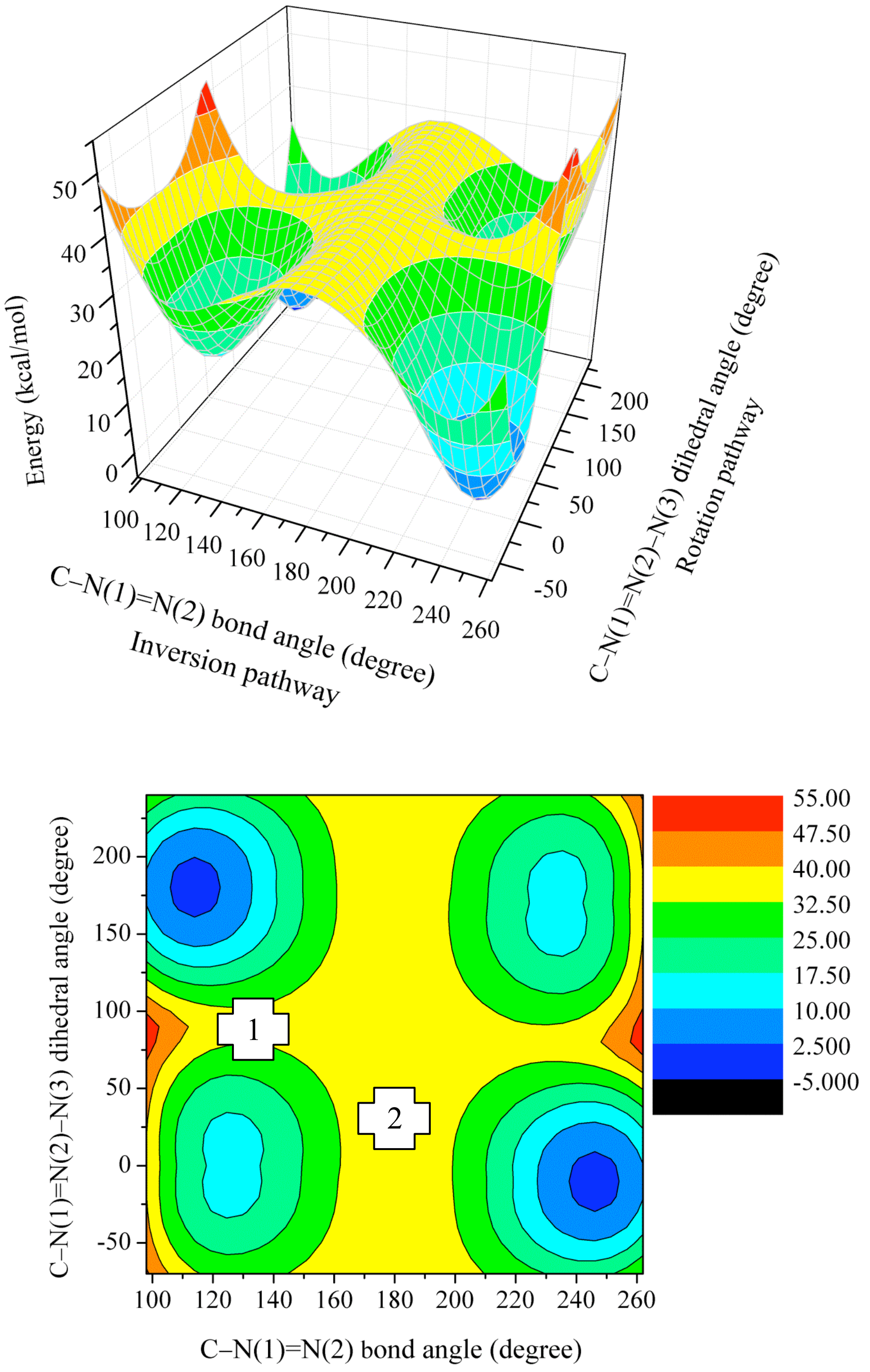


Figure 3-3. Potential energy surface (top) and contour map (bottom) for H-5 in the gas phase. Labeled point 1 and point 2 in the counter map represent saddle points for *cis*-to-*trans* isomerization through the inversion and rotation mechanisms, respectively.

ca. 92˚, with an energy barrier at *ca.* 19.6 kcal/mol. These two saddle points are labeled as point 1 and 2 in the counter map, representing the inversion and rotation isomerization pathways, respectively.

As mentioned in Section 2.2, the observed rate constants for thermal *cis*-to-*trans* isomerization of target triazenes are found to increase as the ring size of the cyclic amine increases, indicating a decrease of the isomerization energy barrier. This trend is reproduced by theoretical calculations of the energy barrier for isomerization of CH_3O-n and H-n in the gas phase. As shown in Figure 3-4, one can see that in both cases the energy barrier for isomerization decreases as the ring size increases from 4 to 7. In addition, as mentioned previously in Section 2.2, the inductive (-I) effect of the oxygen atom present in morpholine decreases the electron-donating character of the nitrogen and therefore decreases the k_{obs} for isomerization. This effect is also reproduced by theoretical calculations, i.e., the relative higher energy barrier for X-6-O in comparison to X-6 is clearly shown in Figure 3-4 (X = CH_3O and H).

Regarding the substituent effects on the isomerization rate constant, the same trend observed experimentally is reproduced by theoretical calculations on the energy barriers for X-4 and X-5 in the gas phase, i.e., the energy barrier decreases as the electron-withdrawing character of the substituent group on the phenyl ring increases (Figure 3-5). The ρ value for X-5 (8 ± 3) is slightly larger than that for X-4 (6.0 ± 0.7), consistent with the Hammett plots shown in Figure 2-3, indicating target substrates with a larger cyclic amine ring are more sensitive to the electronic character of the substituent on the phenyl ring.

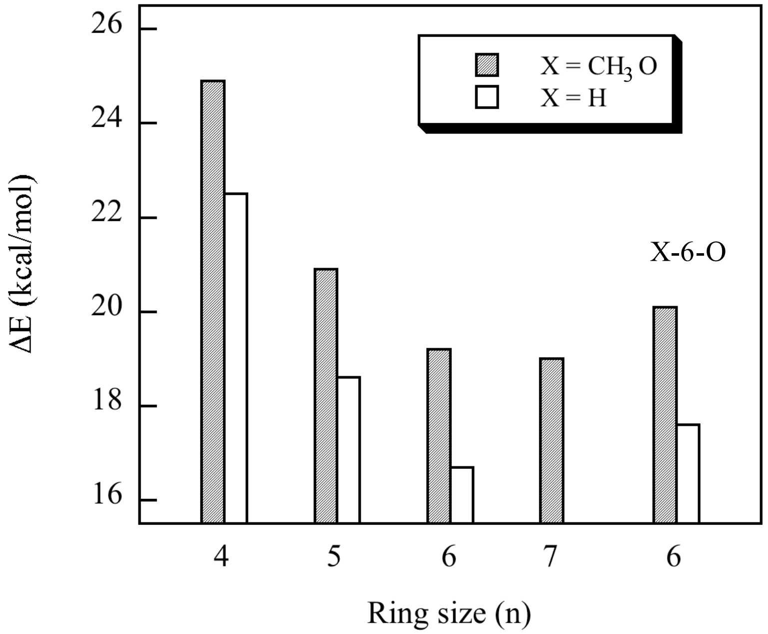


Figure 3-4. Calculated energy barriers for isomerization of CH_3O-n and H-n in gas phase.

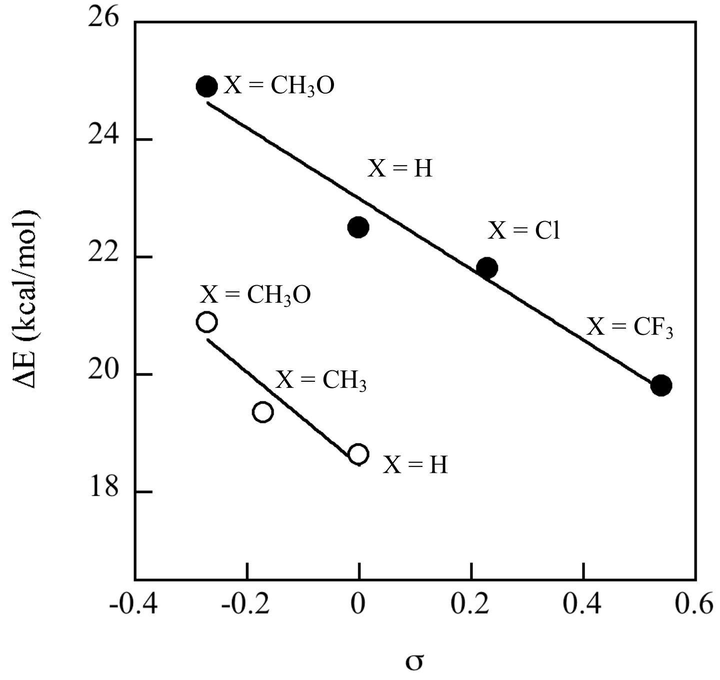


Figure 3-5. Hammett plots for calculated isomerization energy barriers for X-4 (●) and X-5 (○) in the gas phase.

Geometry optimizations of *cis*, *trans*, and transition state forms of target triazenes were also performed in various solvents (data shown in Appendix A). Changes in N(1)=N(2) and N(2)−N(3) bond lengths, C−N(1)=N(2)−N(3) dihedral angles, and dipole moments for *cis*, *trans*, and transition state forms all follow the same trends as those described in the gas phase. Therefore, theoretical calculations in solvents also predict a rotation mechanism for *cis*-to-*trans* isomerization as in the gas phase. The trends shown in the gas phase as a function of phenyl substituent and ring size are also observed for X-5 in cyclohexane and DMSO, and for H-n (n = 4-6) in benzene. In addition, the calculated energy barriers for *cis*-to-*trans* isomerization of H-4, Cl-4, CH_3-5, H-5, and CH_3O-5 in various solvents are found to decrease as the polarity of the solvent increases, consistent with the solvent effect experimentally observed. For example, shown in Figure 3-6 is the calculated energy barrier for *cis*-to-*trans* isomerization of H-5 in various solvents. It can be seen that the isomerization energy barrier in the gas phase is the highest, those in nonpolar solvents (cyclohexane and benzene) are lower, and those in polar solvents (acetonitrile, DMSO and alcohols) are the lowest. Overall, this trend is in good agreement with the experimentally observed solvent effect described in Section 2.2.

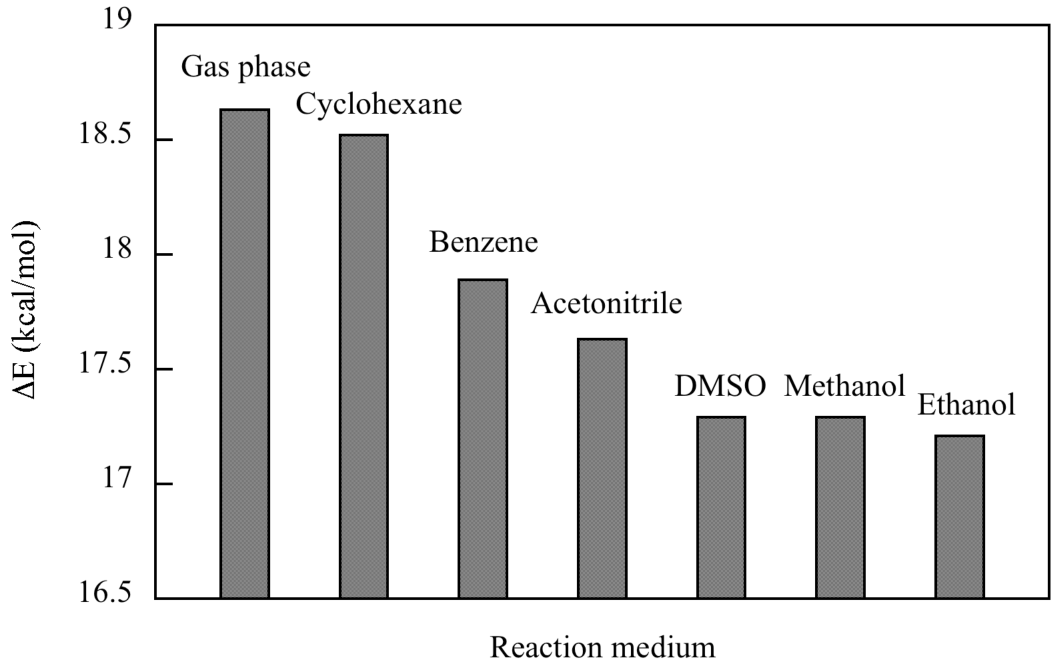


Figure 3-6. Isomerization energy barrier for H-5 in various reaction media.

3.2 Conclusions

The thermal *cis*-to-*trans* isomerization of target substrates is predicted to proceed via a rotation mechanism involving twisting around the C–N(1)=N(2)–N(3) bond and a dipolar transition state, in both the gas phase and solvents. In comparison with the *cis* ground state, the transition states show lengthening of the N(1)=N(2) bond, shortening of the N(2)−N(3) bond, an increase of the C−N(1)=N(2)−N(3) dihedral angle, and an increase in molecular dipole moment. The reaction coordinates for the inversion and rotation pathways, as well as the three dimensional potential energy surface and counter map, all show that the energy barrier for the rotation mechanism is lower than that in the inversion mechanism. Moreover, the cyclic amine ring effect, the phenyl substituent effect, and the solvent effect predicted on the calculated energy barriers for thermal *cis*-to-*trans* isomerization are all in good agreement with those obtained from the experimental studies described in Chapter 2.

4 Experimental

4.1 Synthetic methods

4.1.1 Materials and instruments

Sodium nitrite (Sigma), 4-(trifluoromethyl)aniline (Sigma-Aldrich), *p*-chloroaniline (J. T. Baker), *p*-toluidine hydrochloride (Aldrich), azetidine hydrochloride (Aldrich), pyrrolidine (Aldrich), ethanol (Commercial Alcohols Inc.), petroleum ether (BDH) and all deuterated solvents (Cambridge Isotope Laboratories Inc.) were used as received. Aniline (J. T. Baker) was purified by reduced pressure distillation before use.

Melting points were measured on a Mel-Temp apparatus using open capillaries. ^{1}H NMR spectra were performed on a Bruker AVANCE 300 MHz nuclear magnetic resonance spectrometer in either $CDCl_3$ or acetone-d_6. The chemical shifts are referred to solvent signals (i.e., δ 2.05 for acetone-d_6 and δ 7.27 for $CDCl_3$). Mass spectra were obtained by electronspray ionization on a VG Model 7070E analytical organic mass spectrometer.

4.1.2 Synthesis of target N-(phenylazo) substituted nitrogen heterocycles

Target substrates CH_3O-n, H-n (n = 5-7, 6-O), and CF_3-5 were all synthesized by Kelvin Lau, by coupling of cyclic amines with aryl diazonium ions.[74] The same method was used to prepare CH_3-5, H-4, Cl-4 and CF_3-4; details for each of these compounds are presented below.

4.1.2.1 Synthesis of N-(*p*-methylphenylazo)pyrrolidine (CH_3-5)

p-Toluidine hydrochloride (0.4399 g, 3.1 mmol) and HCl solution (6 mL, 1 mol/L) were mixed in a 25 mL round bottom flask which was placed in an ice bath, and stirred for one hour. Pyrrolidine (0.2371 g, 3.3 mmol) and NaOH solution (3.5 mL, 1 mol/L) were mixed in a 50 mL round bottom flask and cooled in a fridge. A pre-cooled $NaNO_2$ solution prepared by dissolving 0.2011 g $NaNO_2$ in 2.6 mL H_2O was added slowly with a 100 μL syringe over 20 minutes into the 25 mL round bottom flask with constant stirring on ice bath to obtain the phenyl diazonium ions. After this addition, the solution was kept stirring for another 10 minutes and a transparent yellow solution was obtained. Then, the phenyl diazonium solution in the 25 mL flask was added slowly with a pipette into the 50 mL round bottom flask on an ice bath with stirring over 20 minutes. Light brown precipitate was formed. Several drops of NaOH solutions (1 mol/L) were used to maintain the pH between 7 and 8 with stirring for another hour on ice. The crude product was filtered out, washed with cold water, dried in the vacuum overnight at room temperature and recrystallized from ethanol, which yielded pale yellow crystals (0.4716 g, 83.1%); mp 79-80 °C (78.5-80 °C in ref. 25); ^1H NMR (300 MHz, $CDCl_3$, ppm) at R.T.: δ 7.30-7.27 (AA' of AA'BB', 2H, $H_{\textit{ortho to N(1)}}$), 7.12-7.09 (BB' of AA'BB', 2H, $H_{\textit{meta to N(1)}}$), 3.76 (br, 4H, $C\mathbf{H_2}NC\mathbf{H_2}$), 2.31 (s, 3H, CH_3), 2.00 (m, 4H, $C\mathbf{H_2}CH_2NCH_2C\mathbf{H_2}$).

4.1.2.2 Synthesis of N-(phenylazo)azetidine (H-4)

Distilled aniline (0.27 mL, 2.9 mmol) and HCl solution (9 mL, 1 mol/L) were mixed in a

25 mL round bottom flask which was placed in an ice bath, and stirred for one hour. Azetidine hydrochloride (0.2993 g, 3.2 mmol) and NaOH solution (6.5 mL, 1 mol/L) were mixed in a 50 mL round bottom flask and cooled in a fridge. A pre-cooled $NaNO_2$ solution prepared by dissolving 0.213 g $NaNO_2$ (2.9 mmol) in 1.5 mL H_2O was added slowly with a 100 μl syringe over 30 minutes into the 25 mL round bottom flask with constant stirring on ice bath to obtain the phenyl diazonium ions. After this addition, the solution was kept stirring for another 30 minutes and a transparent yellow solution was obtained. Then, the phenyl diazonium solution in the 25 mL flask was added slowly with a pipette into the 50 mL round bottom flask on an ice bath with stirring over 20 minutes. Several drops of NaOH solutions (1 mol/L) were used to maintain the pH between 7 and 8, with stirring for another hour on ice. A yellow oil was obtained. Ethyl ether (20-25 mL × 4 times) was used to extract the oil product from the reaction medium. The ethyl ether phase was dried with anhydrous sodium sulfate and then the ethyl ether was removed by evaporation, yielding a yellow oil (0.1386 g, yield 29.7 %); ^{1}H NMR (300 MHz, acetone-d_6, ppm) at R.T.: δ 7.36 (d, 2H, J = 7.4 Hz, $H_{\textit{ortho to N(1)}}$), 7.30 (t, 2H, J = 7.4 Hz, $H_{\textit{meta to N(1)}}$), 7.14 (t, 1H, J = 7.4 Hz, $H_{\textit{para to N(1)}}$), 4.24 (app. t, 4H, J = 7.1 Hz, $C\mathbf{H_2}NC\mathbf{H_2}$), 2.36 (app. quintet, 2H, J = 7.5 Hz, $CH_2C\mathbf{H_2}CH_2$); MS m/z (rel. intensity) (EI): 161 (M, 37), 105 (48), 77 (100); HRMS calc. for $C_9H_{11}N_3$ 161.0953; found: 161.0949.

4.1.2.3 Synthesis of N-(*p*-chlorophenylazo)azetidine (Cl-4)

p-Chloroaniline (0.3828 g, 3.0 mmol) and HCl solution (9 mL, 1 mol/L) were mixed in a 25 mL round bottom flask which was placed in an ice bath, and stirred for one hour.

Azetidine hydrochloride (0.3183 g, 3.3 mmol) and NaOH solution (6.6 mL, 1 mol/L) were mixed in a 50 mL round bottom flask and cooled in a fridge. A pre-cooled $NaNO_2$ solution prepared by dissolving 0.207 g $NaNO_2$ in 2 mL H_2O was added slowly with a 100 μl syringe over 20 minutes into the 25 mL round bottom flask with constant stirring on ice bath to obtain the *p*-chlorophenyl diazonium ions. After this addition, the solution was kept stirring for another 15 minutes and a transparent yellow solution was obtained. Then, the *p*-chlorophenyl diazonium solution in the 25 mL flask was added slowly with a pipette into the 50 mL round bottom flask on an ice bath with stirring over 20 minutes. Light brown precipitate was formed. Several drops of NaOH solutions (1 mol/L) were used to maintain the pH between 7 and 8 with stirring for another 20 minutes on ice. The crude product was filtered out, washed with cold water, dried in the vacuum overnight at room temperature, and recrystallized from ethanol, which yielded a light brown powder (0.2188 g, 37.3 %): mp 56-57°C; ^{1}H NMR (300 MHz, acetone-d_6, ppm) at R.T.: δ 7.38-7.29 (AA'BB', 4H, Ar), 4.27 (br, 4H, $C\mathbf{H_2}NC\mathbf{H_2}$), 2.38 (app. quintet, 2H, J = 7.5 Hz, $CH_2C\mathbf{H_2}CH_2$); MS m/z (rel. intensity) (EI): 195 [M (^{35}Cl), 26], 139 (44), 113 (32), 111 (100); HRMS calc. for $C_9H_{10}{}^{35}ClN_3$ 195.0563; found: 195.0564.

4.1.2.4 Synthesis of N-(*p*-trifluoromethylphenylazo)azetidine (CF_3-4)

4-(Trifluoromethyl)aniline (0.4354 g, 2.7 mmol) and HCl solution (8 mL, 1 mol/L) were mixed in a 25 mL round bottom flask which was placed in an ice bath, and stirred for one hour. Azetidine hydrochloride (0.2809 g, 3.0 mmol) and NaOH solution (6 mL, 1 mol/L) were mixed in a 50 mL round bottom flask and cooled in a fridge. A pre-cooled $NaNO_2$

solution prepared by dissolving 0.2109 g $NaNO_2$ in 2 mL H_2O was added slowly with a 100 μl syringe over 20 minutes into the 25 mL round bottom flask with constant stirring on ice bath to obtain the *p*-trifluoromethylphenyl diazonium ions. After this addition, the solution was kept stirring for another 15 minutes and a transparent yellow solution was obtained. Then, the *p*-trifluoromethylphenyl diazonium solution in the 25 mL flask was added slowly with a pipette into the 50 mL round bottom flask on an ice bath with stirring over 15 minutes. A light yellow precipitate was formed. Several drops of NaOH solutions (1 mol/L) were used to maintain the pH between 7 and 8 with stirring for another 10 minutes on ice. The crude product was filtered out, washed with cold water, dried in the vacuum overnight at room temperature, and recrystallized with petroleum ether (60-80°C), which yielded bright yellow crystals (0.3750 g, 60.6 %): mp 78-77°C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) at R.T.: δ 7.57-7.54 (AA' of AA'BB', 2H, $H_{\textit{meta to N(1)}}$), 7.49-7.46 (BB' of AA'BB', 2H, $H_{\textit{ortho to N(1)}}$), 4.37 (app. t, 4H, J = 7.3 Hz, $C\mathbf{H_2}NC\mathbf{H_2}$), 2.41 (app. quintet, 2H, J = 7.6 Hz, $CH_2C\mathbf{H_2}CH_2$); MS m/z (rel. intensity) (EI): 229(M, 19), 173 (30), 145 (100); HRMS calc. for $C_{10}H_{10}F_3N_3$, observed: 229.0827; found: 229.0824

4.2 Kinetic studies

4.2.1 Materials and instruments

Benzene, cyclohexane, DMSO, methanol, 2-propanol, acetonitrile and toluene, (OmniSolv, EM Science), as well as ACS grade solvents DMF (Caledon), ethanol (Commercial Alcohols Inc.), 1-propanol (BDH), 1-butanol (EM Science) and 1-octanol (J. T. Baker) were all used as received. Ultra pure water was obtained by passing deionized water through a Millipore Milli-Q system.

Irradiations were carried out using a photochemical reactor containing one 350 nm UV lamp (RPR-3500, Southern N.E. Ultraviolet Co.) Kinetic traces were recorded using a Varian Cary 1 Bio UV-visible spectrophotometer.

4.2.2 Sample preparation and experimental methods

Sample solutions are kept in 7 x 7 mm^2 quartz cells, either having an absorbance of 0.5 ± 0.05 at 350 nm or a concentration of 1.05 x 10^{-4} mol/L. Concentrated stock solutions of target triazenes are prepared in acetonitrile in a 1 mL volumetric flask, then 64 μl of this stock solution are added to the desired solvent in a 5 mL flask. All sample solutions are irradiated for 30 seconds in the photochemical reactor, where the *trans* triazenes photoisomerize to the *cis* forms. Then the samples are immediately placed in the UV-visible spectrophotometer for kinetic measurements, which are carried out by monitoring the absorbance at 325 nm as a function of time. Kinetic runs for *cis*-to-*trans* isomerization of each solution are carried out at least twice (typically four times) and the average values for rate constants and photolysis yields are presented. The temperature during the kinetic study is controlled at 21.0 ± 0.1 ˚C, using a circulating water-bath.

Kinetic traces are fitted to a first-order exponential equation as shown in Eq. 4-1, using the general curve fitting procedure of Kaleidagraph^{TM} from Synergy Software, where A_i and A_f represent the initial and final absorbances (Figure 4-1), k_{obs} is the first-order rate constant and t is time.

$$A = A_f + (A_i - A_f)\exp(-k_{obs}t) \qquad \text{Eq. 4-1}$$

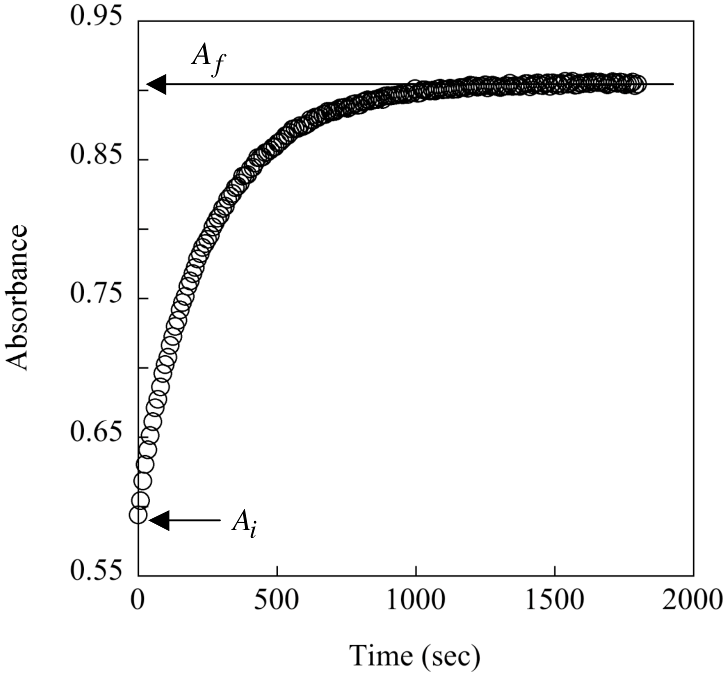


Figure 4-1. Typical kinetic trace for thermal *cis*-to-*trans* isomerization of target triazenes recorded by UV-visible spectroscopy

According to Beer's law, absorbance is directly proportional to the concentration of the light-absorbing species. Thus, a change in the absorbance upon irradiation reflects a change in the concentration of the target *trans* triazenes. The percent decomposition of triazenes was calculated by comparing the absorbance before irradiation (A_0) and after isomerization (A_f), as shown in Eq. 4-2.

$$\% \, Decomposition = (1 - \frac{A_f}{A_0}) \times 100\% \qquad \text{Eq. 4-2}$$

4.3 Theoretical studies

All calculations were done on a Linux work station using the Gaussian 03 package of programs.[75] Molecular geometry optimizations were performed by using *ab initio* density-functional theory (DFT) with the B3LYP functional and the 6-31G* basis set. Only one imaginary frequency was obtained for each optimized structure corresponding to a transition-state, using QST2 or QST3 methods. In the case of QST2 method, transition states are generated freely based on the entered starting *cis* isomer and target *trans* isomer, both of which have been previously optimized. In the case of QST3 method, a proposed transition state is added in the input file after the starting *cis* and target *trans* isomers. Calculations in various solvents were performed using the default method (PCM). The cartesian coordinates, imaginary frequencies (where applicable), and energies for all optimized structures are given in Appendix B.

In order to test the method of choice (i.e., DFT-B3LYP/6-31G*), optimization of *trans*-(2,6-*cis*-dimethyl-N-phenylazo)piperidine (Figure 4-2) was performed and compared with experimental X-ray data of this compound.[24] The reason why target triazenes were not used for comparison is that no related X-ray data could be found. The results in Table 4-1 show that this method reproduces the structural experimental data very well.

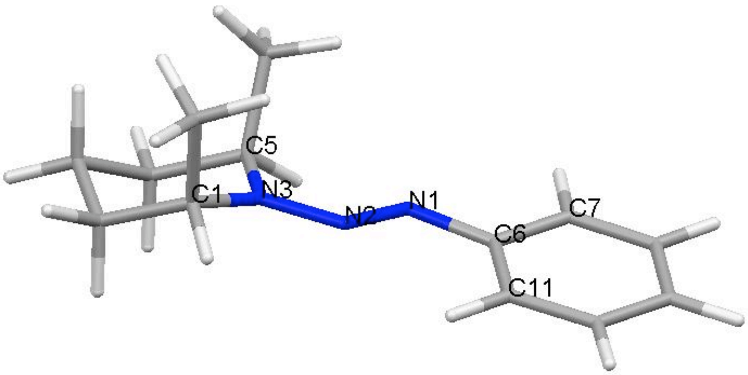


Figure 4-2. X-ray structure of *trans*-(2,6-*cis*-dimethyl-N-phenylazo)piperidine

Table 4-1. Geometrical parameters for *trans*-(2,6-*cis*-dimethyl-N-phenylazo)piperidine using DFT-B3LYP/6-31G* method

Parameter	Theoretical	X-ray	Parameter	Theoretical	X-ray
C6-N1	1.417	1.422	C5-N3-C1	123.3	123.1
N1=N2	1.269	1.260	C7-C6-C11-N1	-179.3	179.0
N2-N3	1.335	1.338	C11-C6-N1=N2	7.6	7.4
C6-N1=N2	113.7	112.5	C6-N1=N2-N3	-176.3	-175.6
N1=N2-N3	115.6	114.3	N1=N2-N3-C5	-2.4	-2.8
N2-N3-C5	121.9	122.7	N1=N2-N3-C1	-169.5	-170.4
N2-N3-C1	113.5	113.0	C5=N3-N2-C1	167.1	167.6

For all calculated structures (i.e., *cis* and *trans* forms and transition states), corresponding potential energy values (E_{ele}) were corrected by zero-point energy (ZPE) as shown in Eq. 4-3. There are two corrections included in this equation: one is the ZPE, as E_{ele} corresponds to the electronic energy state at absolute 0 K whereas at room temperature molecules are predominantly in their lowest vibrational energy state (higher than E_{ele} by the value of ZPE); the other correction is the scale factor f (0.9804),[76] as calculations performed are for the most abundant elements without consideration of isotopes, which have lower ZPE values due to their heavier masses.[77] Energy barriers were all calculated using the corrected potential energy values (E).

$$E = E_{ele} + ZPE \times f \qquad \text{Eq. 4-3}$$

Reaction coordinates for isomerization via inversion and rotation mechanisms were generated, respectively, by relaxed scanning of the C−N(1)=N(2) bond angle (from 116° to 255° at a 2° interval) and C−N1=N2-N3 dihedral angle (from 12° to 182° at a 10° interval). The three-dimensional potential energy surface was generated by relaxed scanning of the C−N1=N2 bond angle (from 98° to 178°, at a 5° interval) together with that of the C−N(1)=N(2)−N(3) dihedral angle (from −70° to 240°, at a 10° interval). The remaining points in the potential energy surface (C−N1=N2 bond angle from 182° to 262°) are found through symmetry. For each step calculation during scanning, the C−N(1)=N(2) bond angle and C−N(1)=N(2)−N(3) dihedral angle were fixed at the setting values, while the rest of the geometric parameters were optimized.

References

(1) Kolar, G. F. In *Chemical Carcinogens*; 2nd ed.; Searle, C. E., Ed.; ACS: Washington, D. C., 1984; Vol. 2, (a) p 870, (b) p 872-907.

(2) Lazny, R.; Sienkiewicz, M.; Brase, S. *Tetrahedron* **2001**, *57*, 5825-5832.

(3) Kimball, D. B.; Haley, M. M. *Angew. Chem. Int. Ed.* **2002**, *41*, 3338-3351.

(4) Carvalho, E.; Francisco, A. P.; Iley, J.; Rosa, E. *Bioorg. Med. Chem.* **2000**, *8*, 1719-1725.

(5) Lippert, T. W., A.; Stebani, J.; Nuyken, O.; Ihlemann, J. *Angew. Makromol. Chem.* **1993**, *213*, 127-155.

(6) Hahn, C.; Lippert, T.; Wokaun, A. *J. Phys. Chem. B* **1999**, *103*, 1287-1294.

(7) Hahn, C.; Kunz, T.; Dahn, U.; Nuyken, O.; Wokaun, A. *Appl. Surf. Sci.* **1998**, *127*, 899-904.

(8) Lippert, T.; Hauer, M.; Phipps, C. R.; Wokaun, A. *Appl. Phys. A: Mater.* **2003**, *77*, 259-264.

(9) Fardel, R.; Feurer, P.; Lippert, T.; Nagel, M.; Nueesch, F. A.; Wokaun, A. *Appl. Surf. Sci.* **2007**, *254*, 1332-1337.

(10) Lippert, T.; Stebani, J.; Nuyken, O.; Stasko, A.; Wokaun, A. *J. Photochem. Photobiol. A: Chem.* **1994**, *78*, 139-148.

(11) Pham, V. P.; Galstyan, T.; Granger, A.; Lessard, R. A. *Jpn. J. Appl. Phys. Pt. 1, No. 1B* **1997**, *36*, 429-438.

(12) Oliveira, O. N.; dos Santos, D. S.; Balogh, D. T.; Zucolotto, V.; Mendonca, C. R. *Adv. Colloid Interface Sci.* **2005**, *116*, 179-192.

(13) Dugave, C.; Demange, L. *Chem. Rev.* **2003**, *103*, 2475-2532.

(14) Liu, Z. F.; Hashimoto, K.; Fujishima, A. *Nature (London, U. K.)* **1990**, *347*, 658-660.

(15) Rochon, P.; Gosselin, J.; Natansohn, A.; Xie, S. *Appl. Phys. Lett.* **1992**, *60*, 4-5.

(16) Baro, J.; Dudek, D.; Luther, K.; Troe, J. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 1155-1161.

(17) Baro, J.; dudek, D.; Luther, K.; Troe, J. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 1161-1164.

(18) Scaiano, J. C.; Chen, C. P.; McGarry, P. F. *J. Photochem. Photobiol., A* **1991**, *62*, 75-81.

(19) Vaughan, K. *Org. Prep. Proc. Int.* **2001**, *33*, 59-74.

(20) Smith, R. H.; Michejda, C. J. *Synthesis* **1983**, 476-477.

(21) Elks, J.; Hey, D. H. *J. Chem. Soc.* **1943**, 441-445.

(22) Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. In *Organic Chemistry*; Oxford University Press: Oxford, 2001, 597-600.

(23) Sieh, D. H.; Wilbur, D. J.; Michejda, C. J. *J. Am. Chem. Soc.* **1980**, *102*, 3883-3887.

(24) Lunazzi, L.; Cerioni, G.; Foresti, E.; Macciantelli, D. *J. Chem. Soc. Perkin Trans. 2* **1978**, 686-691.

(25) Foster, N. I.; Heindel, N. D.; Burns, H. D.; Muhr, W. *Synthesis* **1980**, *7*, 572-573.

(26) Patrick, T. B. W., Richard P. ; DeGonia, David J. *J. Org. Chem.* **1985**, *50*, 2232-2235.

(27) Ludwig, M.; Bednarova, I.; Parik, P. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1654-1672.

(28) Hardie, R. L.; Thomson, R. H. *J. Chem. Soc.* **1958**, 1286-1291.

(29) Svoboda, P.; Pytela, O.; Vecera, M. *Collect. Czech. Chem. Comm.* **1986**, *52*, 2217-2224.

(30) Pytela, O.; Svoboda, P.; Vecera, M. *Collect. Czech. Chem. Commun.* **1987**, *52*, 2492-2499.

(31) Michejda, C. J., Jr.; Denlinger, C. L.; Kupper, R.; Koepke, S. R.; Smith, R. H., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 1056-1059.

(32) Akhtar, M. H.; McDaniel, R. S.; Feser, M.; Oehlschlager, A. C. *Tetrahedron* **1968**, *24*, 3899-3906.

(33) Marullo, N. P.; Mayfield, C. B.; Wagener, E. H. *J. Am. Chem. Soc.* **1968**, *90*, 510-511.

(34) Foster, N.; Pestel, B. *Magn. Reson. Chem.* **1985**, *23*, 83-85.

(35) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*; 3rd ed.; VCH: New York, 1987.

(36) Lippert, T.; Wokaun, A.; Dauth, J.; Nuyken, O. *Magn. Reson. Chem.* **1992**, *30*, 1178-1185.

(37) Tontini, A.; Gatti, G.; Diamantini, G.; Tarzia, G. *J. Chem. Soc. Perkin Trans. 2* **1998**, 2361-2363.

(38) Patrick, T. B.; Willaredt, R. P. *J. Org. Chem.* **1983**, *48*, 4415-4416.

(39) Nguyen, M.-T.; Hoesch, L. *Helv. Chim. Acta.* **1986**, *69*, 1627-1637.

(40) Barra, M.; Chen, N. *J. Org. Chem.* **2000**, *65*, 5739-5744.

(41) Chen, N.; Barra, M.; Lee, I.; Chahal, N. *J. Org. Chem.* **2002**, *67*, 2271-2276.

(42) Barra, M.; Srivastava, S.; Brockman, E. *J. Phys. Org. Chem.* **2004**, *17*, 1057-1060.

(43) Zhang, H.; Barra, M. *J. Phys. Org. Chem.* **2005**, *18*, 498-503.

(44) Barra, M.; Lim, H. *Trends Org. Chem.* **2006**, *11*, 17-28.

(45) Neidle, S. W., Derry E. V. *Acta Crystallogr., Sect. B: Struct. Sci.* **1992**, *B48*, 213-217.

(46) Bortolus, P.; Monti, S. *J. Phys. Chem.* **1979**, *86*, 648-652.

(47) Tamai, N.; Miyasaka, H. *Chem. Rev.* **2000**, *100*, 1875-1980.

(48) Rau, H. In *Photochromism Molecules and Systems*; Durr, H., Bouas-Lauran, H., Eds.; Elsevier: New York, 1990, 165-192.

(49) Kessler, H. *Tetrahedron* **1974**, *30*, 1861-1870.

(50) Asano, T.; Okada, T. *J. Org. Chem.* **1984**, *49*, 4387-4391.

(51) Asano, T.; Okada, T. *J. Org. Chem.* **1986**, *51*, 4454-4458.

(52) Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219-235.

(53) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275-311.

(54) Yoshikawa, K.; Hashimoto, M.; Morishima, I. *J. Am. Chem. Soc.* **1974**, *96*, 288-289.

(55) Hirao, H.; Ohwada, T. *J. Phys. Chem. A* **2003**, *107*, 2875-2881.

(56) Nakamura, S.; Hirao, H.; Ohwada, T. *J. Org. Chem.* **2004**, *69*, 4309-4316.

(57) Ohwada, T.; Hirao, H.; Ogawa, A. *J. Org. Chem.* **2004**, *64*, 7486-7494.

(58) Panitz, J. C.; Lippert, T.; Stebani, J.; Nuyken, O.; Wokaun, A. *J. Phys. Chem.* **1993**, *97*, 5246-5253.

(59) Rakotondradany, F.; Williams, C. I.; Whitehed, M. A.; Jean-Claude, B. J. *J. Mol. Struct. (Theochem)* **2001**, *535*, 217-234.

(60) Schmiedekamp, A.; Smith, R. H. J.; Michejda, C. J. *J.Org. Chem.* **1988**, *53*, 3433-3436.

(61) Richard, R. M.; Ball, D. W. *J. Mol. Model.* **2008**, *14*, 21-27.

(62) Hameed, A. J. *J. Mol. Struct (Theochem)* **2005**, *725*, 97-101.

(63) Dabbagh, H. A.; Teimouri, A.; Chermahini, A. N.; Shiasi, R. *Spectrochimi. Acta, Part A* **2007**, *67*, 437-443.

(64) Turro, N. J. In *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Company, Inc.: Menlo Park, 1978, p243-245.

(65) Kleinpeter, E. *J. Mol. Struct.* **1996**, *380*, 139-156.

(66) Pinto, B. M.; Grindley, T. B.; Szarek, W. A. *Magn. Reson. Chem.* **1986**, *24*, 323-331.

(67) Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. In *Organic Chemistry* Oxford University Press, 2001, 1090-1100.

(68) Nishimura, N.; Sueyoshi, T.; Yamanaka, H.; Imai, E.; Yamamoto, S.; Hasegawa, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1381-1387.

(69) Marcandalli, B.; Liddo, L. P.-D.; Dede, C. D. F.; Bellobono, I. R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 589-593.

(70) Kikuchi, O.; Azuki, M.; Inadomi, Y.; Morhashi, K. *J. Mol. Struct (Theochem)* **1999**, *468*, 95-104.

(71) Crecca, C. R.; Roitberg, A. E. *J. Phys. Chem. A* **2006**, *110*, 8188.

(72) Anet, F. A. L.; Ji, X. *Tetrahedron Lett.* **1984**, *25*, 1419-1420.

(73) Wang, L.; Wang, X. *J. Mol. Struct. (Theochem)* **2007**, *806*, 179-186.

(74) Fu, J.; Lau, K.; Barra, M. *J. Org. Chem.* **2008**, submitted for publication.

(75) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; J. A. Montgomery, J.; T. Vreven; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; J. Tomasi; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; N. Rega; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; O. Yazyev; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; P. Y. Ayala; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford CT, 2004.

(76) Foresman, J. B.; Frisch, A. In *Exploring Chemistry With Electronic Structure Methods*; 2nd ed.; Gaussian: Pittsburgh, 1996, p 64.

(77) Carey, F. A.; Sundberg, R. J. In *Advanced Organic Chemistry Part A: Structure and Mechanisms*; 4th ed.; Kluwer Academic / Plenum Publishers: New York, 2000, p 222-224.

Appendix A. Selected optimized parameters for *cis* and *trans* isomers and transition states of target substrates calculated in various solvents by PCM method.

	CH_3-5						CH_3O-5					
	Cyclohexane			DMSO			Cyclohexane			DMSO		
	Cis	TS	*Trans*	*Cis*	TS	*Trans*	*Cis*	TS	*Trans*	*Cis*	TS	*Trans*
N1=N2 (Å)	1.260	1.283	1.276	1.267	1.300	1.280	1.260	1.282	1.275	1.266	1.301	1.279
N2-N3 (Å)	1.358	1.306	1.317	1.344	1.290	1.312	1.365	1.308	1.320	1.351	1.291	1.315
C-N1=N2-N3 (°)	11.8	91.8	-179.6	12.2	92.0	-179.6	11.4	91.8	-179.7	12.0	92.1	-179.3
Dipole (D)	4.316	6.910	3.309	5.385	8.440	3.882	4.021	6.352	2.738	4.956	7.835	3.312
$\Delta E_{TS\text{-}Cis}$ (kcal/mol)		18.8			17.9			20.4			19.4	

H-4

	Cyclohexane			Benzene			Acetonitrile			DMSO		
	Cis	TS	*Trans*	*Cis*	TS	*Trans*	*Cis*	TS	*Trans*	*Cis*	TS	*Trans*
C-N1 (Å)	1.428	1.362	1.418	1.428	1.362	1.418	1.430	1.365	1.419	1.430	1.364	1.419
N1=N2 (Å)	1.260	1.281	1.270	1.260	1.283	1.269	1.265	1.303	1.273	1.265	1.303	1.273
N2-N3 (Å)	1.350	1.301	1.329	1.350	1.299	1.329	1.340	1.280	1.323	1.340	1.280	1.323
C-N1=N2-N3 (°)	7.8	89.6	176.9	7.7	89.7	176.9	7.9	90.1	176.6	7. 9	90.1	176.6
Dipole (D)	4.299	6.855	2.817	4.360	7.008	2.854	5.239	8.626	3.314	5.265	8.648	3.312
$\Delta E_{TS\text{-}Cis}$ (kcal/mol)		22.1			22.0			21.0			21.0	

Cl-4

	Cyclohexane			Benzene			Acetonitrile			DMSO		
	Cis	TS	*Trans*	*Cis*	TS	*Trans*	*Cis*	TS	*Trans*	*Cis*	TS	*Trans*
C-N1 (Å)	1.425	1.359	1.415	1.425	1.359	1.415	1.427	1.360	1.416	1.427	1.360	1.416
N1=N2 (Å)	1.261	1.286	1.271	1.261	1.288	1.272	1.306	1.276	1.266	1.266	1.307	1.276
N2-N3 (Å)	1.347	1.295	1.324	1.346	1.293	1.323	1.335	1.277	1.317	1.336	1.276	1.317
C-N1=N2-N3 (°)	8.1	89.4	176.9	8.1	89.5	176.9	8.3	89.8	176.8	8.2	89.9	176.8
Dipole (D)	4.353	9.290	5.373	4.433	9.460	5.457	5.266	11.209	6.350	5.236	11.253	6.373
$\Delta E_{TS\text{-}Cis}$ (kcal/mol)		21.0			20.9			19.5			19.5	

	H-5								
	Cyclohexane			Benzene			Acetonitrile		
	Cis	TS	Trans	Cis	TS	Trans	Cis	TS	Trans
N1=N2 (Å)	1.261	1.283	1.27607	1.261	1.285	1.276	1.267	1.301	1.281
N2-N3 (Å)	1.355	1.305	1.316	1.354	1.304	1.316	1.342	1.289	1.311
C-N1=N2-N3 (°)	12.1	91.7	-179.5	12.2	91.7	-179.5	12.8	91.8	-178.4
Dipole (D)	4.353	7.107	3.744	4.425	7.240	3.795	5.376	8.677	4.326
$\Delta E_{TS\text{-}Cis}$ (kcal/mol)		18.5			17.9			17.6	
	DMSO			Methanol			Ethanol		
	Cis	TS	Trans	Cis	TS	Trans	Cis	TS	Trans
N1=N2 (Å)	1.267	1.301	1.281	1.267	1.300	1.280	1.266	1.300	1.280
N2-N3 (Å)	1.342	1.289	1.311	1.344	1.290	1.311	1.343	1.290	1.311
C-N1=N2-N3 (°)	12.6	91.8	-178.6	12.6	91.8	-179.0	12.6	91.8	-178.8
Dipole (D)	5.397	8.699	4.334	5.322	8.640	4.317	5.320	8.617	4.309
$\Delta E_{TS\text{-}Cis}$ (kcal/mol)		17.3			17.3			17.2	

Appendix B. Cartesian coordinates, imaginary frequencies (where applicable), and energies for all optimized structures.

cis-CH_3O-4

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-2.383022	1.343348	0.332518
7	-1.216721	1.790288	0.194521
6	-0.038717	0.986457	0.165058
6	0.230792	-0.049373	1.081299
6	0.988942	1.404289	-0.689341
6	1.480727	-0.653029	1.114657
1	-0.537991	-0.361653	1.780599
6	2.234668	0.778201	-0.687229
1	0.797222	2.235164	-1.361977
6	2.488289	-0.256513	0.222602
1	1.701982	-1.441905	1.827184
1	2.999461	1.115645	-1.377440
6	-4.058106	-0.377186	0.065087
6	-2.128700	-1.002079	-0.655292
6	-3.550287	-1.610595	-0.723819
1	-4.581616	0.365727	-0.547494
1	-4.635626	-0.567622	0.975479
1	-1.792155	-0.530305	-1.586288
1	-1.324920	-1.632329	-0.266524
1	-3.965287	-1.735053	-1.726100
1	-3.643578	-2.550869	-0.175694
7	-2.652293	0.005185	0.318720
8	3.671727	-0.930169	0.327301
6	4.735285	-0.555069	-0.532624
1	4.471865	-0.699019	-1.589099
1	5.032429	0.490374	-0.375646
1	5.571301	-1.209169	-0.278111

E = -628.25416898; ZPE = 0.223238
Number of imaginary freq = 0

trans-CH_3O-4

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	1.891745	0.533740	-0.209966
7	1.117834	-0.467501	-0.243363
6	-0.257215	-0.143634	-0.153872
6	-0.789416	1.160947	-0.131259
6	-1.138152	-1.226898	-0.090824
6	-2.156836	1.358241	-0.039333
1	-0.114712	2.008029	-0.188088
6	-2.518158	-1.038138	0.004127
1	-0.721873	-2.229633	-0.114559
6	-3.034333	0.261715	0.031062
1	-2.580067	2.358163	-0.022867
1	-3.171203	-1.901927	0.053486
6	4.261806	0.991662	0.256926
6	3.792711	-1.099125	-0.018023
6	5.081656	-0.324998	0.370107
1	3.975807	1.424008	1.223577
1	4.665002	1.779588	-0.387896
1	3.272268	-1.582647	0.818364
1	3.851229	-1.802192	-0.853923
1	5.484866	-0.543835	1.360580
1	5.879712	-0.405648	-0.371271
7	3.180777	0.202870	-0.356208
8	-4.361543	0.573114	0.119869
6	-5.294972	-0.491207	0.194969
1	-5.257655	-1.126372	-0.700309
1	-5.127094	-1.114167	1.083818
1	-6.278979	-0.023430	0.263611

E = -628.27317003; ZPE = 0.223466
Number of imaginary freq = 0

ts-CH_3O-4

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	2.026178	0.112834	-0.903927
7	1.013215	0.854891	-0.750690
6	-0.214654	0.416478	-0.363738
6	-0.578150	-0.942746	-0.289859
6	-1.221251	1.382674	-0.245874
6	-1.901431	-1.307888	-0.081413
1	0.179065	-1.709213	-0.419163
6	-2.546024	1.024797	0.000549
1	-0.949491	2.428880	-0.351461
6	-2.894132	-0.329888	0.080540
1	-2.193018	-2.352897	-0.037736
1	-3.294769	1.801561	0.106317
6	4.005005	-1.028839	-0.234008
6	3.734632	0.838914	0.800613
6	4.884941	-0.194442	0.730898
1	4.297150	-0.955868	-1.287842
1	3.836846	-2.079644	0.023170
1	3.900596	1.743063	0.202652
1	3.372718	1.129694	1.789998
1	5.826594	0.171090	0.316220
1	5.079111	-0.688403	1.685655
7	2.863334	-0.145410	0.086907
8	-4.157852	-0.798548	0.301152
6	-5.206849	0.144582	0.447572
1	-5.042430	0.802269	1.311669
1	-5.326319	0.759477	-0.454380
1	-6.114845	-0.439680	0.607971

E = -628.21238314; ZPE = 0.221054
Number of imaginary freq = 1 (-621.559 Hz)

cis-CH_3O-5

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	2.006538	1.551740	0.178648
7	0.825644	1.885422	-0.092226
6	-0.324251	1.051169	0.003865
6	-0.600168	0.233100	1.117542
6	-1.331841	1.236189	-0.950495
6	-1.834209	-0.390417	1.246942
1	0.151355	0.107072	1.890682
6	-2.560657	0.585129	-0.845199
1	-1.139446	1.903849	-1.785269
6	-2.819975	-0.233302	0.261426
1	-2.058684	-1.011181	2.109120
1	-3.308716	0.738469	-1.614722
6	1.851324	-0.880824	-0.405773
6	3.833338	0.107004	0.593757
6	3.066861	-1.804630	-0.611301
1	1.472672	-0.485049	-1.356512
1	1.019477	-1.385560	0.092941
6	4.276481	-0.862327	-0.506505
1	4.032225	-0.312453	1.589406
1	4.286261	1.099170	0.541591
1	3.105690	-2.555571	0.186938
1	3.011975	-2.338900	-1.564890
1	5.209120	-1.383497	-0.269346
1	4.419422	-0.317797	-1.447878
7	2.377210	0.249440	0.400197
8	-3.989127	-0.907473	0.477118
6	-5.027218	-0.768880	-0.478680
1	-5.854855	-1.379647	-0.113070
1	-5.358885	0.274278	-0.567754
1	-4.718450	-1.132886	-1.467991

E = -667.59346250; ZPE = 0.253187
Number of imaginary freq = 0

trans-CH_3O-5

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-1.500596	0.509691	-0.105808
7	-0.725311	-0.498831	-0.068067
6	0.648843	-0.162529	-0.045613
6	1.174883	1.144963	-0.067177
6	1.542052	-1.237179	0.002888
6	2.544110	1.352940	-0.039606
1	0.493822	1.987944	-0.105370
6	2.923844	-1.037656	0.031536
1	1.133699	-2.243422	0.018658
6	3.432267	0.264911	0.010614
1	2.959288	2.356384	-0.055689
1	3.583961	-1.896787	0.069642
6	-3.318990	-1.167845	-0.030145
6	-3.801520	1.240124	-0.089756
6	-4.837869	-0.940540	-0.115311
1	-3.003012	-1.623891	0.918586
1	-2.917479	-1.793816	-0.834047
6	-5.034099	0.487652	0.433892
1	-3.979511	1.648717	-1.096051
1	-3.477526	2.061539	0.555840
1	-5.164943	-0.988400	-1.160847
1	-5.402238	-1.693081	0.443050
1	-5.973619	0.946128	0.111907
1	-5.022737	0.474514	1.530213
7	-2.785012	0.192503	-0.124173
8	4.761624	0.586812	0.035669
6	5.702864	-0.470623	0.090426
1	5.579250	-1.076548	0.998371
1	5.629406	-1.125165	-0.788791
1	6.686767	0.002526	0.105019

E = -667.61744102; ZPE = 0.25331
Number of imaginary freq = 0

ts-CH_3O-5

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	1.804781	-1.284885	0.450665
7	0.737688	-0.801438	0.945838
6	-0.519255	-0.552360	0.490498
6	-0.886535	-0.794309	-0.858667
6	-1.502415	-0.039069	1.370317
6	-2.184835	-0.532577	-1.288566
1	-0.146296	-1.198332	-1.543770
6	-2.788615	0.217493	0.912869
1	-1.231885	0.145712	2.405647
6	-3.150181	-0.022968	-0.417950
1	-2.441102	-0.733024	-2.327025
1	-3.524241	0.611847	1.610648
6	2.422049	1.051393	-0.048067
6	4.031744	-0.778190	-0.340106
6	3.807563	1.619823	-0.400100
1	2.079012	1.302786	0.965282
1	1.628501	1.345108	-0.740774
6	4.791753	0.506851	0.017347
1	4.154818	-1.030859	-1.401369
1	4.287630	-1.653824	0.259310
1	3.878156	1.799661	-1.479179
1	4.000679	2.570004	0.105732
1	5.757752	0.577154	-0.490304
1	4.972244	0.543418	1.097955
7	2.633417	-0.407241	-0.078815
8	-4.478669	0.244623	-0.874474
6	-5.262065	0.753451	0.208246
1	-6.285815	0.824375	-0.094747
1	-5.183152	0.093323	1.046639
1	-4.903405	1.723388	0.482994

E = -667.55838103; ZPE = 0.251351
Number of imaginary freq = 1 (-573.729 Hz)

cis-CH_3O-6

```
---------------------------------------------
 Atomic       Coordinates (Angstroms)
 Number       X           Y           Z
 --------------------------------------------
    6      -4.127713   -0.743036   -0.665639
    6      -3.762014   -1.755157    0.429453
    6      -2.253507   -1.720959    0.711989
    6      -1.769141   -0.294651    0.995483
    6      -3.593397    0.649574   -0.322061
    1      -2.005393   -2.358142    1.570011
    1      -4.307761   -1.503737    1.350628
    1      -4.076275   -2.765977    0.142603
    1      -3.697902   -1.061710   -1.624556
    1      -5.215279   -0.690348   -0.798534
    1      -2.235281    0.085478    1.921575
    1      -0.690887   -0.284299    1.139613
    1      -4.091099    1.031354    0.587066
    1      -3.787642    1.361172   -1.127484
    1      -1.701971   -2.114063   -0.152010
    7      -1.628606    1.898741   -0.158896
    7      -0.403747    2.141829   -0.067789
    6       0.657386    1.190600   -0.085961
    6       0.733093    0.115531   -0.995506
    6       1.781581    1.487953    0.692565
    6       1.892541   -0.638147   -1.094940
    1      -0.120171   -0.116654   -1.622991
    6       2.937356    0.709170    0.625717
    1       1.739956    2.345799    1.357253
    6       2.999920   -0.359094   -0.276974
    1       1.966394   -1.459673   -1.801071
    1       3.781562    0.957707    1.258705
    7      -2.136801    0.593496   -0.125764
    8       4.079574   -1.177104   -0.443633
    6       5.231477   -0.937330    0.348936
    1       5.652425    0.058845    0.158808
    1       5.012542   -1.036771    1.420503
    1       5.958786   -1.697335    0.057717
 --------------------------------------------
E = -706.90877052; ZPE = 0.282198
Number of imaginary freq = 0
```

trans-CH_3O-6

```
---------------------------------------------
 Atomic       Coordinates (Angstroms)
 Number       X           Y           Z
 --------------------------------------------
    6      -4.694646    1.154065   -0.191166
    6      -5.293497   -0.240257    0.042218
    6      -4.330959   -1.324298   -0.462512
    6      -2.937336   -1.188525    0.162289
    6      -3.311446    1.264152    0.455861
    1      -4.721722   -2.325099   -0.241718
    1      -5.475811   -0.382889    1.117735
    1      -6.265780   -0.329526   -0.457107
    1      -4.602708    1.340959   -1.269211
    1      -5.346713    1.933747    0.220915
    1      -2.962957   -1.450821    1.234353
    1      -2.216184   -1.854752   -0.312677
    1      -3.414566    1.231213    1.555151
    1      -2.812964    2.202283    0.199374
    1      -4.237544   -1.248775   -1.553919
    7      -1.131373    0.477773    0.057192
    7      -0.353023   -0.519647    0.051744
    6       1.020304   -0.177074    0.008794
    6       1.533243    1.125918   -0.147964
    6       1.921032   -1.239542    0.125720
    6       2.900737    1.343144   -0.174719
    1       0.843588    1.956514   -0.249031
    6       3.301302   -1.030506    0.101315
    1       1.520697   -2.242557    0.240309
    6       3.798046    0.268341   -0.049196
    1       3.308097    2.342356   -0.297126
    1       3.969631   -1.878587    0.197578
    7      -2.443349    0.180556    0.003288
    8       5.123854    0.597982   -0.090902
    6       6.075990   -0.445217    0.027281
    1       5.986176   -0.968057    0.989074
    1       5.980173   -1.175448   -0.787647
    1       7.055352    0.033599   -0.031925
 --------------------------------------------
E = -706.93632119; ZPE = 0.282889
Number of imaginary freq = 0
```

ts-CH_3O-6

```
---------------------------------------------
 Atomic       Coordinates (Angstroms)
 Number       X           Y           Z
 --------------------------------------------
    6      -4.431039   -1.067433   -0.437115
    6      -4.822291   -0.421281    0.899582
    6      -3.569269   -0.038248    1.699464
    6      -2.604550    0.805490    0.858775
    6      -3.452450   -0.177686   -1.207580
    1      -3.841952    0.525043    2.600636
    1      -5.416092    0.483451    0.703431
    1      -5.459475   -1.096232    1.483739
    1      -3.957424   -2.041165   -0.254503
    1      -5.318650   -1.248720   -1.055596
    1      -3.075023    1.769952    0.598201
    1      -1.700624    1.020640    1.424586
    1      -3.945374    0.769495   -1.490156
    1      -3.114021   -0.660072   -2.127134
    1      -3.045744   -0.944315    2.031397
    7      -1.300221    0.569939   -1.170256
    7      -0.280551    1.158535   -0.705686
    6       0.895452    0.581352   -0.340342
    6       1.152956   -0.802215   -0.430954
    6       1.965666    1.444879   -0.080917
    6       2.437481   -1.289754   -0.245110
    1       0.340488   -1.485123   -0.652851
    6       3.253108    0.957300    0.146122
    1       1.776036    2.514007   -0.059758
    6       3.496645   -0.418580    0.058952
    1       2.649442   -2.351625   -0.325633
    1       4.053585    1.655054    0.364078
    7      -2.261958    0.087530   -0.385547
    8       4.713602   -1.008367    0.242626
    6       5.823326   -0.177190    0.542948
    1       6.022223    0.538804   -0.265448
    1       5.673978    0.372678    1.481786
    1       6.678701   -0.846768    0.649687
 --------------------------------------------
E = -706.87675152; ZPE = 0.280767
Number of imaginary freq = 1 (-566.87 Hz)
```

cis-CH_3O-6-O

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	4.118695	-0.790277	0.577644
6	2.384691	-1.713702	-0.692478
6	1.779829	-0.333763	-0.954755
6	3.589567	0.620596	0.339744
1	2.215018	-2.367058	-1.553549
1	3.706685	-1.188236	1.519909
1	5.210253	-0.782780	0.648350
1	2.181118	0.075380	-1.896123
1	0.698668	-0.423885	-1.050221
1	4.075422	1.053138	-0.549588
1	3.805469	1.264255	1.196414
1	1.900276	-2.163121	0.190097
7	1.630459	1.876144	0.166530
7	0.408804	2.120983	0.061694
6	-0.658407	1.177280	0.086654
6	-0.745472	0.106672	1.000382
6	-1.776728	1.480380	-0.698255
6	-1.910688	-0.638406	1.096650
1	0.102635	-0.128774	1.633628
6	-2.937606	0.709748	-0.635102
1	-1.725474	2.336052	-1.364961
6	-3.011926	-0.354938	0.271457
1	-1.994126	-1.456445	1.805663
1	-3.776888	0.961613	-1.273172
7	2.131124	0.561144	0.165302
8	-4.096924	-1.164376	0.435145
6	-5.244655	-0.919754	-0.363179
1	-5.659979	0.079356	-0.176939
1	-5.021478	-1.023648	-1.433292
1	-5.977285	-1.674736	-0.072671
8	3.789820	-1.652128	-0.503995

E = -742.79755669; ZPE = 0.258235
Number of imaginary freq = 0

trans-CH_3O-6-O

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-4.733623	1.037342	-0.137892
6	-4.370768	-1.259458	-0.399396
6	-2.937455	-1.170879	0.125103
6	-3.332719	1.252333	0.430980
1	-4.810406	-2.225634	-0.135735
1	-4.720435	1.188828	-1.229893
1	-5.439800	1.744194	0.307085
1	-2.894126	-1.450347	1.190183
1	-2.277837	-1.846566	-0.422854
1	-3.381062	1.238904	1.532147
1	-2.916841	2.213267	0.115396
1	-4.366785	-1.163376	-1.497588
7	-1.138586	0.501175	0.012302
7	-0.364836	-0.497847	0.005163
6	1.011033	-0.163837	-0.018922
6	1.532663	1.137358	-0.160174
6	1.902822	-1.233225	0.101495
6	2.901386	1.346294	-0.168357
1	0.849234	1.972763	-0.263940
6	3.284314	-1.032448	0.096400
1	1.494847	-2.234418	0.204000
6	3.790485	0.264709	-0.038519
1	3.316552	2.343615	-0.278651
1	3.946418	-1.885030	0.195125
7	-2.451990	0.196829	-0.057420
8	5.117557	0.586444	-0.060507
6	6.063069	-0.462422	0.067135
1	5.955090	-0.989384	1.024635
1	5.976409	-1.187412	-0.753301
1	7.045256	0.012234	0.025965
8	-5.212042	-0.264862	0.170507

E = -742.82460388; ZPE = 0.258834
Number of imaginary freq = 0

ts-CH_3O-6-O

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-4.378997	-0.607523	-0.705475
6	-2.871201	-1.557631	0.826120
6	-2.206183	-0.208966	1.122346
6	-3.809477	0.797815	-0.486722
1	-2.856345	-2.192203	1.716283
1	-3.866684	-1.088160	-1.554690
1	-5.449542	-0.557440	-0.922245
1	-2.650624	0.242999	2.020223
1	-1.130828	-0.311664	1.272536
1	-4.411767	1.323595	0.267943
1	-3.795436	1.386051	-1.407780
1	-2.322042	-2.068344	0.019015
7	-1.528937	1.505079	-0.555601
7	-0.399027	1.565048	-0.000735
6	0.808455	0.930974	-0.079193
6	1.013328	-0.171100	-0.948521
6	1.897805	1.363074	0.702585
6	2.253629	-0.791992	-1.022505
1	0.193604	-0.516863	-1.572019
6	3.136815	0.727232	0.624433
1	1.763141	2.208087	1.370543
6	3.328420	-0.356700	-0.239003
1	2.407956	-1.630119	-1.696362
1	3.947074	1.094802	1.244827
7	-2.435210	0.680007	-0.018718
8	4.508466	-1.051115	-0.390103
6	5.621390	-0.622642	0.367459
1	5.901525	0.414337	0.132217
1	5.435946	-0.701592	1.448602
1	6.446482	-1.285829	0.097803
8	-4.237734	-1.396866	0.467520

E = -742.76403319; ZPE = 0.256669
Number of imaginary freq = 1 (-575.621 Hz)

cis-CH$_3$O-7

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	-1.533702	-0.990220	1.177590
7	-0.459462	-0.595181	1.699911
6	0.749744	-0.282313	1.022631
6	1.478152	0.835256	1.470703
6	1.362475	-1.154850	0.111539
6	2.746650	1.102876	0.978912
1	1.028518	1.485101	2.215797
6	2.653458	-0.909199	-0.363641
1	0.832522	-2.044509	-0.215666
6	3.347814	0.230625	0.057815
1	3.305007	1.973759	1.308169
1	3.101223	-1.610768	-1.058537
8	4.604266	0.576094	-0.354017
6	5.269906	-0.282059	-1.265058
1	5.415647	-1.285630	-0.843236
1	4.723383	-0.367741	-2.214109
1	6.243645	0.174979	-1.451124
6	-3.155231	-1.480162	-0.421625
6	-1.304338	0.024811	-1.122094
6	-4.281524	-0.496376	-0.072149
1	-3.198971	-1.752610	-1.482692
1	-3.281649	-2.399590	0.156032
6	-1.606011	1.487248	-0.740322
1	-1.810761	-0.217067	-2.061298
1	-0.234921	-0.096407	-1.304505
6	-4.157572	0.916481	-0.671007
1	-4.330503	-0.407923	1.020664
1	-5.228665	-0.951829	-0.393626
6	-2.983078	1.732953	-0.093864
1	-1.518766	2.071021	-1.667192
1	-0.825247	1.863837	-0.069938
1	-4.089460	0.865919	-1.768327
1	-5.091768	1.450261	-0.454802
1	-3.206509	2.803935	-0.179489
1	-2.917248	1.524680	0.981921
7	-1.788589	-0.991730	-0.168493

E = -746.21562084; ZPE = 0.311917

Number of imaginary freq = 0

trans-CH$_3$O-7

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	-1.050820	-0.674876	-0.566592
7	-0.288395	0.337010	-0.641262
6	1.071008	0.053855	-0.368079
6	1.611291	-1.228181	-0.143228
6	1.932200	1.154638	-0.332618
6	2.962848	-1.385454	0.116306
1	0.956004	-2.091483	-0.176782
6	3.295937	1.006222	-0.072101
1	1.513475	2.140376	-0.513098
6	3.818380	-0.271045	0.155298
1	3.389999	-2.368769	0.289751
1	3.931744	1.884038	-0.052040
8	5.132703	-0.543304	0.416935
6	6.042232	0.542192	0.465752
1	6.090879	1.073823	-0.494303
1	5.778227	1.256508	1.257367
1	7.018987	0.106625	0.685431
6	-3.271032	-1.491343	-0.566631
6	-2.816712	0.893765	-1.240721
6	-3.887713	-1.360960	0.835255
1	-4.061292	-1.473679	-1.328104
1	-2.740687	-2.443728	-0.657357
6	-3.033180	1.840194	-0.037802
1	-3.762575	0.728474	-1.766605
1	-2.110035	1.342329	-1.944627
6	-4.483400	0.019602	1.168032
1	-3.114576	-1.596712	1.578831
1	-4.663339	-2.133485	0.932903
6	-3.432271	1.145475	1.277925
1	-3.810203	2.560943	-0.326890
1	-2.117423	2.413192	0.137331
1	-5.258291	0.287996	0.434020
1	-5.003025	-0.068873	2.130572
1	-3.799940	1.918669	1.964400
1	-2.530454	0.730989	1.747787
7	-2.321730	-0.438500	-0.903347

E = -746.24378386; ZPE = 0.311917

Number of imaginary freq = 0

ts-CH$_3$O-7

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	-1.134761	-0.971711	-0.003801
7	-0.290932	-0.514508	0.818216
6	1.052848	-0.298909	0.420044
6	1.409474	0.763724	-0.432339
6	2.074183	-1.075428	0.980700
6	2.738828	1.010810	-0.736378
1	0.625944	1.390261	-0.846171
6	3.417493	-0.822325	0.693172
1	1.808125	-1.882515	1.656953
6	3.756115	0.220812	-0.175739
1	3.021672	1.822879	-1.399380
1	4.181894	-1.440892	1.149744
8	5.032003	0.555702	-0.534605
6	6.100036	-0.198771	0.012010
1	6.127230	-0.127455	1.107771
1	6.037971	-1.256806	-0.276735
1	7.014421	0.233116	-0.399359
6	-2.937457	-0.791850	-1.503255
6	-2.140841	1.285004	-0.351519
6	-4.200542	-1.168255	-0.713546
1	-3.193539	-0.124859	-2.335648
1	-2.484884	-1.691691	-1.928977
6	-2.904195	1.500659	0.972314
1	-2.718338	1.700133	-1.183365
1	-1.186269	1.815743	-0.320535
6	-4.842836	-0.032328	0.104103
1	-3.947582	-1.989151	-0.029818
1	-4.932029	-1.569156	-1.429156
6	-3.979492	0.444365	1.291721
1	-3.366102	2.495744	0.912310
1	-2.191364	1.538681	1.802762
1	-5.099032	0.814697	-0.550266
1	-5.797799	-0.406041	0.494920
1	-4.631111	0.857574	2.072047
1	-3.495314	-0.433955	1.738442
7	-1.901679	-0.116205	-0.718191

E = -746.1835274; ZPE = 0.310031

Number of imaginary freq = 1 (-600.441 Hz)

cis-H-4

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-1.348591	1.423351	-0.470368
7	-0.134083	1.699714	-0.301339
6	0.896857	0.725484	-0.145340
6	1.086484	-0.328227	-1.055861
6	1.869481	0.966229	0.837300
6	2.220878	-1.134741	-0.962439
1	0.354194	-0.497600	-1.839352
6	2.983246	0.136916	0.942218
1	1.733630	1.809567	1.508102
6	3.166481	-0.916343	0.041558
1	2.363852	-1.940120	-1.678569
1	3.719885	0.322901	1.719528
1	4.043813	-1.552933	0.114722
6	-1.476821	-0.882186	0.647995
6	-3.275656	-0.008196	-0.159685
6	-2.977171	-1.261820	0.702732
1	-1.086613	-0.435147	1.569607
1	-0.773925	-1.641616	0.296526
1	-3.710588	0.830970	0.394834
1	-3.840767	-0.162421	-1.084585
1	-3.426496	-1.265881	1.697787
1	-3.204312	-2.205223	0.201253
7	-1.822376	0.156192	-0.369825

E = -513.73192901; ZPE = 0.190379
Number of imaginary freq = 0

trans-H-4

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-0.953618	0.539033	-0.170026
7	-0.196987	-0.476225	-0.216302
6	1.183005	-0.174882	-0.09445
6	1.732661	1.119121	-0.095805
6	2.035233	-1.281798	0.020698
6	3.108290	1.288583	0.027986
1	1.072521	1.973599	-0.196461
6	3.412133	-1.104755	0.146378
1	1.592600	-2.273429	0.011796
6	3.954888	0.181267	0.151238
1	3.526511	2.292196	0.024088
1	4.061229	-1.971789	0.237524
1	5.028275	0.322523	0.244892
6	-2.893036	-1.059696	-0.090514
6	-3.331367	1.034479	0.232963
6	-4.177973	-0.269929	0.281321
1	-2.413943	-1.590579	0.741478
1	-2.936758	-1.724475	-0.957971
1	-3.078436	1.443255	1.218576
1	-3.693619	1.841287	-0.412701
1	-4.613243	-0.509316	1.253179
1	-4.955637	-0.313373	-0.484229
7	-2.239753	0.239443	-0.351028

E = -513.75052249; ZPE = 0.190705
Number of imaginary freq = 0

ts-H-4

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-1.082073	0.486132	0.971277
7	-0.152096	-0.354971	1.113903
6	1.095532	-0.124167	0.470983
6	1.544062	1.142637	0.059007
6	1.947704	-1.230354	0.340396
6	2.821931	1.286997	-0.477100
1	0.889776	2.001101	0.170223
6	3.218830	-1.079972	-0.209842
1	1.592643	-2.199190	0.679189
6	3.662900	0.179484	-0.619851
1	3.162866	2.271176	-0.788862
1	3.866641	-1.946668	-0.312746
1	4.656214	0.298636	-1.043792
6	-2.438689	-1.012956	-0.568273
6	-3.307802	0.868550	0.042057
6	-3.830042	-0.354739	-0.760073
1	-2.403007	-1.803254	0.191123
1	-1.910910	-1.355512	-1.462382
1	-3.683301	0.927946	1.070236
1	-3.395007	1.851156	-0.433015
1	-4.669463	-0.887447	-0.309237
1	-4.064596	-0.127280	-1.802256
7	-1.955603	0.285476	-0.031224

E = -513.69418214; ZPE = 0.188438
Number of imaginary freq = 1 (-568.502 Hz)

cis-H-5

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 ---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 ---------------------------------------------
    7      0.974024    1.587453    0.238298
    7     -0.238462    1.739200   -0.057483
    6     -1.242498    0.731719   -0.021248
    6     -1.448180   -0.086787    1.103678
    6     -2.190564    0.720626   -1.056717
    6     -2.571046   -0.911696    1.171287
    1     -0.737784   -0.056028    1.924392
    6     -3.292617   -0.128023   -0.993569
    1     -2.045593    1.387254   -1.901854
    6     -3.491050   -0.947608    0.121481
    1     -2.725019   -1.531671    2.051060
    1     -4.008797   -0.138974   -1.811221
    1     -4.359339   -1.598227    0.176320
    6      1.197159   -0.838625   -0.378796
    6      3.003461    0.435060    0.636758
    6      2.540043   -1.568260   -0.579284
    1      0.761562   -0.511648   -1.330978
    1      0.451376   -1.458418    0.126441
    6      3.597004   -0.457809   -0.456668
    1      3.244766    0.046209    1.635514
    1      3.308220    1.482438    0.591918
    1      2.683309   -2.312892    0.212899
    1      2.574037   -2.095745   -1.537433
    1      4.591961   -0.838024   -0.205793
    1      3.673112    0.103361   -1.395972
    7      1.546998    0.363459    0.416784
 ---------------------------------------------
E = -553.07152668; ZPE = 0.220344
Number of imaginary freq = 0
```

trans-H-5

```
 ---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 ---------------------------------------------
    7     -0.580935    0.506075   -0.093705
    7      0.182826   -0.511502   -0.036826
    6      1.561553   -0.187571   -0.012375
    6      2.094838    1.114010   -0.027093
    6      2.437887   -1.281583    0.033149
    6      3.473375    1.302163    0.002614
    1      1.419149    1.961478   -0.061335
    6      3.817600   -1.086025    0.062781
    1      2.010419   -2.279921    0.044393
    6      4.343083    0.207084    0.047675
    1      3.875301    2.312557   -0.008874
    1      4.482693   -1.945202    0.097757
    1      5.418285    0.363006    0.071171
    6     -2.418509   -1.148568   -0.015768
    6     -2.871669    1.264270   -0.125901
    6     -3.932659   -0.904413   -0.135344
    1     -2.126965   -1.599733    0.942542
    1     -2.005773   -1.783916   -0.806334
    6     -4.123907    0.535846    0.383823
    1     -3.018928    1.648053   -1.146584
    1     -2.554415    2.097754    0.507102
    1     -4.239635   -0.967906   -1.186084
    1     -4.516889   -1.639930    0.425071
    1     -5.050283    0.999124    0.032320
    1     -4.136963    0.543070    1.480122
    7     -1.865542    0.205467   -0.108416
 ---------------------------------------------
E = -553.09522392; ZPE = 0.220629
Number of imaginary freq = 0
```

ts-H-5

```
 ---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 ---------------------------------------------
    7      0.718222   -0.651925    0.984629
    7     -0.228930    0.153780    1.219172
    6     -1.448938    0.039408    0.502299
    6     -1.916607   -1.157659   -0.068913
    6     -2.270884    1.176235    0.473827
    6     -3.176224   -1.201031   -0.662824
    1     -1.291675   -2.044036   -0.032170
    6     -3.523052    1.128287   -0.134871
    1     -1.906531    2.088466    0.937164
    6     -3.983557   -0.060721   -0.705756
    1     -3.530231   -2.133256   -1.096370
    1     -4.144479    2.019923   -0.156929
    1     -4.963232   -0.101102   -1.173929
    6      1.985241    1.113819   -0.263811
    6      2.813830   -1.182444   -0.064904
    6      3.402996    1.009669   -0.857781
    1      1.944316    1.757212    0.624715
    1      1.244338    1.495433   -0.972853
    6      4.011233   -0.229195   -0.171488
    1      2.681068   -1.761499   -0.990067
    1      2.867193   -1.883383    0.771636
    1      3.344037    0.847357   -1.940656
    1      3.983887    1.921739   -0.691633
    1      4.847639   -0.661791   -0.728429
    1      4.369403    0.031680    0.831609
    7      1.680713   -0.272561    0.130948
 ---------------------------------------------
E = -553.04027000; ZPE = 0.218751
Number of imaginary freq = 1 (-521.091 Hz)
```

cis-H-6

```
---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 --------------------------------------------
    6       3.490103   -0.249015    0.639811
    6       3.259426   -1.383493   -0.368519
    6       1.757719   -1.617133   -0.583834
    6       1.032909   -0.314630   -0.943766
    6       2.724710    1.010926    0.227565
    1       1.590111   -2.348962   -1.383708
    1       3.724522   -1.113956   -1.328115
    1       3.746456   -2.305971   -0.030283
    1       3.149403   -0.561620    1.635751
    1       4.558025   -0.012204    0.720779
    1       1.399354    0.065664   -1.913198
    1      -0.034659   -0.491110   -1.039366
    1       3.125912    1.400146   -0.724812
    1       2.818456    1.801171    0.974878
    1       1.307267   -2.027380    0.329312
    7       0.553186    1.869493    0.194788
    7      -0.697161    1.899885    0.114976
    6      -1.568510    0.773345    0.087045
    6      -1.548641   -0.195120    1.106607
    6      -2.607145    0.760185   -0.855447
    6      -2.541556   -1.171292    1.156626
    1      -0.759459   -0.170612    1.851419
    6      -3.580275   -0.236992   -0.811631
    1      -2.635501    1.536979   -1.613942
    6      -3.554699   -1.205711    0.194398
    1      -2.523032   -1.911075    1.953023
    1      -4.370928   -0.247044   -1.557407
    1      -4.322418   -1.973204    0.235425
    7       1.292867    0.706731    0.089824
 --------------------------------------------
E = -592.38659946; ZPE = 0.249620
Number of imaginary freq = 0
```

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```
---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 --------------------------------------------
    6      -3.775862    1.183339   -0.199030
    6      -4.393072   -0.206311    0.012463
    6      -3.432334   -1.296599   -0.481959
    6      -2.051150   -1.182502    0.173997
    6      -2.405670    1.276367    0.478402
    1      -3.838462   -2.294902   -0.278770
    1      -4.598060   -0.354971    1.083028
    1      -5.356062   -0.281491   -0.506588
    1      -3.659339    1.376274   -1.273624
    1      -4.428592    1.966970    0.204227
    1      -2.102983   -1.454505    1.242193
    1      -1.325309   -1.849386   -0.292448
    1      -2.532452    1.239943    1.574655
    1      -1.890193    2.208909    0.236048
    1      -3.314806   -1.212413   -1.570376
    7      -0.230123    0.469163    0.083828
    7       0.542113   -0.534145    0.061305
    6       1.918024   -0.196170    0.006417
    6       2.428935    1.101001   -0.175592
    6       2.809489   -1.270377    0.135749
    6       3.804804    1.306741   -0.213523
    1       1.738772    1.929976   -0.286414
    6       4.186409   -1.057224    0.097318
    1       2.397144   -2.266279    0.268388
    6       4.690875    0.232616   -0.076853
    1       4.191628    2.313000   -0.355450
    1       4.865327   -1.899707    0.201172
    1       5.763788    0.401722   -0.110863
    7      -1.539575    0.183780    0.043508
 --------------------------------------------
E = -592.41384079; ZPE = 0.250169
Number of imaginary freq = 0
```

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```
---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 --------------------------------------------
    6       3.421713   -0.976573   -0.702844
    6       3.837429    0.490965   -0.878820
    6       2.601789    1.401765   -0.880930
    6       1.729402    1.178660    0.360278
    6       2.554167   -1.150117    0.546592
    1       2.897229    2.457382   -0.920162
    1       4.502960    0.781304   -0.052515
    1       4.409841    0.620369   -1.805152
    1       2.853129   -1.308548   -1.581552
    1       4.302926   -1.624422   -0.621128
    1       2.260791    1.512199    1.268346
    1       0.804657    1.748921    0.295367
    1       3.155751   -0.944018    1.449335
    1       2.164600   -2.166816    0.633074
    1       1.997750    1.202239   -1.775706
    7       0.359466   -0.699296    1.247953
    7      -0.634749    0.050848    1.437291
    6      -1.751731   -0.012703    0.560907
    6      -2.070972   -1.146552   -0.206895
    6      -2.622322    1.086433    0.558579
    6      -3.239047   -1.165274   -0.964705
    1      -1.400904   -1.999737   -0.198877
    6      -3.782969    1.063809   -0.213075
    1      -2.370652    1.948442    1.169388
    6      -4.098095   -0.061795   -0.977155
    1      -3.480474   -2.047340   -1.552731
    1      -4.445883    1.925201   -0.211905
    1      -5.005418   -0.082049   -1.574534
    7       1.400642   -0.247957    0.495778
 --------------------------------------------
E = -592.35859073; ZPE = 0.248260
Number of imaginary freq = 1 (-516.945 Hz)
```

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Atomic Number	Coordinates (Angstroms) X	Y	Z
6	3.469444	-0.328071	0.565201
6	1.860643	-1.596301	-0.567515
6	1.041061	-0.348880	-0.902966
6	2.724003	0.966114	0.251594
1	1.769864	-2.331435	-1.372596
1	3.149444	-0.711763	1.548007
1	4.548549	-0.151377	0.591531
1	1.348448	0.044880	-1.884994
1	-0.013763	-0.609429	-0.948612
1	3.113790	1.398835	-0.683588
1	2.856198	1.697078	1.052802
1	1.476334	-2.044080	0.363556
7	0.565831	1.855620	0.194755
7	-0.680950	1.896677	0.097318
6	-1.562190	0.776468	0.079504
6	-1.568003	-0.168972	1.120067
6	-2.580354	0.750034	-0.884120
6	-2.566919	-1.139139	1.169463
1	-0.793695	-0.132992	1.879789
6	-3.559156	-0.241640	-0.840120
1	-2.588705	1.510888	-1.658990
6	-3.559309	-1.188831	0.186478
1	-2.569174	-1.862057	1.981273
1	-4.333888	-0.263906	-1.602007
1	-4.331475	-1.951792	0.227271
7	1.289316	0.672530	0.132212
8	3.244170	-1.306416	-0.441120

E = -628.27514288; ZPE = 0.225540
Number of imaginary freq = 0

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Atomic Number	Coordinates (Angstroms) X	Y	Z
6	3.813616	1.076102	0.147532
6	3.475722	-1.220258	0.447316
6	2.057430	-1.166219	-0.121893
6	2.427863	1.260472	-0.468139
1	3.937646	-2.184972	0.219117
1	3.764937	1.248704	1.235334
1	4.523448	1.783912	-0.289874
1	2.050629	-1.471448	-1.180281
1	1.388996	-1.835484	0.422936
1	2.509960	1.228334	-1.566518
1	1.986742	2.219119	-0.181847
1	3.437116	-1.099421	1.542323
7	0.237288	0.487088	-0.057190
7	-0.528276	-0.519022	-0.025297
6	-1.907773	-0.190685	0.006232
6	-2.427891	1.102286	0.189611
6	-2.789350	-1.269732	-0.145122
6	-3.805299	1.299943	0.206145
1	-1.744257	1.934004	0.318929
6	-4.167937	-1.064392	-0.129149
1	-2.369023	-2.262262	-0.277550
6	-4.682114	0.221429	0.046083
1	-4.200558	2.302527	0.349963
1	-4.840366	-1.909564	-0.250729
1	-5.756370	0.384113	0.063550
7	1.548385	0.199131	0.008997
8	4.317967	-0.225202	-0.120327

E = -628.30190136; ZPE = 0.226106
Number of imaginary freq = 0

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Atomic Number	Coordinates (Angstroms) X	Y	Z
6	3.432456	1.176521	-0.112305
6	2.993839	-0.575665	1.376705
6	1.956449	-1.185287	0.431991
6	2.431324	0.619800	-1.120642
1	3.505040	-1.367373	1.932305
1	2.933948	1.915991	0.535925
1	4.263622	1.665596	-0.628396
1	2.440203	-1.929078	-0.221210
1	1.185063	-1.684353	1.013815
1	2.951716	-0.045234	-1.828222
1	1.958063	1.425489	-1.686864
1	2.485369	0.087468	2.095596
7	0.339761	-0.311409	-1.204314
7	-0.697823	-0.934368	-0.844103
6	-1.800240	-0.391192	-0.261663
6	-1.885595	0.986620	0.004816
6	-2.943553	-1.192415	-0.132025
6	-3.095390	1.538356	0.421323
1	-1.006482	1.610918	-0.119430
6	-4.141718	-0.634562	0.311381
1	-2.875410	-2.247341	-0.380779
6	-4.224877	0.732078	0.587885
1	-3.155582	2.605733	0.618136
1	-5.017655	-1.267734	0.425424
1	-5.163343	1.167477	0.919129
7	1.380857	-0.108732	-0.396396
8	3.999963	0.137309	0.674182

E = -628.24572841; ZPE = 0.224073
Number of imaginary freq = 1 (-524.356 Hz)

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Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	-2.375264	1.298784	-0.429226
7	-1.233243	1.799326	-0.263047
6	-0.032004	1.043474	-0.143043
6	0.335881	0.036589	-1.052184
6	0.909569	1.482845	0.800950
6	1.607677	-0.532117	-1.001072
1	-0.369115	-0.286926	-1.811335
6	2.169511	0.897800	0.877873
1	0.637191	2.291927	1.471867
6	2.511245	-0.107960	-0.027740
1	1.894688	-1.301363	-1.710526
1	2.887918	1.227561	1.620961
6	-2.052473	-1.014580	0.634309
6	-3.993668	-0.478605	-0.141385
6	-3.453896	-1.670798	0.690480
1	-1.738844	-0.525219	1.563815
1	-1.225405	-1.620714	0.255879
1	-4.576065	0.250118	0.433076
1	-4.524545	-0.717869	-1.068232
1	-3.882820	-1.779675	1.688427
1	-3.504134	-2.629461	0.169757
7	-2.599956	-0.033986	-0.352220
17	4.108784	-0.841008	0.051096

E = -973.32792939; ZPE = 0.180700

Number of imaginary freq = 0

trans-Cl-4

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	1.836832	-0.520927	-0.181227
7	1.112788	0.520246	-0.220058
6	-0.275205	0.257001	-0.135821
6	-0.863329	-1.019863	-0.163185
6	-1.101848	1.384054	-0.031565
6	-2.243883	-1.160535	-0.076408
1	-0.228801	-1.894269	-0.254519
6	-2.485658	1.252699	0.057664
1	-0.637124	2.365095	-0.019114
6	-3.046849	-0.022678	0.035262
1	-2.700299	-2.144780	-0.098915
1	-3.121750	2.127469	0.140968
6	3.829879	1.008165	-0.036450
6	4.193153	-1.109958	0.238160
6	5.081451	0.164401	0.332207
1	3.362410	1.543724	0.798952
1	3.906524	1.683437	-0.893429
1	3.920705	-1.543718	1.207528
1	4.532815	-1.905217	-0.433428
1	5.507842	0.363405	1.316920
1	5.872826	0.201702	-0.419293
7	3.131938	-0.261030	-0.324469
17	-4.794843	-0.204975	0.142084

E = -973.34718415; ZPE = 0.181047

Number of imaginary freq = 0

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Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	-2.009850	-0.325845	-1.040192
7	-1.121854	0.567597	-1.136503
6	0.187838	0.295895	-0.660406
6	0.713784	-0.995439	-0.481711
6	1.022720	1.404574	-0.457553
6	2.042241	-1.169366	-0.103156
1	0.079089	-1.859040	-0.649423
6	2.347969	1.239336	-0.064707
1	0.613854	2.397834	-0.615707
6	2.849373	-0.050606	0.108942
1	2.450677	-2.165789	0.030344
1	2.988558	2.099445	0.098878
6	-3.249647	0.852566	0.841192
6	-4.116016	-0.954335	0.028113
6	-4.592304	0.106529	1.058243
1	-3.315790	1.755682	0.222693
1	-2.642522	1.070350	1.724047
1	-4.596451	-0.879909	-0.954120
1	-4.114781	-1.999579	0.353605
1	-5.488979	0.661849	0.777185
1	-4.713431	-0.287616	2.069451
7	-2.785915	-0.318813	0.053675
17	4.525138	-0.272278	0.599438

E = -973.29151555; ZPE = 0.178996

Number of imaginary freq = 1 (-564.046 Hz)

cis-CF_3-4

```
 ---------------------------------------------
 Atomic        Coordinates (Angstroms)
 Number        X             Y             Z
 ---------------------------------------------
    7      3.054288   -1.255066   -0.431419
    7      1.942665   -1.820885   -0.264012
    6      0.702387   -1.136341   -0.142112
    6      0.264827   -0.188656   -1.084894
    6     -0.193305   -1.585399    0.841799
    6     -1.032639    0.311061   -1.023558
    1      0.940032    0.140824   -1.868180
    6     -1.479312   -1.063856    0.915704
    1      0.139366   -2.344645    1.542829
    6     -1.905947   -0.112589   -0.017489
    1     -1.365713    1.041511   -1.754143
    1     -2.157572   -1.397784    1.694087
    6      2.586333    1.043881    0.618332
    6      4.564800    0.617677   -0.138292
    6      3.947209    1.780461    0.681924
    1      2.287423    0.550804    1.550502
    1      1.732153    1.596359    0.218574
    1      5.193571   -0.066841    0.441379
    1      5.078520    0.883793   -1.067412
    1      4.359605    1.917344    1.683310
    1      3.947282    2.738502    0.157854
    7      3.203228    0.082755   -0.345305
    6     -3.316499    0.402127    0.016877
    9     -4.147323   -0.339662   -0.754286
    9     -3.829819    0.385822    1.268252
    9     -3.398754    1.674097   -0.438788
 ---------------------------------------------
E = -850.7701749; ZPE = 0.195107
Number of imaginary freq = 0
```

trans-CF_3-4

```
 ---------------------------------------------
 Atomic        Coordinates (Angstroms)
 Number        X             Y             Z
 ---------------------------------------------
    7      2.526304   -0.511536   -0.173985
    7      1.815799    0.540309   -0.229217
    6      0.424721    0.291146   -0.167584
    6     -0.175341   -0.979834   -0.224744
    6     -0.390773    1.427210   -0.061461
    6     -1.557282   -1.100660   -0.160454
    1      0.451820   -1.858362   -0.323946
    6     -1.774764    1.304109    0.004226
    1      0.085749    2.402014   -0.032227
    6     -2.364389    0.038097   -0.044406
    1     -2.018376   -2.081838   -0.212554
    1     -2.397889    2.188994    0.083070
    6      4.542592    0.989472   -0.024824
    6      4.874067   -1.135427    0.259309
    6      5.779207    0.127578    0.354479
    1      4.084130    1.545993    0.801551
    1      4.631622    1.649678   -0.892272
    1      4.598929   -1.571799    1.226519
    1      5.201105   -1.930515   -0.418637
    1      6.200006    0.323487    1.342128
    1      6.577196    0.151404   -0.390390
    7      3.822470   -0.270478   -0.295063
    6     -3.853414   -0.107437    0.083846
    9     -4.239369   -0.239427    1.377214
    9     -4.512780    0.966303   -0.408498
    9     -4.313856   -1.199392   -0.569350
 ---------------------------------------------
E = -850.78934391; ZPE = 0.195475
Number of imaginary freq = 0
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ts-CF_3-4

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 Atomic        Coordinates (Angstroms)
 Number        X             Y             Z
 ---------------------------------------------
    7     -2.849015    0.669363   -1.044694
    7     -1.820659    1.152379   -0.468463
    6     -0.528269    0.777900   -0.323402
    6     -0.033263   -0.436707   -0.870867
    6      0.374722    1.609971    0.385621
    6      1.299683   -0.784614   -0.710506
    1     -0.709381   -1.085273   -1.419722
    6      1.699684    1.239475    0.536941
    1      0.007974    2.539877    0.808226
    6      2.183120    0.038410   -0.002995
    1      1.658428   -1.717746   -1.135006
    1      2.373338    1.886967    1.090048
    6     -3.508273   -0.438927    1.131430
    6     -5.002753   -0.446656   -0.459265
    6     -5.007029   -0.847445    1.046375
    1     -3.271419    0.467495    1.701048
    1     -2.791576   -1.222979    1.389955
    1     -5.591557    0.435919   -0.726139
    1     -5.200742   -1.251417   -1.173188
    1     -5.674850   -0.250976    1.669995
    1     -5.193832   -1.907335    1.226191
    7     -3.568367   -0.139032   -0.313159
    6      3.626518   -0.321734    0.117755
    9      4.382254    0.168411   -0.901714
    9      3.820323   -1.664786    0.115035
    9      4.179098    0.161760    1.258488
 ---------------------------------------------
E = -850.73705231; ZPE = 0.193498
Number of imaginary freq = 1 (-521.504 Hz)
```

cis-CH_3-5

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
7	-1.551554	1.564315	-0.297593
7	-0.367892	1.867741	-0.002323
6	0.747108	0.983409	0.006408
6	1.061305	0.143626	-1.074537
6	1.684437	1.125332	1.041906
6	2.272976	-0.547264	-1.096428
1	0.363088	0.047100	-1.900700
6	2.874655	0.406822	1.020652
1	1.459043	1.804152	1.859401
6	3.197521	-0.440606	-0.050638
1	2.501242	-1.186526	-1.946900
1	3.576147	0.516345	1.845321
6	-1.497672	-0.847463	0.407337
6	-3.429888	0.170760	-0.662394
6	-2.747975	-1.721678	0.623867
1	-1.115660	-0.436398	1.349924
1	-0.678208	-1.393648	-0.067446
6	-3.924544	-0.745553	0.460975
1	-3.619497	-0.278333	-1.647035
1	-3.853308	1.177068	-0.655885
1	-2.797671	-2.501098	-0.145885
1	-2.728660	-2.220402	1.597776
1	-4.868143	-1.245492	0.221833
1	-4.069326	-0.164416	1.379850
7	-1.975850	0.274630	-0.437163
6	4.512827	-1.183190	-0.085176
1	5.342012	-0.519061	-0.364114
1	4.759934	-1.609814	0.894081
1	4.491581	-2.001454	-0.812503

E = -592.38939443; ZPE = 0.247827
Number of imaginary freq = 0

trans-CH_3-5

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
7	1.049196	-0.491724	-0.106956
7	0.307150	0.541836	-0.058739
6	-1.077600	0.248186	-0.033487
6	-1.643457	-1.039535	-0.064514
6	-1.934603	1.354402	0.024767
6	-3.023775	-1.196415	-0.035154
1	-0.990153	-1.903751	-0.114454
6	-3.317611	1.183948	0.054239
1	-1.492998	2.346531	0.043771
6	-3.890600	-0.092375	0.027658
1	-3.443564	-2.200500	-0.062610
1	-3.962535	2.059106	0.097735
6	2.920658	1.124657	-0.025138
6	3.323884	-1.297777	-0.107739
6	4.431044	0.847876	-0.115858
1	2.621375	1.583622	0.927284
1	2.537107	1.768093	-0.823810
6	4.581615	-0.591087	0.419489
1	3.484398	-1.698867	-1.119771
1	2.975001	-2.115586	0.529106
1	4.757828	0.895142	-1.161487
1	5.020733	1.576073	0.448474
1	5.504590	-1.077074	0.090252
1	4.573680	-0.588223	1.515885
7	2.341123	-0.217336	-0.126022
6	-5.387993	-0.284914	0.083510
1	-5.725437	-1.033155	-0.643627
1	-5.712383	-0.632123	1.073990
1	-5.919299	0.649482	-0.125355

E = -592.41305066; ZPE = 0.248097
Number of imaginary freq = 0

ts-CH_3-5

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
7	1.355574	-1.148547	-0.727008
7	0.324985	-1.233527	0.013445
6	-0.932005	-0.715033	-0.007027
6	-1.347048	0.198112	-1.010814
6	-1.866735	-1.084423	0.989960
6	-2.644073	0.704641	-1.003505
1	-0.644676	0.483209	-1.789240
6	-3.152672	-0.559494	0.975576
1	-1.559577	-1.785646	1.760140
6	-3.561432	0.340116	-0.016013
1	-2.937764	1.398569	-1.788654
1	-3.850508	-0.860556	1.753999
6	2.060779	0.683996	0.767119
6	3.579734	-0.225399	-0.932750
6	3.459581	1.304761	0.924263
1	1.757518	0.044432	1.607797
1	1.261898	1.414265	0.611156
6	4.405161	0.283657	0.257312
1	3.661938	0.452201	-1.792616
1	3.813504	-1.239092	-1.263338
1	3.507889	2.263904	0.395634
1	3.708304	1.493208	1.972417
1	5.358783	0.721159	-0.050915
1	4.617152	-0.544278	0.943759
7	2.206893	-0.194278	-0.407835
6	-4.991217	0.912221	-0.019207
1	-5.657314	0.205111	-0.467771
1	-5.300464	1.105058	0.986815
1	-5.009295	1.823997	-0.578884

E = -592.35709730; ZPE = 0.246325
Number of imaginary freq = 1 (-539.018 Hz)

cis-CH_3O-5 in cyclohexane

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
7	2.008753	1.552316	0.177219
7	0.825368	1.889245	-0.093361
6	-0.325142	1.053767	0.002793
6	-0.601731	0.242102	1.120973
6	-1.330721	1.231673	-0.955317
6	-1.835579	-0.382523	1.251192
1	0.147043	0.121089	1.898547
6	-2.559824	0.580667	-0.848275
1	-1.138117	1.892736	-1.796493
6	-2.820014	-0.231800	0.262821
1	-2.059444	-0.999130	2.117678
1	-3.305650	0.729369	-1.621307
6	1.848461	-0.881546	-0.400561
6	3.839438	0.108324	0.585673
6	3.060692	-1.810868	-0.599117
1	1.468317	-0.494054	-1.353995
1	1.018015	-1.377571	0.108588
6	4.274177	-0.871994	-0.507385
1	4.034048	-0.305189	1.584487
1	4.299606	1.096974	0.526210
1	3.098470	-2.553353	0.207050
1	3.000829	-2.353710	-1.547531
1	5.205145	-1.394550	-0.266919
1	4.416283	-0.336506	-1.454171
7	2.382757	0.256900	0.390423
8	-3.989125	-0.905638	0.480126
6	-5.026943	-0.773362	-0.480806
1	-5.854243	-1.383631	-0.113753
1	-5.358640	0.268947	-0.574856
1	-4.713684	-1.142179	-1.466462

E = -667.59823226; ZPE = 0.252897

Number of imaginary freq = 0

trans-CH_3O-5 in cyclohexane

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
7	-1.501738	0.501255	-0.098332
7	-0.724290	-0.508445	-0.057247
6	0.649563	-0.167999	-0.038924
6	1.173265	1.140904	-0.059515
6	1.547310	-1.240036	0.005074
6	2.542668	1.352481	-0.036165
1	0.491724	1.984485	-0.093481
6	2.929065	-1.037237	0.029272
1	1.143552	-2.249082	0.020622
6	3.434417	0.266841	0.008825
1	2.953644	2.358684	-0.051439
1	3.590429	-1.895969	0.063612
6	-3.327097	-1.168835	-0.022609
6	-3.799578	1.241622	-0.097658
6	-4.843998	-0.934747	-0.122472
1	-3.022681	-1.625771	0.929443
1	-2.920664	-1.795368	-0.823921
6	-5.039290	0.496715	0.418310
1	-3.963124	1.638523	-1.110760
1	-3.480079	2.067908	0.544033
1	-5.161372	-0.986406	-1.170852
1	-5.415575	-1.682408	0.435128
1	-5.973127	0.957716	0.083714
1	-5.038268	0.489473	1.514824
7	-2.784221	0.189589	-0.110272
8	4.763296	0.591937	0.029862
6	5.708547	-0.465456	0.081722
1	5.586770	-1.071590	0.989317
1	5.633681	-1.118066	-0.798343
1	6.691232	0.010073	0.095004

E = -667.62113290; ZPE = 0.252961

Number of imaginary freq = 0

ts-CH_3O-5 in cyclohexane

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
7	-1.805252	-1.267006	0.488434
7	-0.761750	-1.272424	-0.256522
6	0.496522	-0.772125	-0.076680
6	0.862941	-0.035253	1.080340
6	1.492461	-0.984914	-1.053820
6	2.157556	0.446026	1.236981
1	0.122336	0.140279	1.856417
6	2.787131	-0.492797	-0.889148
1	1.238015	-1.547911	-1.947746
6	3.134370	0.228081	0.259199
1	2.430030	1.003057	2.130461
1	3.516458	-0.684252	-1.669701
6	-2.441621	0.797102	-0.700168
6	-3.996030	-0.313873	0.844286
6	-3.814238	1.490065	-0.742831
1	-2.161733	0.295355	-1.636632
1	-1.614725	1.457030	-0.423371
6	-4.800823	0.415305	-0.239437
1	-4.035286	0.223581	1.800513
1	-4.274768	-1.355646	1.013974
1	-3.820703	2.353479	-0.067431
1	-4.056749	1.852117	-1.745881
1	-5.731785	0.838447	0.147837
1	-5.052809	-0.281421	-1.047477
7	-2.624246	-0.262428	0.311449
8	4.383414	0.756195	0.518153
6	5.399555	0.528124	-0.438650
1	6.299916	1.007638	-0.047425
1	5.595074	-0.544663	-0.579102
1	5.151190	0.971909	-1.413608

E = -667.56394656; ZPE = 0.251123

Number of imaginary freq = 1 (-570.411 Hz)

cis-CH_3O-5 in DMSO

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	2.014130	1.556384	0.164506
7	0.825431	1.899551	-0.103353
6	-0.325800	1.062422	-0.003844
6	-0.608710	0.279212	1.132990
6	-1.322519	1.211124	-0.976754
6	-1.842259	-0.346632	1.268087
1	0.132145	0.178834	1.923307
6	-2.552373	0.561046	-0.862593
1	-1.125638	1.844646	-1.840063
6	-2.819188	-0.222985	0.267721
1	-2.067962	-0.943544	2.149936
1	-3.289182	0.687393	-1.649354
6	1.837726	-0.887515	-0.377598
6	3.851823	0.113337	0.562264
6	3.041453	-1.831279	-0.559903
1	1.445329	-0.529690	-1.337377
1	1.014729	-1.357831	0.166270
6	4.265779	-0.902785	-0.504475
1	4.038644	-0.276952	1.571655
1	4.328329	1.092584	0.475584
1	3.078531	-2.551226	0.266458
1	2.967899	-2.397509	-1.493574
1	5.191514	-1.428908	-0.251961
1	4.407867	-0.396878	-1.467597
7	2.395597	0.275382	0.362165
8	-3.989653	-0.893068	0.493210
6	-5.019288	-0.794382	-0.486270
1	-5.848614	-1.395926	-0.109498
1	-5.351359	0.243522	-0.615642
1	-4.690977	-1.192572	-1.454785

E = -667.60679527; ZPE = 0.252265
Number of imaginary freq = 0

trans-CH_3O-5 in DMSO

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	-1.503452	0.482473	-0.101683
7	-0.722571	-0.528499	-0.033914
6	0.651100	-0.180197	-0.023492
6	1.168611	1.132203	-0.025135
6	1.557944	-1.247076	-0.002078
6	2.538081	1.351504	-0.009351
1	0.485212	1.976484	-0.037740
6	2.939419	-1.037142	0.014031
1	1.164667	-2.262101	0.000928
6	3.437312	0.270585	0.010384
1	2.939853	2.363380	-0.009412
1	3.603242	-1.895588	0.029626
6	-3.343106	-1.170412	0.012157
6	-3.794144	1.241984	-0.139770
6	-4.856068	-0.925161	-0.113932
1	-3.056697	-1.605915	0.979781
1	-2.932328	-1.818041	-0.770446
6	-5.045402	0.522879	0.382413
1	-3.936977	1.598555	-1.170372
1	-3.477556	2.088173	0.477130
1	-5.159735	-1.004956	-1.164646
1	-5.439388	-1.651494	0.459562
1	-5.969491	0.981928	0.019248
1	-5.058771	0.548977	1.478722
7	-2.783173	0.181401	-0.098954
8	4.764746	0.603219	0.026650
6	5.719536	-0.452517	0.053712
1	5.606615	-1.072495	0.952307
1	5.639045	-1.089537	-0.836434
1	6.699018	0.029364	0.066775

E = -667.62783433; ZPE = 0.252277
Number of imaginary freq = 0

ts-CH_3O-5 in DMSO

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	1.693609	-0.736602	0.961911
7	0.736707	-0.000949	1.365127
6	-0.540866	-0.111528	0.750503
6	-1.016125	-1.269483	0.101631
6	-1.418932	0.967467	0.912067
6	-2.319224	-1.326405	-0.374144
1	-0.361351	-2.129127	-0.016930
6	-2.726564	0.924567	0.423434
1	-1.064234	1.857383	1.429195
6	-3.184399	-0.229519	-0.224270
1	-2.691141	-2.221171	-0.870308
1	-3.369235	1.788068	0.561927
6	2.780633	1.184865	-0.221262
6	3.692928	-1.089179	-0.325738
6	4.129501	1.185865	-0.964166
1	2.817598	1.742521	0.723852
1	1.960035	1.597953	-0.815776
6	4.842379	-0.083412	-0.458974
1	3.475862	-1.577645	-1.286037
1	3.855211	-1.864966	0.427244
1	3.959331	1.115483	-2.045214
1	4.696220	2.102205	-0.773397
1	5.627380	-0.432532	-1.136428
1	5.293126	0.099844	0.524127
7	2.557548	-0.243905	0.074515
8	-4.442629	-0.391064	-0.736302
6	-5.363671	0.687137	-0.604905
1	-6.232589	0.338331	-0.037981
1	-4.910602	1.541247	-0.085610
1	-5.683599	0.998854	-1.604173

E = -667.57425690; ZPE = 0.250633
Number of imaginary freq = 1 (-549.162 Hz)

cis-CH_3-5 in cyclohexane

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
7	-1.553033	1.569376	-0.294399
7	-0.365601	1.875759	-0.003551
6	0.748806	0.989020	0.006346
6	1.065076	0.157498	-1.080445
6	1.681308	1.119737	1.047718
6	2.274730	-0.537817	-1.102277
1	0.371211	0.069827	-1.912348
6	2.870474	0.398397	1.025444
1	1.454203	1.790442	1.872759
6	3.195164	-0.441726	-0.051378
1	2.503930	-1.171799	-1.957272
1	3.568482	0.499408	1.855057
6	-1.493133	-0.845184	0.403851
6	-3.438426	0.178262	-0.644874
6	-2.734852	-1.735501	0.598745
1	-1.119451	-0.446636	1.355267
1	-0.667649	-1.373847	-0.079545
6	-3.920631	-0.767204	0.459315
1	-3.626408	-0.249515	-1.639127
1	-3.871499	1.180321	-0.613652
1	-2.776362	-2.495806	-0.190371
1	-2.709970	-2.256567	1.560761
1	-4.859391	-1.270667	0.208957
1	-4.069605	-0.207784	1.391024
7	-1.983030	0.287204	-0.420887
6	4.507867	-1.189269	-0.085384
1	5.343207	-0.522242	-0.337849
1	4.740007	-1.638368	0.887446
1	4.492651	-1.990417	-0.831603

E = -592.39349962; ZPE = 0.247594
Number of imaginary freq = 0

trans-CH_3-5 in cyclohexane

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
7	1.049834	-0.482165	-0.097854
7	0.305697	0.553009	-0.048476
6	-1.078662	0.254577	-0.028814
6	-1.641362	-1.035283	-0.058521
6	-1.941370	1.357751	0.024075
6	-3.021771	-1.197347	-0.033651
1	-0.986536	-1.899459	-0.103488
6	-3.324391	1.182436	0.048907
1	-1.505042	2.353250	0.042653
6	-3.893209	-0.096266	0.023463
1	-3.437097	-2.204030	-0.059868
1	-3.972243	2.056462	0.088127
6	2.929012	1.125601	-0.016180
6	3.320355	-1.299252	-0.112886
6	4.436753	0.841436	-0.124890
1	2.644040	1.586870	0.939529
1	2.538970	1.768485	-0.812508
6	4.586811	-0.600466	0.402414
1	3.463308	-1.689101	-1.131600
1	2.977411	-2.121185	0.522044
1	4.751549	0.892306	-1.174070
1	5.034956	1.564518	0.437091
1	5.502599	-1.089410	0.057935
1	4.592363	-0.603235	1.498908
7	2.339702	-0.213973	-0.107354
6	-5.390220	-0.294100	0.075074
1	-5.722504	-1.045404	-0.651265
1	-5.716058	-0.640830	1.065278
1	-5.924009	0.638139	-0.136924

E = -592.41613644; ZPE = 0.247729
Number of imaginary freq = 0

ts-CH_3-5 in cyclohexane

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
7	1.355574	-1.148547	-0.727008
7	0.324985	-1.233527	0.013445
6	-0.932005	-0.715033	-0.007027
6	-1.347048	0.198112	-1.010814
6	-1.866735	-1.084423	0.989960
6	-2.644073	0.704641	-1.003505
1	-0.644676	0.483209	-1.789240
6	-3.152672	-0.559494	0.975576
1	-1.559577	-1.785646	1.760140
6	-3.561432	0.340116	-0.016013
1	-2.937764	1.398569	-1.788654
1	-3.850508	-0.860556	1.753999
6	2.060779	0.683996	0.767119
6	3.579734	-0.225399	-0.932750
6	3.459581	1.304761	0.924263
1	1.757518	0.044432	1.607797
1	1.261898	1.414265	0.611156
6	4.405161	0.283657	0.257312
1	3.661938	0.452201	-1.792616
1	3.813504	-1.239092	-1.263338
1	3.507889	2.263904	0.395634
1	3.708304	1.493208	1.972417
1	5.358783	0.721159	-0.050915
1	4.617152	-0.544278	0.943759
7	2.206893	-0.194278	-0.407835
6	-4.991217	0.912221	-0.019207
1	-5.657314	0.205111	-0.467771
1	-5.300464	1.105058	0.986815
1	-5.009295	1.823997	-0.578884

E = -592.36194742; ZPE = 0.246029
Number of imaginary freq = 1 (-534.467 Hz)

cis-CH$_3$-5 in DMSO

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	1.555624	-1.575770	-0.290075
7	0.360609	-1.889013	-0.010218
6	-0.752768	-0.996715	0.004742
6	-1.073336	-0.176507	-1.089620
6	-1.676941	-1.111736	1.055588
6	-2.279945	0.525657	-1.109460
1	-0.385996	-0.098720	-1.929997
6	-2.865458	-0.387188	1.033177
1	-1.445796	-1.768768	1.892461
6	-3.193760	0.442989	-0.050783
1	-2.510329	1.154414	-1.969451
1	-3.556976	-0.475570	1.871206
6	1.486712	0.848478	0.390128
6	3.453725	-0.191078	-0.616040
6	2.719571	1.755138	0.561348
1	1.108304	0.479603	1.351273
1	0.664132	1.350959	-0.124080
6	3.917325	0.796655	0.457388
1	3.634021	0.207202	-1.623647
1	3.902014	-1.185143	-0.550863
1	2.755435	2.490945	-0.250876
1	2.684653	2.303236	1.507931
1	4.849351	1.303574	0.189594
1	4.071450	0.270929	1.407846
7	1.997611	-0.310043	-0.387681
6	-4.503255	1.196816	-0.083356
1	-5.342479	0.532261	-0.329980
1	-4.729754	1.649471	0.889082
1	-4.486157	1.994336	-0.833355

E = -592.40105191; ZPE = 0.247006
Number of imaginary freq = 0

trans-CH$_3$-5 in DMSO

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	1.052127	-0.466313	-0.096740
7	0.303746	0.570795	-0.042711
6	-1.080302	0.264230	-0.024456
6	-1.638094	-1.029070	-0.051857
6	-1.951447	1.362467	0.024092
6	-3.018696	-1.198928	-0.030203
1	-0.981552	-1.893608	-0.092625
6	-3.334480	1.180202	0.045665
1	-1.524037	2.363594	0.041531
6	-3.896952	-0.102176	0.021662
1	-3.427415	-2.209615	-0.054834
1	-3.986495	2.052826	0.081046
6	2.943429	1.127088	-0.010649
6	3.314882	-1.301952	-0.118833
6	4.447814	0.830069	-0.124845
1	2.666341	1.583837	0.949717
1	2.557420	1.776658	-0.803946
6	4.587389	-0.615126	0.395505
1	3.449547	-1.683330	-1.141367
1	2.966069	-2.123746	0.513210
1	4.759617	0.883571	-1.174826
1	5.051349	1.545970	0.440752
1	5.496504	-1.110106	0.041982
1	4.597894	-0.624234	1.492088
7	2.338782	-0.207393	-0.105916
6	-5.393315	-0.307684	0.068718
1	-5.718661	-1.063309	-0.656264
1	-5.719842	-0.654599	1.058660
1	-5.930700	0.621748	-0.146363

E = -592.42182514; ZPE = 0.247079
Number of imaginary freq = 0

ts-CH$_3$-5 in DMSO

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	1.355574	-1.148547	-0.727008
7	0.324985	-1.233527	0.013445
6	-0.932005	-0.715033	-0.007027
6	-1.347048	0.198112	-1.010814
6	-1.866735	-1.084423	0.989960
6	-2.644073	0.704641	-1.003505
1	-0.644676	0.483209	-1.789240
6	-3.152672	-0.559494	0.975576
1	-1.559577	-1.785646	1.760140
6	-3.561432	0.340116	-0.016013
1	-2.937764	1.398569	-1.788654
1	-3.850508	-0.860556	1.753999
6	2.060779	0.683996	0.767119
6	3.579734	-0.225399	-0.932750
6	3.459581	1.304761	0.924263
1	1.757518	0.044432	1.607797
1	1.261898	1.414265	0.611156
6	4.405161	0.283657	0.257312
1	3.661938	0.452201	-1.792616
1	3.813504	-1.239092	-1.263338
1	3.507889	2.263904	0.395634
1	3.708304	1.493208	1.972417
1	5.358783	0.721159	-0.050915
1	4.617152	-0.544278	0.943759
7	2.206893	-0.194278	-0.407835
6	-4.991217	0.912221	-0.019207
1	-5.657314	0.205111	-0.467771
1	-5.300464	1.105058	0.986815
1	-5.009295	1.823997	-0.578884

E = -592.37097743; ZPE = 0.245491
Number of imaginary freq = 1 (-506.37 Hz)

cis-H-4 in acetonitrile

```
---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 --------------------------------------------
    7      -1.350820    1.420012   -0.472246
    7      -0.127571    1.700759   -0.312229
    6       0.903537    0.724216   -0.148603
    6       1.086546   -0.340537   -1.047934
    6       1.880500    0.975970    0.828587
    6       2.221401   -1.147973   -0.949915
    1       0.352568   -0.521699   -1.830565
    6       2.996742    0.147894    0.936155
    1       1.748483    1.823860    1.498633
    6       3.173942   -0.916804    0.046021
    1       2.357959   -1.964963   -1.657205
    1       3.738235    0.342429    1.709780
    1       4.052804   -1.554754    0.122076
    6      -1.480065   -0.899529    0.625671
    6      -3.291589   -0.004042   -0.153757
    6      -2.985452   -1.253275    0.712577
    1      -1.050412   -0.486511    1.545004
    1      -0.808996   -1.662614    0.223354
    1      -3.741108    0.833365    0.391401
    1      -3.840217   -0.172940   -1.086110
    1      -3.407597   -1.230448    1.719221
    1      -3.240553   -2.199504    0.230265
    7      -1.835115    0.176122   -0.352477
 -------------------------------------------
```

E = -513.74414639; ZPE = 0.189426
Number of imaginary freq = 0

trans-H-4 in acetonitrile

```
---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 --------------------------------------------
    7      -0.952935    0.516984   -0.119908
    7      -0.188769   -0.497058   -0.212936
    6       1.190539   -0.185442   -0.092239
    6       1.734225    1.112455   -0.121321
    6       2.053883   -1.284120    0.041085
    6       3.110379    1.294535   -0.002289
    1       1.073224    1.966445   -0.240558
    6       3.430847   -1.094919    0.161770
    1       1.623058   -2.283715    0.053343
    6       3.966174    0.195609    0.141766
    1       3.520905    2.303250   -0.027934
    1       4.086204   -1.958071    0.268957
    1       5.040723    0.346229    0.231086
    6      -2.926740   -1.055678   -0.133251
    6      -3.337502    1.040309    0.254753
    6      -4.201397   -0.253846    0.247919
    1      -2.483015   -1.645271    0.678822
    1      -2.966526   -1.665585   -1.041307
    1      -3.111914    1.432010    1.253468
    1      -3.665401    1.857842   -0.396050
    1      -4.644377   -0.517678    1.209974
    1      -4.972457   -0.261282   -0.525555
    7      -2.232992    0.238989   -0.303356
 --------------------------------------------
```

E = -513.75974752; ZPE = 0.189598
Number of imaginary freq = 0

ts-H-4 in acetonitrile

```
---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 --------------------------------------------
    7      -1.085305    0.415246    1.007419
    7      -0.142710   -0.428167    1.112190
    6       1.099581   -0.155177    0.471065
    6       1.515639    1.129880    0.078977
    6       1.979224   -1.238514    0.316656
    6       2.789106    1.315739   -0.458619
    1       0.843587    1.975367    0.204453
    6       3.246339   -1.046448   -0.233239
    1       1.652167   -2.226805    0.635160
    6       3.658306    0.231898   -0.622163
    1       3.103032    2.315520   -0.755982
    1       3.915712   -1.897070   -0.353504
    1       4.648930    0.383647   -1.047462
    6      -2.439357   -0.982832   -0.636606
    6      -3.307732    0.869548    0.082592
    6      -3.829210   -0.309832   -0.783582
    1      -2.406250   -1.836005    0.051265
    1      -1.905284   -1.239176   -1.556044
    1      -3.703472    0.895896    1.104272
    1      -3.363078    1.869859   -0.359479
    1      -4.661264   -0.867621   -0.349668
    1      -4.072946   -0.027686   -1.810197
    7      -1.960916    0.265565    0.015633
 --------------------------------------------
```

E = -513.70888451; ZPE = 0.187604
Number of imaginary freq = 1 (-532.672 Hz)

cis-H-4 in benzene

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	−1.349717	1.423551	−0.468801
7	−0.131886	1.702343	−0.304062
6	0.899200	0.726820	−0.145699
6	1.088421	−0.326177	−1.057266
6	1.870272	0.965975	0.839151
6	2.222124	−1.134325	−0.962895
1	0.358005	−0.494564	−1.844095
6	2.984163	0.135865	0.944125
1	1.734170	1.807523	1.513891
6	3.167390	−0.916946	0.042309
1	2.364739	−1.940050	−1.679922
1	3.720288	0.320602	1.723413
1	4.044825	−1.554831	0.115880
6	−1.475797	−0.890118	0.637978
6	−3.281082	−0.007088	−0.154153
6	−2.977115	−1.264678	0.700501
1	−1.074207	−0.457868	1.561522
1	−0.781259	−1.647518	0.266218
1	−3.720683	0.827193	0.403987
1	−3.842246	−0.160194	−1.081694
1	−3.417627	−1.268418	1.699467
1	−3.211270	−2.205804	0.197919
7	−1.826996	0.165244	−0.361551

E = -513.73694291; ZPE = 0.190018
Number of imaginary freq = 0

trans-H-4 in benzene

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	−0.953619	0.530586	−0.154338
7	−0.193804	−0.484549	−0.214662
6	1.185749	−0.178727	−0.093397
6	1.733139	1.116880	−0.103019
6	2.042527	−1.282570	0.026400
6	3.108979	1.291092	0.019112
1	1.072711	1.971526	−0.208764
6	3.419473	−1.101028	0.150312
1	1.604363	−2.277349	0.023526
6	3.959333	0.186820	0.148092
1	3.524075	2.296846	0.008876
1	4.071029	−1.966804	0.245776
1	5.033190	0.331625	0.240256
6	−2.905573	−1.059078	−0.101718
6	−3.334261	1.037580	0.236718
6	−4.186673	−0.263536	0.270791
1	−2.438586	−1.607998	0.725542
1	−2.948384	−1.707715	−0.981739
1	−3.090760	1.444440	1.225309
1	−3.684549	1.845285	−0.414463
1	−4.624221	−0.507953	1.240376
1	−4.962217	−0.297251	−0.497442
7	−2.237265	0.238356	−0.334855

E = -513.75423730; ZPE = 0.190268
Number of imaginary freq = 0

ts-H-4 in benzene

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	1.215393	−0.071255	−1.245924
7	0.158278	−0.641488	−0.845048
6	−1.080398	−0.290213	−0.406639
6	−1.457760	1.070138	−0.269507
6	−2.029788	−1.288001	−0.084178
6	−2.736588	1.397831	0.171589
1	−0.740163	1.846256	−0.519750
6	−3.297742	−0.931080	0.358185
1	−1.750076	−2.331688	−0.191243
6	−3.670641	0.410688	0.493588
1	−3.002821	2.448893	0.263504
1	−4.008923	−1.717967	0.599809
1	−4.664567	0.678496	0.839045
6	2.132919	−0.229195	1.103384
6	3.546271	0.334273	−0.456921
6	3.676201	−0.044831	1.048258
1	1.760530	−1.258080	1.182042
1	1.577259	0.405854	1.798609
1	3.942366	−0.394895	−1.170455
1	3.882189	1.338194	−0.733267
1	4.251087	−0.952578	1.239897
1	4.053072	0.761854	1.679506
7	2.084216	0.226744	−0.299636

E = -513.70000970; ZPE = 0.188132
Number of imaginary freq = 1 (-564.44 Hz)

cis-H-4 in cyclohexane

```
---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 --------------------------------------------
    7       -1.349009    1.423021   -0.469992
    7       -0.131584    1.701833   -0.303665
    6        0.899141    0.726075   -0.144999
    6        1.086380   -0.328964   -1.054669
    6        1.872513    0.967331    0.837012
    6        2.220385   -1.136799   -0.961082
    1        0.354260   -0.499174   -1.839301
    6        2.986610    0.137499    0.941307
    1        1.737840    1.810260    1.510150
    6        3.167876   -0.917234    0.041441
    1        2.361418   -1.944074   -1.676568
    1        3.724413    0.323927    1.718494
    1        4.045417   -1.554904    0.114441
    6       -1.476938   -0.889154    0.640181
    6       -3.280633   -0.008129   -0.158797
    6       -2.979057   -1.260345    0.704638
    1       -1.073752   -0.455858    1.562536
    1       -0.784278   -1.648902    0.269700
    1       -3.723448    0.828920    0.392598
    1       -3.837835   -0.167201   -1.087708
    1       -3.419760   -1.256013    1.703513
    1       -3.215066   -2.204643    0.208944
    7       -1.826103    0.164571   -0.361627
 --------------------------------------------
E = -513.73632703; ZPE = 0.190068
Number of imaginary freq = 0
```

trans-H-4 in cyclohexane

```
---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 --------------------------------------------
    7       -0.953644    0.533639   -0.153379
    7       -0.194433   -0.481679   -0.214434
    6        1.185308   -0.177467   -0.093237
    6        1.734153    1.117387   -0.103407
    6        2.040642   -1.282305    0.026869
    6        3.110142    1.289994    0.018526
    1        1.074416    1.972401   -0.209445
    6        3.417740   -1.102384    0.150652
    1        1.601083   -2.276321    0.024262
    6        3.959108    0.184771    0.147865
    1        3.526476    2.295118    0.007819
    1        4.068238   -1.968794    0.246363
    1        5.033047    0.328297    0.239812
    6       -2.902887   -1.058754   -0.103659
    6       -3.335358    1.036070    0.239093
    6       -4.185802   -0.266397    0.269479
    1       -2.435206   -1.607911    0.723018
    1       -2.943830   -1.706439   -0.984434
    1       -3.092703    1.440349    1.228975
    1       -3.686983    1.845363   -0.409405
    1       -4.624087   -0.513747    1.237991
    1       -4.960560   -0.299587   -0.499545
    7       -2.237376    0.240294   -0.334830
 --------------------------------------------
E = -513.75373315; ZPE = 0.190318
Number of imaginary freq = 0
```

ts-H-4 in cyclohexane

```
---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 --------------------------------------------
    7       -1.082911    0.465161    0.983110
    7       -0.148896   -0.377095    1.115249
    6        1.096839   -0.133899    0.471611
    6        1.534961    1.138659    0.065147
    6        1.957708   -1.232953    0.333429
    6        2.811298    1.295960   -0.472313
    1        0.875295    1.993319    0.181246
    6        3.227463   -1.069617   -0.217451
    1        1.611503   -2.208160    0.666064
    6        3.661304    0.195762   -0.621579
    1        3.143581    2.285151   -0.780049
    1        3.882012   -1.931513   -0.325861
    1        4.653714    0.325028   -1.046580
    6       -2.438902   -1.004878   -0.588894
    6       -3.307864    0.869853    0.052476
    6       -3.829440   -0.341430   -0.768124
    1       -2.404990   -1.815568    0.148670
    1       -1.908231   -1.320615   -1.491275
    1       -3.691688    0.921535    1.077897
    1       -3.383017    1.857196   -0.414863
    1       -4.666715   -0.881189   -0.321727
    1       -4.066486   -0.098321   -1.806217
    7       -1.957505    0.278848   -0.014520
 --------------------------------------------
E = -513.69929322; ZPE = 0.188178
Number of imaginary freq = 1 (-565.854 Hz)
```

cis-H-4 in DMSO

```
---------------------------------------------
 Atomic       Coordinates (Angstroms)
 Number       X            Y            Z
 --------------------------------------------
    7     -1.349942     1.423190    -0.469285
    7     -0.126213     1.703929    -0.313410
    6      0.904224     0.726715    -0.148168
    6      1.088513    -0.333679    -1.052563
    6      1.877987     0.972411     0.833094
    6      2.221691    -1.143476    -0.954768
    1      0.356214    -0.509667    -1.838079
    6      2.992524     0.141992     0.940335
    1      1.744206     1.816218     1.507974
    6      3.171425    -0.918346     0.045434
    1      2.359345    -1.957347    -1.665450
    1      3.731174     0.331167     1.718033
    1      4.048870    -1.558176     0.121818
    6     -1.478795    -0.901928     0.624380
    6     -3.290957    -0.001142    -0.146335
    6     -2.982808    -1.264386     0.698841
    1     -1.057702    -0.495370     1.550639
    1     -0.800620    -1.657214     0.219554
    1     -3.738738     0.826686     0.414964
    1     -3.843338    -0.153485    -1.079435
    1     -3.410294    -1.264392     1.703465
    1     -3.229981    -2.202128     0.196152
    7     -1.835555     0.180703    -0.344612
 --------------------------------------------
E = -513.74424026; ZPE = 0.189415
Number of imaginary freq = 0
```

trans-H-4 in DMSO

```
---------------------------------------------
 Atomic       Coordinates (Angstroms)
 Number       X            Y            Z
 --------------------------------------------
    7     -0.952808     0.518413    -0.116924
    7     -0.189091    -0.495295    -0.216993
    6      1.190187    -0.184890    -0.094254
    6      1.735123     1.112397    -0.126041
    6      2.052279    -1.284036     0.043389
    6      3.111260     1.293546    -0.005021
    1      1.075148     1.966639    -0.249082
    6      3.429164    -1.095757     0.166136
    1      1.620446    -2.283159     0.057466
    6      3.965740     0.194244     0.143648
    1      3.522778     2.301803    -0.032911
    1      4.083537    -1.959227     0.276798
    1      5.040282     0.344089     0.234375
    6     -2.925901    -1.054332    -0.140376
    6     -3.337277     1.038573     0.262771
    6     -4.200472    -0.255895     0.247894
    1     -2.480549    -1.649038     0.667020
    1     -2.966512    -1.658144    -1.052445
    1     -3.110445     1.423159     1.263966
    1     -3.666534     1.860612    -0.381634
    1     -4.642324    -0.526671     1.208551
    1     -4.972427    -0.258266    -0.524733
    7     -2.232961     0.241895    -0.302690
 --------------------------------------------
E = -513.75974981; ZPE = 0.189588
Number of imaginary freq = 0
```

ts-H-4 in DMSO

```
---------------------------------------------
 Atomic       Coordinates (Angstroms)
 Number       X            Y            Z
 --------------------------------------------
    7      1.156540    -1.145972    -0.682701
    7      0.100562    -1.380238     0.021504
    6     -1.028913    -0.536757    -0.011279
    6     -1.078046     0.820579    -0.396639
    6     -2.228816    -1.169257     0.380068
    6     -2.300083     1.495786    -0.429696
    1     -0.180239     1.336402    -0.717306
    6     -3.435736    -0.479156     0.368561
    1     -2.187689    -2.216817     0.671761
    6     -3.480923     0.860422    -0.038358
    1     -2.322366     2.538320    -0.745181
    1     -4.350372    -0.991406     0.663924
    1     -4.426092     1.400261    -0.051605
    6      2.045468     0.551195     0.955829
    6      3.377396    -0.092663    -0.633925
    6      3.532900     0.832381     0.608525
    1      1.884537    -0.156765     1.780295
    1      1.383523     1.411191     1.091008
    1      3.844495    -1.078365    -0.531127
    1      3.641305     0.341302    -1.603539
    1      4.257527     0.492833     1.350447
    1      3.727074     1.875587     0.349976
    7      1.929870    -0.137750    -0.349826
 --------------------------------------------
E = -513.70901223; ZPE = 0.187594
Number of imaginary freq = 1 (-531.721 Hz)
```

cis-H-5 in acetonitrile

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	0.974848	1.596305	0.247350
7	-0.250764	1.755681	-0.031098
6	-1.250161	0.738863	-0.011288
6	-1.459858	-0.081671	1.112000
6	-2.187687	0.721810	-1.057122
6	-2.577156	-0.917392	1.167166
1	-0.759350	-0.048517	1.944334
6	-3.287391	-0.133086	-1.003615
1	-2.037792	1.383352	-1.908665
6	-3.489498	-0.956324	0.109368
1	-2.731945	-1.543330	2.045063
1	-3.996103	-0.148962	-1.830461
1	-4.354867	-1.615014	0.155559
6	1.191365	-0.838687	-0.361578
6	3.028491	0.458585	0.589602
6	2.523677	-1.593814	-0.529100
1	0.753580	-0.551889	-1.325500
1	0.445128	-1.419716	0.185877
6	3.599315	-0.496549	-0.461165
1	3.258214	0.111558	1.606069
1	3.355883	1.496386	0.494698
1	2.655836	-2.302310	0.297315
1	2.545996	-2.162846	-1.463585
1	4.586398	-0.882174	-0.188638
1	3.684770	0.017697	-1.426435
7	1.568439	0.398779	0.367856

E = -553.08367164; ZPE = 0.219381
Number of imaginary freq = 0

trans-H-5 in acetonitrile

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-0.582406	0.470629	-0.128475
7	0.188696	-0.541337	0.016825
6	1.565044	-0.201615	0.011467
6	2.083019	1.106314	0.078148
6	2.460871	-1.282403	-0.039187
6	3.460855	1.314571	0.079376
1	1.398946	1.948602	0.131017
6	3.839239	-1.067367	-0.037946
1	2.052946	-2.290750	-0.083254
6	4.347892	0.232931	0.020217
1	3.847528	2.331762	0.132543
1	4.517000	-1.918882	-0.081216
1	5.423077	0.403849	0.024770
6	-2.439352	-1.148049	0.107576
6	-2.862474	1.246738	-0.259349
6	-3.947092	-0.900094	-0.066709
1	-2.174740	-1.511757	1.109977
1	-2.018785	-1.853917	-0.617143
6	-4.130910	0.587537	0.297924
1	-2.976861	1.501982	-1.322842
1	-2.552004	2.145624	0.281075
1	-4.233450	-1.068387	-1.111701
1	-4.547895	-1.568149	0.557248
1	-5.042321	1.021419	-0.123390
1	-4.166037	0.710016	1.387179
7	-1.861998	0.187454	-0.093117

E = -553.10466547; ZPE = 0.219583
Number of imaginary freq = 0

ts-H-5 in acetonitrile

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	0.814867	-0.773446	-1.098571
7	-0.218971	-1.179133	-0.420951
6	-1.395451	-0.523412	-0.213166
6	-1.645712	0.790981	-0.694992
6	-2.437307	-1.173598	0.500792
6	-2.879070	1.402384	-0.473794
1	-0.866722	1.312956	-1.247931
6	-3.656466	-0.540386	0.711485
1	-2.262332	-2.179714	0.877697
6	-3.899065	0.753955	0.228909
1	-3.040153	2.408918	-0.860930
1	-4.434343	-1.068161	1.263516
1	-4.856688	1.241388	0.398476
6	1.666004	0.150629	1.018177
6	3.054041	0.111526	-1.015353
6	3.071195	0.693614	1.323528
1	1.431888	-0.795486	1.524612
1	0.855888	0.853773	1.229058
6	3.963475	0.090787	0.218566
1	3.044430	1.099920	-1.491901
1	3.266334	-0.648446	-1.770135
1	3.071970	1.787534	1.254818
1	3.399811	0.419408	2.329851
1	4.883788	0.658944	0.058192
1	4.235028	-0.942556	0.464594
7	1.721425	-0.145615	-0.431168

E = -553.05484854; ZPE = 0.217894
Number of imaginary freq = 1 (-488.266 Hz)

cis-H-5 in benzene

```
---------------------------------------------
 Atomic       Coordinates (Angstroms)
 Number       X            Y            Z
 --------------------------------------------
    7       0.974667    1.593560    0.236034
    7      -0.243104    1.748123   -0.053282
    6      -1.245019    0.736549   -0.019994
    6      -1.454323   -0.074454    1.109776
    6      -2.185747    0.713653   -1.062106
    6      -2.573395   -0.905494    1.175500
    1      -0.750976   -0.034292    1.937384
    6      -3.285576   -0.139021   -0.999500
    1      -2.037803    1.372387   -1.914267
    6      -3.487194   -0.952260    0.120094
    1      -2.729347   -1.521172    2.058931
    1      -3.996575   -0.159002   -1.822618
    1      -4.353418   -1.607139    0.173901
    6       1.192142   -0.838166   -0.370087
    6       3.013525    0.446220    0.614679
    6       2.528683   -1.583352   -0.550463
    1       0.759922   -0.529638   -1.329901
    1       0.442358   -1.438085    0.152233
    6       3.595871   -0.480001   -0.456309
    1       3.250014    0.080483    1.623145
    1       3.329407    1.489061    0.542813
    1       2.664300   -2.308376    0.261016
    1       2.557554   -2.134466   -1.495400
    1       4.586695   -0.863307   -0.194218
    1       3.677407    0.056547   -1.409561
    7       1.555102    0.380454    0.395393
 --------------------------------------------
E = -553.07644610; ZPE = 0.219969
Number of imaginary freq = 0
```

trans-H-5 in benzene

```
---------------------------------------------
 Atomic       Coordinates (Angstroms)
 Number       X            Y            Z
 --------------------------------------------
    7      -0.582224    0.495834   -0.093939
    7       0.184849   -0.522256   -0.027795
    6       1.562585   -0.192119   -0.008428
    6       2.091744    1.112026   -0.015675
    6       2.445655   -1.282250    0.026097
    6       3.470193    1.306302    0.008861
    1       1.413964    1.959065   -0.039972
    6       3.825129   -1.080900    0.050617
    1       2.024421   -2.284375    0.032588
    6       4.345692    0.214873    0.041992
    1       3.867179    2.319568    0.003288
    1       4.494061   -1.938458    0.076703
    1       5.421067    0.375461    0.061882
    6      -2.426541   -1.150411   -0.001167
    6      -2.869002    1.263883   -0.140507
    6      -3.938561   -0.900136   -0.131589
    1      -2.143111   -1.593503    0.963370
    1      -2.012339   -1.793427   -0.785048
    6      -4.125981    0.546270    0.371200
    1      -3.006409    1.630077   -1.168614
    1      -2.552178    2.105060    0.482553
    1      -4.239571   -0.973800   -1.183429
    1      -4.527880   -1.627152    0.434616
    1      -5.047725    1.009894    0.008171
    1      -4.144654    0.566167    1.467370
    7      -1.864381    0.200737   -0.101394
 --------------------------------------------
E = -553.09901335; ZPE = 0.220208
Number of imaginary freq = 0
```

ts-H-5 in benzene

```
 --------------------------------------------
-
 Atomic       Coordinates (Angstroms)
 Number       X            Y            Z
 --------------------------------------------
    7       0.827925   -0.072271   -1.338600
    7      -0.204813   -0.725990   -0.944222
    6      -1.404294   -0.318412   -0.447474
    6      -1.708601    1.051144   -0.225730
    6      -2.401750   -1.278564   -0.141977
    6      -2.956055    1.423675    0.270054
    1      -0.961361    1.804741   -0.461491
    6      -3.635806   -0.880011    0.356002
    1      -2.181885   -2.329888   -0.308826
    6      -3.933759    0.472169    0.570169
    1      -3.162493    2.482103    0.422784
    1      -4.381611   -1.640885    0.580456
    1      -4.902891    0.773386    0.958572
    6       1.667057   -0.321496    0.965362
    6       3.090804    0.588582   -0.820297
    6       3.092612   -0.087964    1.492722
    1       1.370200   -1.378544    0.926731
    1       0.891053    0.217679    1.515549
    6       3.975139   -0.100516    0.226851
    1       3.155002    1.681390   -0.741584
    1       3.276991    0.297918   -1.855938
    1       3.154946    0.888845    1.986190
    1       3.386111   -0.847853    2.222271
    1       4.929642    0.414083    0.367121
    1       4.185055   -1.130887   -0.083120
    7       1.738196    0.152014   -0.431866
 ---- ---------------------------------------
E = -553.04616463; ZPE = 0.218453
Number of imaginary freq = 1 (-513.233 Hz)
```

cis-H-5 in cyclohexane

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	0.974539	1.593603	0.235330
7	-0.242897	1.747548	-0.053697
6	-1.244803	0.736241	-0.019782
6	-1.454498	-0.074647	1.110062
6	-2.185414	0.713535	-1.062006
6	-2.573938	-0.905208	1.175494
1	-0.751251	-0.034448	1.937607
6	-3.285295	-0.138911	-0.999725
1	-2.037107	1.372574	-1.913712
6	-3.487397	-0.951937	0.119884
1	-2.730452	-1.520611	2.058902
1	-3.996083	-0.158750	-1.822896
1	-4.353740	-1.606494	0.173581
6	1.192459	-0.838204	-0.370457
6	3.012928	0.446180	0.615275
6	2.529190	-1.583047	-0.550898
1	0.760642	-0.529013	-1.330263
1	0.442335	-1.438808	0.150642
6	3.596003	-0.479394	-0.455957
1	3.250166	0.080508	1.623616
1	3.327964	1.489261	0.543578
1	2.664856	-2.308382	0.260303
1	2.558569	-2.133934	-1.495949
1	4.586961	-0.862475	-0.194028
1	3.677548	0.057549	-1.408969
7	1.554670	0.379616	0.396400

E = -553.07586687; ZPE = 0.220011
Number of imaginary freq = 0

trans-H-5 in cyclohexane

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-0.582202	0.497898	-0.093667
7	0.184425	-0.520429	-0.033193
6	1.562198	-0.191357	-0.010863
6	2.092400	1.112249	-0.022862
6	2.444030	-1.282154	0.030597
6	3.470873	1.305368	0.004792
1	1.415218	1.959445	-0.053273
6	3.823535	-1.081912	0.058178
1	2.021568	-2.283592	0.040200
6	4.345197	0.213322	0.045386
1	3.868833	2.318116	-0.004544
1	4.491629	-1.939801	0.089848
1	5.420556	0.373031	0.067457
6	-2.425278	-1.150088	-0.010115
6	-2.869637	1.264708	-0.132139
6	-3.937836	-0.900044	-0.133776
1	-2.137943	-1.598006	0.951034
1	-2.013390	-1.788929	-0.798556
6	-4.124372	0.542887	0.379269
1	-3.011604	1.639034	-1.156735
1	-2.550570	2.101321	0.495874
1	-4.242518	-0.966892	-1.185021
1	-4.524990	-1.631128	0.429436
1	-5.047897	1.008197	0.022976
1	-4.139083	0.555350	1.475604
7	-1.864576	0.201956	-0.105298

E = -553.09854782; ZPE = 0.220259
Number of imaginary freq = 0

ts-H-5 in cyclohexane

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	0.719923	-0.658050	0.983004
7	-0.231420	0.143979	1.228997
6	-1.449597	0.035479	0.506754
6	-1.918158	-1.159291	-0.069510
6	-2.269635	1.174247	0.477685
6	-3.175637	-1.198318	-0.669480
1	-1.296790	-2.049039	-0.032474
6	-3.520113	1.130513	-0.135907
1	-1.905798	2.086470	0.943582
6	-3.981001	-0.056146	-0.712381
1	-3.529468	-2.129372	-1.107445
1	-4.139629	2.024377	-0.157890
1	-4.959489	-0.093247	-1.184948
6	1.984693	1.116984	-0.253606
6	2.816362	-1.181222	-0.067055
6	3.395449	1.012597	-0.862691
1	1.953666	1.758247	0.636879
1	1.236524	1.498105	-0.955154
6	4.011153	-0.226699	-0.184425
1	2.671743	-1.756509	-0.992549
1	2.879319	-1.884287	0.767211
1	3.323959	0.851513	-1.945017
1	3.977653	1.924611	-0.700763
1	4.840692	-0.658762	-0.751913
1	4.380156	0.032402	0.815304
7	1.683835	-0.270696	0.143551

E = -553.04543986; ZPE = 0.218498
Number of imaginary freq = 1 (-515.211 Hz)

cis-H-5 in DMSO

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	0.975285	1.598714	0.241890
7	-0.250825	1.758057	-0.035006
6	-1.249965	0.740746	-0.012772
6	-1.461761	-0.072965	1.115072
6	-2.184032	0.715695	-1.061366
6	-2.577605	-0.910490	1.171918
1	-0.764202	-0.032951	1.949573
6	-3.282625	-0.140642	-1.005780
1	-2.032463	1.371640	-1.917018
6	-3.486639	-0.957459	0.111535
1	-2.733958	-1.531423	2.053155
1	-3.988758	-0.162851	-1.834768
1	-4.351033	-1.617436	0.159055
6	1.189278	-0.838201	-0.360983
6	3.028065	0.459573	0.586930
6	2.519884	-1.597598	-0.521160
1	0.755488	-0.554155	-1.327566
1	0.439874	-1.415109	0.186435
6	3.597735	-0.502253	-0.458400
1	3.256278	0.117307	1.605349
1	3.357715	1.496209	0.486913
1	2.648892	-2.300800	0.310284
1	2.542405	-2.172835	-1.451838
1	4.583824	-0.888292	-0.182903
1	3.684884	0.006608	-1.426383
7	1.567977	0.401178	0.364508

E = -553.08377352; ZPE = 0.219372
Number of imaginary freq = 0

trans-H-5 in DMSO

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-0.582880	0.473052	-0.121892
7	0.188357	-0.541213	0.005604
6	1.564747	-0.201091	0.006605
6	2.083591	1.107413	0.055774
6	2.460189	-1.282927	-0.023643
6	3.461494	1.314551	0.062740
1	1.400051	1.951009	0.090315
6	3.838769	-1.069030	-0.016479
1	2.051658	-2.291480	-0.055785
6	4.348169	0.231518	0.025857
1	3.848628	2.332227	0.101990
1	4.516018	-1.921669	-0.042998
1	5.423457	0.401756	0.034352
6	-2.439363	-1.150050	0.083386
6	-2.862955	1.252412	-0.230551
6	-3.947218	-0.898330	-0.082593
1	-2.172370	-1.529168	1.079512
1	-2.021006	-1.844866	-0.653088
6	-4.129406	0.580526	0.316461
1	-2.982687	1.535728	-1.286271
1	-2.548522	2.136463	0.331627
1	-4.235327	-1.042399	-1.130767
1	-4.547072	-1.580497	0.526848
1	-5.042393	1.023876	-0.091389
1	-4.160405	0.678053	1.408367
7	-1.862354	0.188307	-0.097719

E = -553.10456664; ZPE = 0.219571
Number of imaginary freq = 0

ts-H-5 in DMSO

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	0.722070	-0.705199	0.952743
7	-0.236146	0.080441	1.247951
6	-1.451723	0.009806	0.513593
6	-1.951806	-1.173179	-0.062299
6	-2.240671	1.171279	0.478843
6	-3.206388	-1.177456	-0.671951
1	-1.359280	-2.083873	-0.018992
6	-3.489135	1.161751	-0.142493
1	-1.855646	2.077721	0.942915
6	-3.979635	-0.012732	-0.721435
1	-3.583443	-2.100505	-1.110860
1	-4.083284	2.074222	-0.169552
1	-4.957123	-0.023065	-1.200561
6	1.991887	1.129812	-0.189006
6	2.815848	-1.181071	-0.123846
6	3.388994	1.044526	-0.830452
1	1.981785	1.733388	0.727948
1	1.231685	1.538078	-0.861725
6	4.011662	-0.226826	-0.221911
1	2.642549	-1.705195	-1.074129
1	2.894521	-1.925397	0.672810
1	3.293204	0.932535	-1.917059
1	3.978861	1.945571	-0.637437
1	4.824410	-0.637593	-0.828196
1	4.403675	-0.016093	0.780609
7	1.693202	-0.273136	0.159301

E = -553.05498747; ZPE = 0.217896
Number of imaginary freq = 1 (-487.935 Hz)

cis-H-5 in ethanol

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	0.974846	1.597823	0.242209
7	-0.250069	1.756802	-0.036750
6	-1.249602	0.740274	-0.013505
6	-1.459473	-0.074753	1.113669
6	-2.185809	0.716992	-1.060241
6	-2.575457	-0.911892	1.171713
1	-0.759427	-0.036638	1.946140
6	-3.284289	-0.139267	-1.003741
1	-2.035773	1.374568	-1.914772
6	-3.486471	-0.957327	0.113009
1	-2.730411	-1.533711	2.052455
1	-3.991993	-0.160224	-1.831280
1	-4.350821	-1.617122	0.161327
6	1.189921	-0.837339	-0.364587
6	3.025692	0.457347	0.591711
6	2.521320	-1.594899	-0.526942
1	0.757492	-0.548567	-1.330388
1	0.439767	-1.418155	0.177849
6	3.597868	-0.498656	-0.457700
1	3.254236	0.110933	1.608682
1	3.353790	1.494951	0.496804
1	2.650163	-2.302044	0.301187
1	2.545552	-2.165787	-1.460255
1	4.584197	-0.884910	-0.183382
1	3.685380	0.014995	-1.423124
7	1.566030	0.398066	0.368606

E = -553.08334374; ZPE = 0.219410

Number of imaginary freq = 0

trans-H-5 in ethanol

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	-0.583192	0.475193	-0.117319
7	0.188189	-0.540167	-0.002094
6	1.564695	-0.200371	0.003173
6	2.084452	1.108102	0.041294
6	2.459307	-1.283095	-0.013564
6	3.462414	1.314060	0.052281
1	1.401602	1.952554	0.063823
6	3.837988	-1.070368	-0.002507
1	2.049874	-2.291403	-0.038013
6	4.348298	0.230019	0.029748
1	3.850257	2.331675	0.082696
1	4.514525	-1.923726	-0.018183
1	5.423602	0.399453	0.040886
6	-2.439100	-1.151183	0.066084
6	-2.863605	1.255291	-0.213255
6	-3.947532	-0.897226	-0.091217
1	-2.168495	-1.543164	1.056234
1	-2.023528	-1.836581	-0.680710
6	-4.128131	0.575923	0.329020
1	-2.987401	1.553855	-1.264290
1	-2.546726	2.131145	0.360213
1	-4.239332	-1.026822	-1.140255
1	-4.545337	-1.587770	0.510742
1	-5.042677	1.024903	-0.069039
1	-4.154960	0.658128	1.422281
7	-1.862728	0.189380	-0.099548

E = -553.10433969; ZPE = 0.219617

Number of imaginary freq = 0

ts-H-5 in ethanol

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	0.816275	-0.733632	-1.124460
7	-0.217545	-1.159083	-0.460863
6	-1.395758	-0.514714	-0.231555
6	-1.653002	0.811444	-0.675866
6	-2.432685	-1.188602	0.467309
6	-2.887650	1.411963	-0.433160
1	-0.878608	1.351823	-1.216939
6	-3.652809	-0.565660	0.700888
1	-2.252321	-2.203966	0.815459
6	-3.902254	0.740692	0.255602
1	-3.053745	2.428171	-0.791702
1	-4.426476	-1.111421	1.241157
1	-4.860804	1.219640	0.442860
6	1.665967	0.123655	1.020812
6	3.057106	0.143700	-1.010275
6	3.073379	0.648853	1.346401
1	1.425678	-0.837272	1.495531
1	0.859031	0.823577	1.253668
6	3.964536	0.078097	0.223609
1	3.053703	1.147124	-1.454420
1	3.266868	-0.592216	-1.789196
1	3.080209	1.744431	1.314151
1	3.398703	0.339732	2.343644
1	4.887969	0.646516	0.083389
1	4.230471	-0.964098	0.436102
7	1.722462	-0.125659	-0.437004

E = -553.05445670; ZPE = 0.217921

Number of imaginary freq = 1 (-489.526 Hz)

cis-H-5 in methanol

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	0.975809	1.588195	0.255228
7	-0.247540	1.748541	-0.030716
6	-1.249761	0.733831	-0.011310
6	-1.450382	-0.100954	1.102935
6	-2.198055	0.734700	-1.047405
6	-2.571161	-0.931832	1.159315
1	-0.740740	-0.082775	1.927834
6	-3.300905	-0.116237	-0.993613
1	-2.054326	1.406675	-1.891876
6	-3.494845	-0.952857	0.110764
1	-2.719641	-1.568462	2.030635
1	-4.018427	-0.118212	-1.813032
1	-4.362783	-1.608228	0.157750
6	1.196465	-0.836974	-0.374362
6	3.022822	0.444658	0.614233
6	2.534723	-1.577013	-0.563327
1	0.756035	-0.528433	-1.330227
1	0.455385	-1.437628	0.158901
6	3.601719	-0.473620	-0.464261
1	3.248606	0.064420	1.619476
1	3.345215	1.486668	0.555624
1	2.673065	-2.307719	0.242489
1	2.560477	-2.118590	-1.513901
1	4.592071	-0.858806	-0.203047
1	3.682197	0.069540	-1.414027
7	1.563037	0.386027	0.386286

E = -553.08359935; ZPE = 0.219384

Number of imaginary freq = 0

trans-H-5 in methanol

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	-0.584817	0.481948	-0.110248
7	0.187708	-0.534340	-0.011410
6	1.564569	-0.197040	-0.001035
6	2.088255	1.110206	0.021976
6	2.455687	-1.282939	-0.000238
6	3.466841	1.311771	0.037989
1	1.408286	1.957361	0.028785
6	3.834990	-1.074479	0.015850
1	2.043177	-2.290245	-0.014414
6	4.349285	0.224637	0.034571
1	3.857874	2.328488	0.056411
1	4.508866	-1.930128	0.014462
1	5.425098	0.390818	0.048990
6	-2.436435	-1.151737	0.042131
6	-2.867586	1.258692	-0.189994
6	-3.946190	-0.898197	-0.103201
1	-2.160256	-1.560987	1.023727
1	-2.023202	-1.822488	-0.719152
6	-4.127902	0.566346	0.345540
1	-2.997036	1.576359	-1.234697
1	-2.549629	2.124298	0.398237
1	-4.242804	-1.008946	-1.153048
1	-4.539375	-1.601257	0.488749
1	-5.045337	1.020644	-0.039604
1	-4.149379	0.627895	1.440275
7	-1.863657	0.193054	-0.101237

E = -553.10481696; ZPE = 0.219602

Number of imaginary freq = 0

ts-H-5 in methanol

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	0.723071	-0.671311	0.968086
7	-0.234272	0.125341	1.233651
6	-1.452613	0.027601	0.506936
6	-1.934491	-1.165150	-0.064085
6	-2.261595	1.175299	0.473469
6	-3.192855	-1.193097	-0.665135
1	-1.325289	-2.064874	-0.024112
6	-3.513514	1.142306	-0.140007
1	-1.889615	2.089498	0.932876
6	-3.986924	-0.042324	-0.712409
1	-3.556077	-2.123552	-1.099962
1	-4.123706	2.044118	-0.165856
1	-4.966955	-0.071175	-1.185508
6	1.992993	1.122883	-0.233345
6	2.818365	-1.183418	-0.090324
6	3.401512	1.022272	-0.847796
1	1.966245	1.752713	0.665360
1	1.243470	1.509349	-0.930586
6	4.014943	-0.230883	-0.193551
1	2.659903	-1.730448	-1.030123
1	2.883891	-1.907751	0.725654
1	3.325331	0.880550	-1.932475
1	3.986513	1.929354	-0.668804
1	4.838567	-0.657068	-0.773994
1	4.388872	0.008027	0.809557
7	1.690333	-0.269983	0.151900

E = -553.05467097; ZPE = 0.217902

Number of imaginary freq = 1 (-486.962 Hz)

cis-H-6 in acetonitrile

```
 ---------------------------------------------------
 Atomic       Coordinates (Angstroms)
 Number       X             Y             Z
 ---------------------------------------------------
    6        3.523482   -0.218728    0.575573
    6        3.228458   -1.427193   -0.324522
    6        1.715050   -1.646647   -0.460222
    6        1.000309   -0.365813   -0.909432
    6        2.773452    1.022743    0.084049
    1        1.501987   -2.439501   -1.187951
    1        3.658699   -1.249233   -1.321048
    1        3.709924   -2.328654    0.073389
    1        3.214844   -0.436207    1.607039
    1        4.598428   -0.000747    0.594781
    1        1.339231   -0.076720   -1.917867
    1       -0.072793   -0.518157   -0.950111
    1        3.145040    1.315900   -0.912140
    1        2.907089    1.869889    0.760174
    1        1.294061   -1.966658    0.502208
    7        0.585449    1.843168    0.261422
    7       -0.677273    1.893289    0.243569
    6       -1.567430    0.781867    0.139182
    6       -1.593579   -0.217559    1.128815
    6       -2.570151    0.809330   -0.841805
    6       -2.593993   -1.189438    1.108842
    1       -0.833735   -0.224094    1.908083
    6       -3.556550   -0.177808   -0.862565
    1       -2.561288    1.603597   -1.586329
    6       -3.574344   -1.180723    0.111077
    1       -2.606827   -1.958719    1.879850
    1       -4.320296   -0.156359   -1.638774
    1       -4.350372   -1.943927    0.098746
    7        1.330079    0.744888    0.008723
 ---------------------------------------------------
E = -592.39792340; ZPE = 0.248463
Number of imaginary freq = 0
```

trans-H-6 in acetonitrile

```
 ---------------------------------------------------
 Atomic       Coordinates (Angstroms)
 Number       X             Y             Z
 ---------------------------------------------------
    6       -3.759423    1.203421   -0.161270
    6       -4.395290   -0.187417   -0.032433
    6       -3.434749   -1.260627   -0.561682
    6       -2.068645   -1.201207    0.132623
    6       -2.407968    1.250296    0.556599
    1       -3.853159   -2.264618   -0.420147
    1       -4.626310   -0.387658    1.024371
    1       -5.345388   -0.225615   -0.578875
    1       -3.613878    1.447632   -1.222339
    1       -4.411830    1.974869    0.265468
    1       -2.149147   -1.530104    1.182154
    1       -1.342164   -1.850144   -0.358269
    1       -2.562724    1.158475    1.644754
    1       -1.877332    2.188135    0.371688
    1       -3.289738   -1.120167   -1.641403
    7       -0.233667    0.439845    0.142546
    7        0.546599   -0.563169    0.071155
    6        1.918875   -0.208342    0.008394
    6        2.412845    1.086539   -0.237317
    6        2.829459   -1.262278    0.185701
    6        3.787251    1.311980   -0.283844
    1        1.713848    1.903527   -0.392942
    6        4.204126   -1.029901    0.138529
    1        2.436935   -2.261724    0.364746
    6        4.690654    0.259135   -0.095299
    1        4.158198    2.318105   -0.476063
    1        4.895998   -1.858605    0.282358
    1        5.762943    0.442772   -0.137525
    7       -1.535657    0.165543    0.099443
 ---------------------------------------------------
E = -592.42223956; ZPE = 0.248924
Number of imaginary freq = 0
```

ts-H-6 in acetonitrile

```
 ---------------------------------------------------
 Atomic       Coordinates (Angstroms)
 Number       X             Y             Z
 ---------------------------------------------------
    6       -3.394605   -0.940196    0.731948
    6       -3.765314    0.535108    0.938124
    6       -2.508948    1.415462    0.893909
    6       -1.701658    1.190417   -0.390745
    6       -2.595968   -1.124609   -0.561361
    1       -2.775325    2.477776    0.956226
    1       -4.459955    0.849819    0.145343
    1       -4.289637    0.668501    1.892090
    1       -2.792265   -1.294799    1.579312
    1       -4.293880   -1.566478    0.684965
    1       -2.267216    1.545611   -1.268104
    1       -0.760548    1.735069   -0.362519
    1       -3.234648   -0.892577   -1.430087
    1       -2.232703   -2.149078   -0.673105
    1       -1.868871    1.190299    1.757527
    7       -0.380548   -0.748865   -1.250844
    7        0.642574   -0.038019   -1.488586
    6        1.742723   -0.052660   -0.585704
    6        2.017060   -1.130753    0.275790
    6        2.637798    1.026856   -0.642000
    6        3.165011   -1.114781    1.066879
    1        1.329311   -1.972001    0.317935
    6        3.780236    1.038175    0.159012
    1        2.422105    1.851941   -1.318646
    6        4.050365   -0.032040    1.016639
    1        3.368520   -1.954148    1.730710
    1        4.462905    1.885365    0.109742
    1        4.942804   -0.024594    1.639998
    7       -1.420713   -0.244055   -0.571474
 ---------------------------------------------------
E = -592.37215860; ZPE = 0.247337
Number of imaginary freq = 1 (-485.976 Hz)
```

cis-H-6 in benzene

```
---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 --------------------------------------------
    6       3.503814   -0.239540    0.621640
    6       3.258185   -1.390738   -0.363622
    6       1.753383   -1.627190   -0.551235
    6       1.023348   -0.332317   -0.927442
    6       2.736939    1.015297    0.197063
    1       1.572465   -2.373711   -1.334500
    1       3.708658   -1.138085   -1.334736
    1       3.749328   -2.307529   -0.015899
    1       3.175458   -0.533678    1.627497
    1       4.572849   -0.002136    0.684491
    1       1.375098    0.029165   -1.908858
    1      -0.045273   -0.509299   -1.002597
    1       3.126406    1.386718   -0.766718
    1       2.841017    1.816917    0.931094
    1       1.316982   -2.019379    0.376790
    7       0.560026    1.862000    0.206930
    7      -0.694215    1.899609    0.134439
    6      -1.570763    0.775730    0.094169
    6      -1.562708   -0.193625    1.113176
    6      -2.599685    0.766269   -0.859111
    6      -2.557636   -1.169004    1.151499
    1      -0.782167   -0.171303    1.868529
    6      -3.576343   -0.228689   -0.825483
    1      -2.618381    1.542360   -1.620125
    6      -3.562097   -1.199387    0.179395
    1      -2.547613   -1.910863    1.947188
    1      -4.360062   -0.236012   -1.579780
    1      -4.332168   -1.966125    0.211813
    7       1.301158    0.714410    0.077992
 --------------------------------------------
E = -592.39113855; ZPE = 0.261199
Number of imaginary freq = 0
```

trans-H-6 in benzene

```
---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 --------------------------------------------
    6      -3.772579    1.188602   -0.191795
    6      -4.394993   -0.200344    0.006842
    6      -3.436969   -1.288496   -0.496590
    6      -2.056765   -1.187568    0.163744
    6      -2.405112    1.272640    0.491765
    1      -3.845540   -2.287966   -0.304094
    1      -4.602615   -0.358057    1.075641
    1      -5.356627   -0.267587   -0.515907
    1      -3.652041    1.389996   -1.264599
    1      -4.422832    1.971742    0.216455
    1      -2.111163   -1.471876    1.228319
    1      -1.334050   -1.851807   -0.311586
    1      -2.535008    1.226337    1.586748
    1      -1.886221    2.205758    0.257988
    1      -3.316527   -1.193514   -1.583979
    7      -0.231322    0.460042    0.094802
    7       0.543776   -0.543970    0.063424
    6       1.918643   -0.200204    0.006877
    6       2.425170    1.097626   -0.187115
    6       2.816146   -1.269287    0.145111
    6       3.800774    1.309327   -0.226503
    1       1.733058    1.924721   -0.306776
    6       4.192617   -1.050492    0.105117
    1       2.409820   -2.267577    0.286456
    6       4.692162    0.240364   -0.080024
    1       4.182883    2.316901   -0.377847
    1       4.875220   -1.890121    0.216462
    1       5.765126    0.413947   -0.115461
    7      -1.537889    0.179085    0.054289
 --------------------------------------------
E = -592.41715604; ZPE = 0.249675
Number of imaginary freq = 0
```

ts-H-6 in benzene

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---------------------------------------------
 Atomic      Coordinates (Angstroms)
 Number      X           Y           Z
 --------------------------------------------
    6      -3.422065   -0.971441    0.702011
    6      -3.830508    0.496967    0.885249
    6      -2.590075    1.400759    0.888648
    6      -1.723281    1.182379   -0.357312
    6      -2.562561   -1.144849   -0.552797
    1      -2.878795    2.458009    0.934357
    1      -4.496888    0.794475    0.062149
    1      -4.398632    0.624727    1.814493
    1      -2.850710   -1.309627    1.576782
    1      -4.305994   -1.615688    0.620822
    1      -2.255218    1.524600   -1.261342
    1      -0.795243    1.746656   -0.290040
    1      -3.166986   -0.931949   -1.451464
    1      -2.177538   -2.163152   -0.643545
    1      -1.984029    1.192430    1.780289
    7      -0.363592   -0.704064   -1.246447
    7       0.637231    0.039641   -1.446488
    6       1.752142   -0.017721   -0.565571
    6       2.062360   -1.143650    0.218078
    6       2.628806    1.077122   -0.572896
    6       3.227377   -1.158993    0.981735
    1       1.388831   -1.995248    0.218754
    6       3.786934    1.057785    0.203586
    1       2.384736    1.935112   -1.194200
    6       4.092979   -0.060010    0.983539
    1       3.460994   -2.035434    1.582669
    1       4.454668    1.916458    0.194162
    1       4.998316   -0.077579    1.585493
    7      -1.403662   -0.246131   -0.509208
 --------------------------------------------
E = -592.36393246; ZPE = 0.247935
Number of imaginary freq = 1 (-509.182 Hz)
```

cis-H-6 in cyclohexane

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
6	3.503635	-0.238370	0.617795
6	3.251665	-1.397046	-0.357320
6	1.745744	-1.629462	-0.542274
6	1.020513	-0.334344	-0.927563
6	2.740079	1.015529	0.183969
1	1.561971	-2.381242	-1.319813
1	3.702357	-1.154525	-1.330911
1	3.739528	-2.312813	-0.002371
1	3.176362	-0.522574	1.626810
1	4.573758	-0.004725	0.676176
1	1.373940	0.018442	-1.911599
1	-0.048835	-0.506708	-1.001704
1	3.129128	1.376711	-0.783938
1	2.847615	1.823659	0.910237
1	1.308251	-2.013044	0.388791
7	0.562083	1.862348	0.211911
7	-0.692326	1.900389	0.145792
6	-1.569343	0.777566	0.098907
6	-1.564824	-0.193784	1.116065
6	-2.594837	0.769519	-0.858047
6	-2.559211	-1.169926	1.148645
1	-0.787295	-0.172016	1.874508
6	-3.571245	-0.225797	-0.829713
1	-2.611070	1.546930	-1.617636
6	-3.560163	-1.198742	0.172980
1	-2.551673	-1.913410	1.942753
1	-4.352255	-0.231841	-1.586731
1	-4.329994	-1.965774	0.201021
7	1.303975	0.717558	0.069977

E = -592.39060026; ZPE = 0.249221

Number of imaginary freq = 0

trans-H-6 in cyclohexane

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
6	-3.771769	1.188918	-0.190330
6	-4.394273	-0.200846	0.002588
6	-3.434755	-1.287485	-0.501418
6	-2.056475	-1.187996	0.163068
6	-2.405895	1.271097	0.496819
1	-3.844003	-2.287465	-0.313062
1	-4.604572	-0.361657	1.070406
1	-5.354668	-0.266825	-0.522579
1	-3.648601	1.393499	-1.262214
1	-4.423460	1.970552	0.218497
1	-2.114002	-1.475268	1.226719
1	-1.331804	-1.850595	-0.311529
1	-2.538816	1.222148	1.591410
1	-1.886298	2.204791	0.267080
1	-3.311339	-1.189289	-1.588169
7	-0.231296	0.460506	0.098398
7	0.543545	-0.543230	0.063952
6	1.918297	-0.199897	0.006811
6	2.424757	1.097333	-0.190804
6	2.815592	-1.268709	0.147849
6	3.800305	1.308839	-0.230721
1	1.732390	1.923763	-0.312666
6	4.191986	-1.050050	0.107403
1	2.408908	-2.266338	0.291776
6	4.691530	0.240249	-0.081228
1	4.182522	2.315823	-0.384947
1	4.874569	-1.889245	0.221074
1	5.764403	0.413637	-0.117148
7	-1.538110	0.178974	0.058383

E = -592.41674485; ZPE = 0.249734

Number of imaginary freq = 0

ts-H-6 in cyclohexane

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
6	-3.417749	-0.966717	0.708825
6	-3.821999	0.503007	0.891570
6	-2.580206	1.405052	0.885194
6	-1.721449	1.181850	-0.365561
6	-2.565574	-1.144059	-0.550575
1	-2.867391	2.462748	0.930130
1	-4.493010	0.799909	0.072019
1	-4.384263	0.633806	1.823944
1	-2.842120	-1.304551	1.580889
1	-4.303689	-1.608977	0.634061
1	-2.258911	1.522245	-1.267064
1	-0.792120	1.744816	-0.306553
1	-3.175126	-0.931628	-1.445977
1	-2.182664	-2.163035	-0.642187
1	-1.968964	1.198155	1.773585
7	-0.364760	-0.713022	-1.245957
7	0.637379	0.027136	-1.451032
6	1.750497	-0.022902	-0.567834
6	2.059111	-1.143176	0.224457
6	2.626838	1.072099	-0.580712
6	3.222120	-1.152762	0.991201
1	1.385765	-1.994833	0.228988
6	3.783086	1.058402	0.198578
1	2.383907	1.925515	-1.208529
6	4.087441	-0.053652	0.987273
1	3.454423	-2.024727	1.598964
1	4.450658	1.917032	0.184688
1	4.991228	-0.066684	1.591497
7	-1.405537	-0.247348	-0.514863

E = -592.36328165; ZPE = 0.247973

Number of imaginary freq = 1 (-510.157 Hz)

cis-H-6 in DMSO

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	3.527359	-0.216726	0.576931
6	3.239910	-1.417737	-0.335064
6	1.727832	-1.645255	-0.469541
6	1.003394	-0.365502	-0.904992
6	2.769014	1.024827	0.099481
1	1.517801	-2.432328	-1.204411
1	3.667007	-1.226585	-1.330473
1	3.728053	-2.319910	0.052952
1	3.221139	-0.447102	1.606321
1	4.600740	0.008684	0.597872
1	1.337132	-0.064053	-1.911547
1	-0.068614	-0.526259	-0.943638
1	3.137163	1.332162	-0.893704
1	2.898348	1.864701	0.785435
1	1.311226	-1.977529	0.490668
7	0.580818	1.843180	0.255956
7	-0.681559	1.893064	0.226968
6	-1.570373	0.779546	0.132009
6	-1.588815	-0.219733	1.121936
6	-2.580788	0.806687	-0.841108
6	-2.589635	-1.191274	1.110010
1	-0.822837	-0.227252	1.895053
6	-3.567108	-0.180601	-0.854514
1	-2.577797	1.600889	-1.585741
6	-3.577551	-1.183084	0.119635
1	-2.596600	-1.960225	1.881387
1	-4.336726	-0.159266	-1.624861
1	-4.353620	-1.946290	0.113671
7	1.326192	0.739967	0.023123

E = -592.39804555; ZPE = 0.248477
Number of imaginary freq = 0

trans-H-6 in DMSO

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-3.762659	1.199240	-0.179886
6	-4.396486	-0.188808	-0.016619
6	-3.439626	-1.271806	-0.532222
6	-2.067722	-1.197382	0.148963
6	-2.405669	1.262125	0.526028
1	-3.855794	-2.273055	-0.366675
1	-4.617717	-0.367365	1.046152
1	-5.351374	-0.238753	-0.553673
1	-3.625742	1.420973	-1.247024
1	-4.412183	1.979256	0.235562
1	-2.138735	-1.505711	1.205442
1	-1.344956	-1.855411	-0.335282
1	-2.551450	1.193008	1.617099
1	-1.877550	2.196326	0.317110
1	-3.304077	-1.153281	-1.615809
7	-0.233189	0.442939	0.125056
7	0.546380	-0.561467	0.070539
6	1.919338	-0.207706	0.008768
6	2.415921	1.090755	-0.212088
6	2.827987	-1.266504	0.164965
6	3.790656	1.313885	-0.257027
1	1.718692	1.912459	-0.349239
6	4.203215	-1.036530	0.119179
1	2.433478	-2.268211	0.326020
6	4.692209	0.255560	-0.090815
1	4.163513	2.322912	-0.429447
1	4.893399	-1.869462	0.245764
1	5.764831	0.437776	-0.131159
7	-1.535666	0.168750	0.084361

E = -592.42213285; ZPE = 0.248918
Number of imaginary freq = 0

ts-H-6 in DMSO

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-3.404354	-0.942755	0.729309
6	-3.783962	0.532070	0.921005
6	-2.530303	1.416442	0.886222
6	-1.706758	1.186719	-0.387020
6	-2.590283	-1.132927	-0.553268
1	-2.800874	2.478242	0.938560
1	-4.469932	0.838711	0.117597
1	-4.320347	0.669609	1.867640
1	-2.810229	-1.288655	1.586024
1	-4.300077	-1.573654	0.676451
1	-2.262276	1.534911	-1.273583
1	-0.768018	1.734963	-0.349623
1	-3.219399	-0.910105	-1.431333
1	-2.221664	-2.156738	-0.652764
1	-1.900001	1.199061	1.759000
7	-0.377655	-0.746976	-1.241611
7	0.642038	-0.031407	-1.479090
6	1.746107	-0.049411	-0.580679
6	2.033690	-1.135153	0.266844
6	2.633449	1.036740	-0.630587
6	3.186369	-1.119632	1.050917
1	1.352717	-1.982038	0.303915
6	3.780487	1.047821	0.163886
1	2.407883	1.867518	-1.296955
6	4.063578	-0.029869	1.007746
1	3.400262	-1.965141	1.703593
1	4.456676	1.900469	0.119870
1	4.959839	-0.023145	1.625603
7	-1.417623	-0.247942	-0.556477

E = -592.37215489; ZPE = 0.247334
Number of imaginary freq = 1 (-486.366 Hz)

cis-H-6 in ethanol

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
6	3.523860	-0.220241	0.581430
6	3.237329	-1.418928	-0.334120
6	1.725383	-1.644190	-0.474701
6	1.004624	-0.361906	-0.909194
6	2.768168	1.023101	0.104245
1	1.517164	-2.429268	-1.212206
1	3.668109	-1.226177	-1.327657
1	3.723034	-2.322710	0.053223
1	3.214380	-0.452498	1.609419
1	4.597552	0.003296	0.605890
1	1.342516	-0.058999	-1.914060
1	-0.067565	-0.520889	-0.952843
1	3.140331	1.331652	-0.887232
1	2.896925	1.862053	0.791468
1	1.304725	-1.978172	0.483139
7	0.580467	1.845258	0.252936
7	-0.681405	1.893797	0.222654
6	-1.569492	0.780213	0.130154
6	-1.588323	-0.215411	1.123890
6	-2.578804	0.802822	-0.844217
6	-2.588594	-1.187361	1.114973
1	-0.823258	-0.218509	1.897843
6	-3.564282	-0.185212	-0.854740
1	-2.575605	1.594621	-1.591292
6	-3.575290	-1.183728	0.123441
1	-2.596272	-1.952942	1.889609
1	-4.332999	-0.167533	-1.625997
1	-4.350902	-1.947322	0.119524
7	1.325851	0.739295	0.023583

E = -592.39762199; ZPE = 0.248526

Number of imaginary freq = 0

trans-H-6 in ethanol

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
6	-3.763403	1.198966	-0.177553
6	-4.396563	-0.189798	-0.017604
6	-3.438773	-1.271255	-0.534733
6	-2.067232	-1.197254	0.147192
6	-2.406513	1.261051	0.528657
1	-3.854438	-2.273063	-0.371374
1	-4.618490	-0.370640	1.044626
1	-5.351072	-0.239156	-0.555373
1	-3.626485	1.423244	-1.244135
1	-4.413440	1.977646	0.239577
1	-2.138516	-1.507267	1.203163
1	-1.343953	-1.854215	-0.337727
1	-2.552354	1.189775	1.619600
1	-1.878910	2.195969	0.321698
1	-3.302733	-1.150556	-1.617992
7	-0.233401	0.444023	0.125697
7	0.546332	-0.560091	0.070547
6	1.919401	-0.206956	0.008620
6	2.416726	1.090737	-0.214621
6	2.827407	-1.265921	0.167116
6	3.791547	1.313052	-0.259473
1	1.720062	1.912513	-0.353735
6	4.202707	-1.036752	0.121472
1	2.432253	-2.267009	0.329933
6	4.692431	0.254633	-0.090813
1	4.164965	2.321462	-0.433781
1	4.892364	-1.869729	0.249941
1	5.765091	0.436193	-0.131126
7	-1.535897	0.169183	0.084776

E = -592.42193545; ZPE = 0.248951

Number of imaginary freq = 0

ts-H-6 in ethanol

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
6	-3.403921	-0.943614	0.729397
6	-3.783749	0.531182	0.921497
6	-2.530547	1.416260	0.886145
6	-1.707358	1.186428	-0.387364
6	-2.589692	-1.133115	-0.553221
1	-2.801713	2.477896	0.938575
1	-4.470236	0.837654	0.118456
1	-4.319912	0.668498	1.868289
1	-2.809795	-1.289648	1.586041
1	-4.299652	-1.574488	0.676484
1	-2.263543	1.534313	-1.273708
1	-0.769008	1.735494	-0.350749
1	-3.219248	-0.910370	-1.431097
1	-2.221073	-2.156861	-0.653439
1	-1.899753	1.199274	1.758645
7	-0.377302	-0.746009	-1.242802
7	0.641702	-0.029338	-1.478224
6	1.745907	-0.048266	-0.580478
6	2.033975	-1.135409	0.265106
6	2.632883	1.038243	-0.628566
6	3.186868	-1.121135	1.048727
1	1.353203	-1.982448	0.300425
6	3.780037	1.048102	0.165618
1	2.406911	1.869844	-1.293646
6	4.063700	-0.031082	1.007317
1	3.401288	-1.967818	1.699593
1	4.455949	1.900956	0.123049
1	4.960091	-0.025183	1.624873
7	-1.417562	-0.247892	-0.555667

E = -592.37177924; ZPE = 0.247367

Number of imaginary freq = 1 (-487.179 Hz)

cis-H-6 in methanol

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	3.517010	-0.226236	0.588495
6	3.233322	-1.418913	-0.335828
6	1.721777	-1.640055	-0.487323
6	1.006964	-0.353383	-0.918548
6	2.767414	1.021811	0.113751
1	1.516584	-2.419905	-1.231186
1	3.670745	-1.221274	-1.325481
1	3.714520	-2.326052	0.049303
1	3.200602	-0.463665	1.613189
1	4.591048	-0.005375	0.620753
1	1.352488	-0.045100	-1.919156
1	-0.065394	-0.509022	-0.970296
1	3.146518	1.334986	-0.873613
1	2.893941	1.856360	0.806768
1	1.294224	-1.979002	0.465709
7	0.579835	1.847276	0.252796
7	-0.682251	1.895255	0.219530
6	-1.568407	0.779796	0.127818
6	-1.577649	-0.219934	1.117561
6	-2.585035	0.804421	-0.838764
6	-2.576576	-1.193194	1.113274
1	-0.805640	-0.225307	1.884758
6	-3.569387	-0.184969	-0.844902
1	-2.589102	1.598739	-1.583223
6	-3.571396	-1.186872	0.129907
1	-2.576902	-1.961837	1.885000
1	-4.344264	-0.165586	-1.610009
1	-4.346195	-1.951406	0.129407
7	1.325073	0.741557	0.022736

E = -592.39786628; ZPE = 0.248476

Number of imaginary freq = 0

trans-H-6 in methanol

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-3.761563	1.204062	-0.144742
6	-4.395387	-0.188947	-0.030400
6	-3.434976	-1.254493	-0.575040
6	-2.066600	-1.201803	0.115349
6	-2.408429	1.244097	0.570159
1	-3.851560	-2.260660	-0.444007
1	-4.623285	-0.401865	1.024597
1	-5.346919	-0.222021	-0.574675
1	-3.619097	1.460820	-1.203254
1	-4.413657	1.969730	0.292724
1	-2.142465	-1.544778	1.160699
1	-1.341205	-1.843283	-0.386861
1	-2.560317	1.139127	1.657517
1	-1.879574	2.184876	0.395193
1	-3.293683	-1.101227	-1.653500
7	-0.233555	0.440533	0.146403
7	0.546669	-0.561880	0.067232
6	1.919072	-0.207915	0.006830
6	2.413265	1.083866	-0.253485
6	2.829124	-1.259723	0.199185
6	3.787777	1.309344	-0.297914
1	1.714353	1.898393	-0.422316
6	4.203799	-1.027209	0.154461
1	2.436366	-2.257185	0.388427
6	4.690684	0.259229	-0.092955
1	4.159080	2.313043	-0.501633
1	4.895510	-1.853785	0.310616
1	5.763050	0.442647	-0.133700
7	-1.535571	0.166078	0.098003

E = -592.42236366; ZPE = 0.261007

Number of imaginary freq = 0

ts-H-6 in methanol

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	3.437021	0.417457	-0.874961
6	3.414395	1.273433	0.400015
6	1.997415	1.345263	0.988910
6	1.422101	-0.058754	1.230530
6	2.846914	-0.975761	-0.615720
1	1.996314	1.886092	1.942549
1	4.097269	0.839071	1.144399
1	3.781730	2.283052	0.182010
1	2.856179	0.908035	-1.667479
1	4.460860	0.296731	-1.247834
1	2.010105	-0.588822	1.992810
1	0.378499	-0.039823	1.540374
1	3.482104	-1.536454	0.084373
1	2.726596	-1.559597	-1.531046
1	1.331458	1.888982	0.306260
7	0.534629	-1.482462	-0.588896
7	-0.609468	-1.528167	0.011743
6	-1.653581	-0.652754	-0.061188
6	-1.616818	0.530751	-0.847627
6	-2.846443	-0.933696	0.655687
6	-2.725339	1.374132	-0.906820
1	-0.719985	0.767213	-1.415786
6	-3.936050	-0.073987	0.583646
1	-2.890578	-1.836816	1.261472
6	-3.895329	1.090784	-0.196163
1	-2.667291	2.270609	-1.524501
1	-4.836558	-0.318423	1.147035
1	-4.753468	1.757270	-0.246894
7	1.514989	-0.851989	-0.009361

E = -592.37207671; ZPE = 0.247343

Number of imaginary freq = 1 (-485.81 Hz)

cis-H-6-O in acetonitrile

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	3.491931	-0.312693	0.545052
6	1.864115	-1.608069	-0.535028
6	1.031558	-0.371680	-0.876725
6	2.739789	0.974344	0.222022
1	1.753112	-2.357325	-1.324942
1	3.186334	-0.686696	1.535375
1	4.570351	-0.127936	0.553773
1	1.309246	0.005616	-1.873361
1	-0.021036	-0.641815	-0.888613
1	3.111911	1.393161	-0.726241
1	2.887670	1.712620	1.014502
1	1.510232	-2.038959	0.415184
7	0.573966	1.842143	0.208892
7	-0.679361	1.893093	0.116478
6	-1.569241	0.775384	0.085807
6	-1.581557	-0.176514	1.120740
6	-2.582234	0.762365	-0.884064
6	-2.586397	-1.143060	1.158607
1	-0.810974	-0.152234	1.888393
6	-3.568126	-0.224633	-0.850193
1	-2.581491	1.523947	-1.662156
6	-3.576527	-1.179117	0.171076
1	-2.593467	-1.874580	1.965615
1	-4.339779	-0.238990	-1.618644
1	-4.353565	-1.940909	0.203034
7	1.300551	0.680504	0.125850
8	3.253187	-1.308006	-0.448029

E = -628.28824855; ZPE = 0.224523

Number of imaginary freq = 0

trans-H-6-O in acetonitrile

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	3.797931	1.098686	0.116832
6	3.477252	-1.187058	0.527742
6	2.074795	-1.181737	-0.081624
6	2.429445	1.234266	-0.546125
1	3.950785	-2.159976	0.365621
1	3.719567	1.318868	1.193561
1	4.508230	1.796109	-0.336980
1	2.099045	-1.546170	-1.120707
1	1.405404	-1.829027	0.488710
1	2.540947	1.147866	-1.638436
1	1.972884	2.201523	-0.317029
1	3.409863	-1.002726	1.611851
7	0.239744	0.458700	-0.117755
7	-0.532277	-0.546182	-0.035013
6	-1.909123	-0.202593	0.003747
6	-2.413543	1.087565	0.250303
6	-2.807988	-1.262044	-0.194944
6	-3.789829	1.304095	0.275802
1	-1.722033	1.907349	0.424135
6	-4.184708	-1.038173	-0.169852
1	-2.405797	-2.257722	-0.373337
6	-4.682498	0.246379	0.064663
1	-4.170684	2.306134	0.469620
1	-4.869190	-1.869816	-0.330612
1	-5.756517	0.422900	0.090729
7	1.544780	0.182927	-0.047633
8	4.325170	-0.212467	-0.075448

E = -628.31231579; ZPE = 0.224988

Number of imaginary freq = 0

ts-H-6-O in acetonitrile

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	3.449013	-0.919536	-0.631847
6	2.667584	1.261940	-0.988477
6	1.727268	1.194482	0.215669
6	2.572849	-1.085801	0.606302
1	3.024975	2.287446	-1.122593
1	2.914122	-1.284861	-1.523148
1	4.376470	-1.488498	-0.517220
1	2.207551	1.635344	1.103300
1	0.815816	1.753023	0.005934
1	3.152826	-0.825569	1.505728
1	2.224155	-2.117910	0.700618
1	2.125937	0.953704	-1.897001
7	0.374167	-0.600549	1.283226
7	-0.623556	0.161250	1.429790
6	-1.748671	0.030986	0.566190
6	-2.029463	-1.137879	-0.163990
6	-2.654325	1.101849	0.531663
6	-3.199885	-1.220534	-0.916844
1	-1.330935	-1.970562	-0.136404
6	-3.817668	1.014359	-0.233649
1	-2.430896	1.997303	1.109102
6	-4.096776	-0.146964	-0.959733
1	-3.411251	-2.129584	-1.478555
1	-4.509665	1.854955	-0.258528
1	-5.005903	-0.216872	-1.554583
7	1.399693	-0.213419	0.488089
8	3.821890	0.445462	-0.812011

E = -628.26044198; ZPE = 0.223192

Number of imaginary freq = 1 (-505.632 Hz)

cis-H-6-0 in benzene

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	3.483415	-0.316470	0.547220
6	1.853967	-1.609578	-0.529654
6	1.028893	-0.370466	-0.881632
6	2.736270	0.971415	0.214239
1	1.746614	-2.363445	-1.315311
1	3.176470	-0.678906	1.541888
1	4.562914	-0.139635	0.554416
1	1.316814	-0.000956	-1.878575
1	-0.025855	-0.632383	-0.900132
1	3.112577	1.380871	-0.736648
1	2.882206	1.719063	0.997648
1	1.488542	-2.034114	0.419477
7	0.572382	1.849288	0.204947
7	-0.677902	1.897744	0.116271
6	-1.564489	0.780305	0.086345
6	-1.585411	-0.161541	1.130006
6	-2.568595	0.752970	-0.891965
6	-2.585640	-1.131734	1.167482
1	-0.823233	-0.123473	1.903310
6	-3.550098	-0.237241	-0.858068
1	-2.564515	1.509679	-1.672441
6	-3.565008	-1.182260	0.170968
1	-2.599185	-1.853456	1.981356
1	-4.314563	-0.260752	-1.631463
1	-4.339021	-1.945026	0.203021
7	1.298281	0.680179	0.119770
8	3.241384	-1.317542	-0.435389

E = -628.28051988; ZPE = 0.225133

Number of imaginary freq = 0

trans-H-6-0 in benzene

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	3.808242	1.084214	0.138627
6	3.476443	-1.209658	0.474971
6	2.063887	-1.171962	-0.109388
6	2.428742	1.252503	-0.494416
1	3.942443	-2.177718	0.269573
1	3.748821	1.271918	1.223082
1	4.518231	1.789202	-0.303331
1	2.068283	-1.497227	-1.161721
1	1.395360	-1.834312	0.444014
1	2.521300	1.202629	-1.591041
1	1.982223	2.214259	-0.226888
1	3.427373	-1.066888	1.566645
7	0.238424	0.477363	-0.078304
7	-0.529767	-0.528680	-0.029836
6	-1.908232	-0.194740	0.004988
6	-2.423261	1.097642	0.209729
6	-2.796018	-1.267384	-0.161771
6	-3.800379	1.301744	0.229904
1	-1.737229	1.926028	0.353571
6	-4.174069	-1.055820	-0.142179
1	-2.381941	-2.261477	-0.309724
6	-4.682792	0.229946	0.053097
1	-4.190639	2.304625	0.390660
1	-4.850610	-1.896867	-0.276567
1	-5.757101	0.397348	0.073953
7	1.546972	0.193840	-0.011683
8	4.321086	-0.221010	-0.104354

E = -628.30611836; ZPE = 0.225652

Number of imaginary freq = 0

ts-H-6-0 in benzene

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	3.452970	-0.886383	-0.679801
6	2.674419	1.309990	-0.918148
6	1.729984	1.176191	0.277491
6	2.570615	-1.119206	0.543676
1	3.036800	2.339372	-0.994595
1	2.921626	-1.207177	-1.590646
1	4.381681	-1.457856	-0.593519
1	2.210418	1.564472	1.189466
1	0.819176	1.747352	0.101818
1	3.147744	-0.907596	1.457836
1	2.220022	-2.153772	0.585185
1	2.132272	1.057169	-1.843749
7	0.371593	-0.673381	1.243831
7	-0.620045	0.082526	1.428839
6	-1.747849	0.000267	0.565403
6	-2.063481	-1.146612	-0.184171
6	-2.623827	1.095058	0.553421
6	-3.236037	-1.182751	-0.935583
1	-1.388430	-1.996936	-0.169558
6	-3.789769	1.054129	-0.210462
1	-2.373961	1.969458	1.148955
6	-4.102078	-0.084362	-0.957273
1	-3.474793	-2.074467	-1.511364
1	-4.458227	1.912167	-0.217415
1	-5.013172	-0.118216	-1.549750
7	1.398823	-0.243594	0.463590
8	3.824570	0.483657	-0.786725

E = -628.25159751; ZPE = 0.223734

Number of imaginary freq = 1 (-520.764 Hz)

cis-Cl-4 in acetonitrile

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	2.380731	1.300584	0.418036
7	1.232441	1.812690	0.266571
6	0.030260	1.054294	0.143506
6	-0.344860	0.071474	1.076200
6	-0.897094	1.465336	-0.827485
6	-1.614623	-0.504336	1.022845
1	0.347569	-0.232502	1.858392
6	-2.157532	0.877841	-0.903525
1	-0.618008	2.250360	-1.527979
6	-2.503072	-0.102946	0.026840
1	-1.905032	-1.259262	1.750288
1	-2.865569	1.186951	-1.669332
6	2.032256	-1.041368	-0.595386
6	4.000979	-0.487710	0.123275
6	3.436161	-1.691036	-0.676214
1	1.672231	-0.598851	-1.530955
1	1.233653	-1.636225	-0.144908
1	4.600802	0.214758	-0.465838
1	4.518344	-0.718245	1.060290
1	3.835890	-1.802005	-1.686038
1	3.505880	-2.644081	-0.147460
7	2.614190	-0.010240	0.318937
17	-4.106596	-0.843026	-0.050683

E = -973.34060538; ZPE = 0.179785
Number of imaginary freq = 0

trans-Cl-4 in acetonitrile

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	1.835922	-0.498817	-0.131522
7	1.106297	0.544872	-0.204497
6	-0.280626	0.272551	-0.124075
6	-0.863265	-1.008016	-0.171595
6	-1.116902	1.394019	-0.009589
6	-2.244629	-1.159413	-0.092227
1	-0.229519	-1.884330	-0.274039
6	-2.501328	1.254361	0.072067
1	-0.663481	2.382935	0.019130
6	-3.050789	-0.025644	0.030827
1	-2.692343	-2.150230	-0.131030
1	-3.141267	2.128969	0.164475
6	3.865541	1.002860	-0.070357
6	4.200469	-1.122446	0.239833
6	5.108320	0.141102	0.287198
1	3.444575	1.589783	0.755453
1	3.929287	1.631601	-0.964162
1	3.964908	-1.555112	1.218974
1	4.497167	-1.917212	-0.452775
1	5.551208	0.352093	1.262200
1	5.885884	0.151203	-0.479503
7	3.122911	-0.258471	-0.272544
17	-4.806063	-0.219943	0.127573

E = -973.35681612; ZPE = 0.179891
Number of imaginary freq = 0

ts-Cl-4 in acetonitrile

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	-2.129606	0.753042	-1.000902
7	-1.122647	1.312818	-0.385525
6	0.133292	0.805530	-0.258926
6	0.524112	-0.454676	-0.790401
6	1.123086	1.569430	0.416629
6	1.831560	-0.914866	-0.654437
1	-0.205593	-1.066665	-1.316129
6	2.423117	1.101764	0.553124
1	0.847026	2.536601	0.831567
6	2.775632	-0.139793	0.016177
1	2.108990	-1.880552	-1.073181
1	3.163240	1.703634	1.076912
6	-2.848967	-0.364892	1.154081
6	-4.221711	-0.528322	-0.540240
6	-4.283720	-0.933815	0.961689
1	-2.742180	0.532182	1.774442
1	-2.063288	-1.083354	1.405401
1	-4.907330	0.259180	-0.867330
1	-4.220611	-1.351590	-1.261012
1	-5.050990	-0.407744	1.532088
1	-4.365973	-2.008432	1.131491
7	-2.862791	-0.006779	-0.282442
17	4.441389	-0.734646	0.194215

E = -973.30780686; ZPE = 0.178052
Number of imaginary freq = 1 (-497.279 Hz)

cis-Cl-4 in benzene

Atomic Number	Coordinates (Angstroms) X	 Y	 Z
7	-2.378019	1.299016	-0.424130
7	-1.233836	1.804731	-0.262931
6	-0.031729	1.048396	-0.142666
6	0.340134	0.054022	-1.063938
6	0.903132	1.473924	0.814390
6	1.611027	-0.517632	-1.012524
1	-0.358725	-0.258637	-1.834703
6	2.163253	0.887752	0.890499
1	0.627673	2.272039	1.498844
6	2.507205	-0.105377	-0.027633
1	1.900411	-1.278553	-1.731580
1	2.876853	1.207519	1.644166
6	-2.042345	-1.026169	0.616606
6	-3.996252	-0.483531	-0.133455
6	-3.444862	-1.679292	0.685896
1	-1.707951	-0.555203	1.548058
1	-1.227196	-1.628590	0.207779
1	-4.585122	0.235260	0.446815
1	-4.522896	-0.720502	-1.063413
1	-3.860113	-1.787313	1.689704
1	-3.504306	-2.636569	0.163598
7	-2.605476	-0.025139	-0.341099
17	4.107372	-0.841898	0.050871

E = -973.33325846; ZPE = 0.180352

Number of imaginary freq = 0

trans-Cl-4 in benzene

Atomic Number	Coordinates (Angstroms) X	 Y	 Z
7	1.836507	-0.512542	-0.161005
7	1.110292	0.529855	-0.215316
6	-0.277202	0.262952	-0.132332
6	-0.863557	-1.015150	-0.168622
6	-1.107567	1.387721	-0.022658
6	-2.244477	-1.160062	-0.084158
1	-0.229704	-1.890361	-0.265455
6	-2.491628	1.253367	0.064271
1	-0.647052	2.371725	-0.003411
6	-3.048089	-0.023758	0.033576
1	-2.697557	-2.146747	-0.113889
1	-3.128986	2.128011	0.152229
6	3.844373	1.006154	-0.051530
6	4.196424	-1.114812	0.240788
6	5.092029	0.155861	0.315436
1	3.394320	1.564231	0.778707
1	3.916918	1.660987	-0.924964
1	3.938105	-1.547338	1.214357
1	4.519794	-1.910266	-0.438628
1	5.523606	0.361185	1.296606
1	5.879138	0.181419	-0.441049
7	3.127962	-0.261042	-0.303471
17	-4.799632	-0.210610	0.137378

E = -973.35116886; ZPE = 0.180599

Number of imaginary freq = 0

ts-Cl-4 in benzene

Atomic Number	Coordinates (Angstroms) X	 Y	 Z
7	-2.011505	-0.295073	-1.052920
7	-1.120507	0.601147	-1.135355
6	0.188027	0.317212	-0.661532
6	0.707439	-0.979777	-0.503418
6	1.027399	1.418817	-0.436832
6	2.034380	-1.167029	-0.123970
1	0.071127	-1.839950	-0.687531
6	2.351579	1.241087	-0.044094
1	0.624897	2.418539	-0.576736
6	2.844304	-0.054650	0.108091
1	2.436515	-2.169098	-0.006093
1	2.995136	2.097059	0.135832
6	-3.244826	0.830691	0.869033
6	-4.111674	-0.960638	0.013397
6	-4.584457	0.074787	1.070884
1	-3.316052	1.756727	0.286242
1	-2.629712	1.011976	1.754757
1	-4.605420	-0.874663	-0.961137
1	-4.091962	-2.011002	0.321575
1	-5.481386	0.636060	0.802720
1	-4.703331	-0.343484	2.072634
7	-2.787670	-0.309880	0.032866
17	4.521467	-0.292854	0.599780

E = -973.29825807; ZPE = 0.178631

Number of imaginary freq = 1 (-542.93 Hz)

cis-Cl-4 in cyclohexane

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
7	-2.378087	1.299401	-0.424060
7	-1.234207	1.804719	-0.263406
6	-0.032083	1.048514	-0.143797
6	0.339661	0.053175	-1.064088
6	0.903179	1.475203	0.812351
6	1.610623	-0.518247	-1.012167
1	-0.359386	-0.260217	-1.834055
6	2.163096	0.888926	0.889163
1	0.627685	2.274397	1.495312
6	2.507047	-0.105480	-0.027660
1	1.900143	-1.279700	-1.730390
1	2.876832	1.209361	1.642195
6	-2.042976	-1.023385	0.621242
6	-3.995527	-0.481874	-0.128988
6	-3.442201	-1.684142	0.678968
1	-1.721424	-0.548715	1.555520
1	-1.219631	-1.620847	0.221837
1	-4.577186	0.234412	0.461713
1	-4.530380	-0.709464	-1.056521
1	-3.861254	-1.809580	1.679129
1	-3.493481	-2.634004	0.142347
7	-2.604557	-0.026118	-0.341655
17	4.106536	-0.842223	0.051566

E = -973.33258918; ZPE = 0.180407
Number of imaginary freq = 0

trans-Cl-4 in cyclohexane

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
7	1.836576	-0.515312	-0.162168
7	1.110955	0.527211	-0.216440
6	-0.276587	0.261351	-0.133252
6	-0.863782	-1.016175	-0.169728
6	-1.105954	1.386639	-0.022925
6	-2.244737	-1.160088	-0.084690
1	-0.230283	-1.891450	-0.267015
6	-2.490032	1.253237	0.064657
1	-0.644549	2.370052	-0.003734
6	-3.047569	-0.023367	0.033802
1	-2.698615	-2.146190	-0.114569
1	-3.126714	2.128083	0.153111
6	3.841061	1.006248	-0.052619
6	4.196416	-1.112918	0.244453
6	5.090062	0.159133	0.316746
1	3.387953	1.562770	0.776928
1	3.913526	1.661793	-0.925471
1	3.935914	-1.541623	1.219080
1	4.523017	-1.910940	-0.430395
1	5.521593	0.367410	1.297350
1	5.877063	0.184073	-0.439772
7	3.128270	-0.262769	-0.306417
17	-4.798987	-0.208955	0.138294

E = -973.35064236; ZPE = 0.180657
Number of imaginary freq = 0

ts-Cl-4 in cyclohexane

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
7	-2.161776	0.619909	-1.074082
7	-1.122741	1.084622	-0.506769
6	0.162004	0.680178	-0.332394
6	0.629079	-0.563616	-0.829480
6	1.080430	1.512231	0.351357
6	1.954246	-0.946571	-0.646390
1	-0.056182	-1.214124	-1.364582
6	2.399018	1.116685	0.531744
1	0.739645	2.469707	0.732369
6	2.837819	-0.112264	0.034927
1	2.298137	-1.899533	-1.037002
1	3.090981	1.765757	1.059153
6	-2.879418	-0.367711	1.139977
6	-4.364314	-0.379105	-0.458309
6	-4.395369	-0.708334	1.064128
1	-2.602931	0.555698	1.662903
1	-2.202262	-1.169518	1.446398
1	-4.905469	0.519760	-0.768638
1	-4.603259	-1.204571	-1.135253
1	-5.037495	-0.053066	1.655066
1	-4.633038	-1.748878	1.291276
7	-2.916165	-0.140029	-0.318260
17	4.516216	-0.609512	0.271689

E = -973.29745942; ZPE = 0.178679
Number of imaginary freq = 1 (-546.347 Hz)

cis-Cl-4 in DMSO

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	2.380270	1.299410	0.421294
7	1.232301	1.810901	0.268614
6	0.029924	1.052909	0.143759
6	-0.344463	0.067697	1.073841
6	-0.898119	1.466907	-0.825212
6	-1.614293	-0.507554	1.021231
1	0.349412	-0.238028	1.854136
6	-2.158688	0.879617	-0.901381
1	-0.619918	2.253938	-1.523807
6	-2.503493	-0.103263	0.027028
1	-1.903923	-1.264210	1.747187
1	-2.867347	1.190757	-1.665739
6	2.035560	-1.036403	-0.602588
6	4.002134	-0.483623	0.117407
6	3.436150	-1.693673	-0.670150
1	1.692563	-0.584607	-1.540305
1	1.226425	-1.628024	-0.167392
1	4.589125	0.219009	-0.484441
1	4.532689	-0.703826	1.049373
1	3.840949	-1.824414	-1.675531
1	3.496448	-2.637976	-0.124625
7	2.613742	-0.012816	0.323933
17	-4.107582	-0.842398	-0.051138

E = -973.34074057; ZPE = 0.179793

Number of imaginary freq = 0

trans-Cl-4 in DMSO

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	1.835287	-0.498335	-0.127406
7	1.106468	0.545292	-0.210391
6	-0.280475	0.273221	-0.127561
6	-0.863358	-1.007057	-0.179762
6	-1.116644	1.394089	-0.006907
6	-2.244650	-1.158918	-0.098368
1	-0.230069	-1.883056	-0.287608
6	-2.500926	1.254097	0.076870
1	-0.663345	2.382968	0.025246
6	-3.050434	-0.025692	0.031218
1	-2.692264	-2.149652	-0.140948
1	-3.140541	2.128416	0.174297
6	3.867088	1.001357	-0.079851
6	4.199033	-1.121771	0.249596
6	5.107654	0.141484	0.289612
1	3.445278	1.598051	0.738449
1	3.933913	1.620038	-0.980422
1	3.961999	-1.547887	1.231240
1	4.496085	-1.921134	-0.437526
1	5.546213	0.360295	1.264843
1	5.888707	0.144643	-0.473613
7	3.122520	-0.260737	-0.270230
17	-4.805861	-0.220064	0.130186

E = -973.35675843; ZPE = 0.179877

Number of imaginary freq = 0

ts-Cl-4 in DMSO

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
7	-2.128157	0.748006	-1.002801
7	-1.121536	1.308200	-0.387591
6	0.133999	0.800549	-0.257569
6	0.524217	-0.463400	-0.780429
6	1.124447	1.569903	0.410751
6	1.832731	-0.920821	-0.645071
1	-0.206665	-1.080037	-1.299247
6	2.425506	1.105165	0.546475
1	0.848440	2.539928	0.819100
6	2.777835	-0.139593	0.016827
1	2.110123	-1.889282	-1.057476
1	3.166465	1.711684	1.063737
6	-2.854864	-0.359986	1.154591
6	-4.224241	-0.526218	-0.542135
6	-4.290765	-0.925594	0.961235
1	-2.747106	0.540131	1.770398
1	-2.072110	-1.079535	1.411833
1	-4.905914	0.262969	-0.873428
1	-4.225362	-1.352270	-1.259719
1	-5.058063	-0.395697	1.528045
1	-4.375855	-1.999427	1.134665
7	-2.863719	-0.009007	-0.283771
17	4.445103	-0.731110	0.193717

E = -973.30798450; ZPE = 0.178046

Number of imaginary freq = 1 (-496.48 Hz)