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Molecular Mechanics and ab Initio Studies of the Structures, Heats of Formation, Conformations, and Strain Energies of Azoalkanes

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Abstract: Ab initio molecular orbital theory has been employed to investigate the structures, energies, and conformations of *trans*- and *cis*-methyldiazene, *trans*-azomethane, diazetine, pyrazoline, 1,2,4,5-tetraazacyclohexa-1,4-diene, and *trans,trans*-1,2,4,5-tetraaza-1,4-pentadiene. A force field has been developed, on the basis of available experimental and theoretical (ab initio) data, to permit molecular mechanics calculations on azoalkanes. Structures, heats of formation, strain energies, and conformations of more than 50 molecules studied by the developed force field are presented. Extensive comparison is made with previous results for analogous alkenes and some striking features are revealed.

Introduction

Azo compounds, characterized by the -N=N- functional group, have attracted considerable attention in the literature.[1] The area of interest almost covers every branch of chemistry. For example, there has been great interest in azo compounds as powerful and selective reducing agents,[2] as sources of free radicals,[3] for study of thermal and photochemical fragmentation,[4] and for a model study of unimolecular reaction theory.[5] The transition-metal chemistry of azo compounds has also been a productive and active field of research.[6] Furthermore, theoretical chemists have been interested in the mechanism of the trans-cis isomerization of diazenes.[7] However, despite the activity in this area, experimental thermochemical and structural data for azo compounds are rather limited, as compared with their isoelectronic alkene analogues. Such information is desirable in order to have a better understanding of azo chemistry.

An alternative source of such data is from theoretical calculations. Recently, the ab initio molecular orbital theory has proven useful in systematic studies of equilibrium geometries, electric dipole moments, charge distributions, relative energies, and conformational analysis of a variety of *small* compounds.[8] However, the computation time required for ab initio calculations is at present a major practical problem to the application of this method to large molecules. Furthermore, there is a sizable error in the calculated total energy (which is directly related to the heat of formation), although it is occasionally possible to derive correct heats of formation from theoretical heats of reactions in conjunction with experimental enthalpies of formation.[9]

The molecular mechanics (MM) or force field method[10] has been shown to be a very reliable, fast, and efficient way of determining molecular structures, energies, and other properties for a wide variety of compounds.[10-16] A handicap of the molecular mechanics method lies in the fact that it is an empirical method and hence a great amount of accurate data must be available for a given class of compounds before the method can be developed.[10] For instance, it is certainly difficult to develop a reliable force field for azo compounds simply on the basis of the existing experimental data.

A promising theoretical approach to study geometries and energies of large molecules would therefore seem to be a combined utilization of the ab initio and molecular mechanics methods. In this work, we first report several ab initio calculations, these calculations being carried out essentially to provide necessary information for the force-field development. Most of the previous theoretical studies have been primarily concerned with the diimine molecule.[17-24] Secondly, we present a force-field method for azoalkanes, which is developed on the basis of experimental and theoretical results. Thirdly, applications of the present molecular mechanics to a study of conformations, structures, heats of formation, and strain energies of a wide range of azoalkanes are reported and discussed. Finally, extensive comparison is made with the available results for the isoelectronic and structurally related alkenes.

Computational Aspects and Results

Ab Initio Calculations. The results presented here were obtained using the modified version of the GAUSSIAN 70 system of programs.[25,26] Geometrical optimization was carried out using a direct search procedure[26] and the minimal STO-3G basis set.[27] Structural parameters[28] of the planar forms of dimethylenediazene (diazetine, **1**), trimethylenediazene (pyrazoline, **2**), and 1,2,4,5-tetraazacyclohexa-1,4-diene (**3**) were fully optimized. The geometry of the boat form of 1,2,4,5-tetraazacylohexa-1,4-diene (**4**) was also fully optimized with the exception that the C-H bond lengths were taken from the theoretical (STO-3G) structure of the planar form. All structural parameters for the eclipsed NNCH conformations of *trans*- and *cis*-methyldiazene (**5** and **6**) were fully optimized assuming C_{3v} local symmetry for the methyl group. The potential barrier hindering rotation of the methyl group was studied for both *cis*- and *trans*-methyldiazenes by optimizing the N_1-C_1 bond length and the $N_2N_1C_1$ and $N_1C_1H_{1,2,3}$[29] bond angles of the staggered forms while the rest of the parameters were kept the same as in the optimized eclipsed forms.[30] The obtained structural parameters for **1**-**6** and total energies are shown in Chart 1. Also included in Chart I are several previous results[17,18] obtained with the STO-3G basis set and they are shown for easy comparison.

A flexible rotor geometric model similar to the one used in methyldiazenes was employed in the study of the rotational potential function along the C_1-N_1 bond of *trans*-ethyldiazene (**11**). Thus, only three parameters (N_1-C_1, $N_2N_1C_1$, and $N_1C_1C_2$[31]) were optimized while other structural parameters were derived from the STO-3G optimized geometries of *trans*-methyldiazene and ethane.[32] Conformations with the dihedral angle ϕ equal to 0 (NNCC syn), 60, 90, 110, 115, 120, and 180° were examined. The obtained rotational potential function is plotted in Figure 1 and the structural and energetic data are presented in Table I.[105]

The rotational potential surface of *trans,trans*-1,2,4,5-tetraaza-1,4-pentadiene (**12**) was also investigated using a

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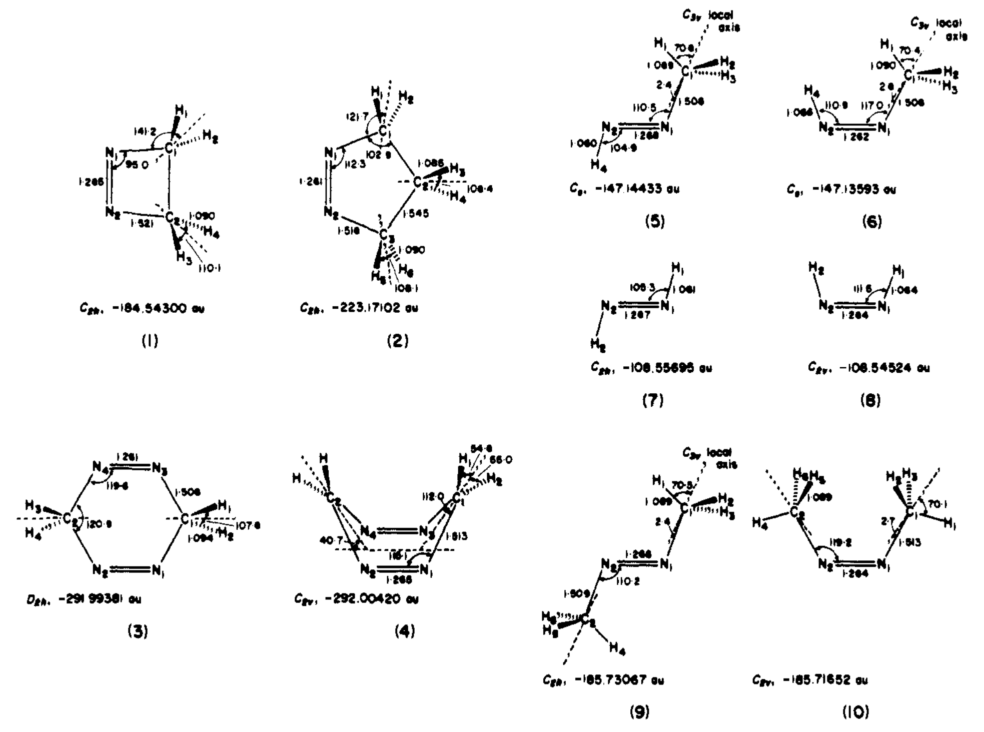
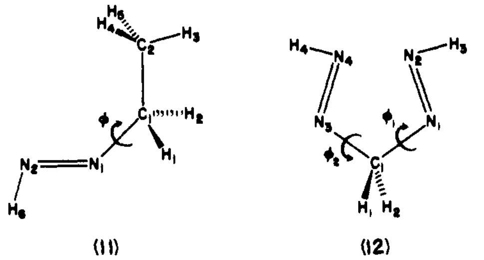
Chart I. Calculated STO-3G Structural Parameters





flexible rotor model. The possible rotational isomerism, referring to the syn,syn (NCNN) C_{2v} conformation, was examined by moving the two azo groups by 60° (or smaller) intervals. For each conformation, the $N_1C_1N_3$, $N_2N_1C_1$, and $N_4N_3C_1$ angles were optimized, while the C–N and H–N bond lengths and the HNN and HCH bond angles were assigned fixed values of 1.512 Å, 1.060 Å, 104.9°, and 109.5°, respectively, on the basis of previous results for *trans*-methyldiazene and *trans*-ethyldiazene. Furthermore, the azo groups were taken to be planar and the HCH plane was assumed to bisect the NCN angle throughout. The structural variations and calculated relative energies are presented in Table II,[105] while the rotational potential energy surface obtained in this manner is depicted in Figure 2.

In order to obtain a reasonable theoretical estimate for the N_{sp^2}–C_{sp^3} stretching force constant, calculations using the extended 4-31G basis set[33] were carried out on *trans*-azomethane. The 4-31G set is the larger and probably more reliable for molecular energetics, but, because of the computational expenses, only four parameters ($N_1{=}N_2$, $C_1{-}N_1$, $N_2N_1C_1$, and $N_1C_1H_{1,2,3}$) of *trans*-azomethane (9) were optimized. The C–H bond length was taken from the 4-31G optimized geometry of methane[32] and the HCH bond angles were kept at 109.5°. The calculated total energy is −187.770 34 au while the optimized structural parameters are 1.222 Å, 1.460 Å, 115.7°, and 177.6°, respectively, for the $N_1{=}N_2$ and $C_1{-}N_1$ bond lengths and the $N_2N_1C_1$ and $N_1C_1H_{1,2,3}$ angles.

The Molecular Mechanics Method

Geometries. The Allinger 1973 force field described previously[10a,34] was used as a starting point to extend these force field calculations to a study of azo hydrocarbons. The Allinger 1973 force field is one of the six force fields for which extensive usage[10a,11-15] has been reported and is currently in use

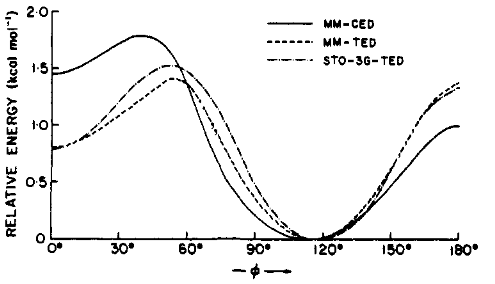


Figure 1. Calculated potential functions describing internal rotation (ϕ) about the C_{sp^3}–N_{sp^2} bond in *trans*-ethyldiazene (TED) and *cis*-ethyldiazene (CED).

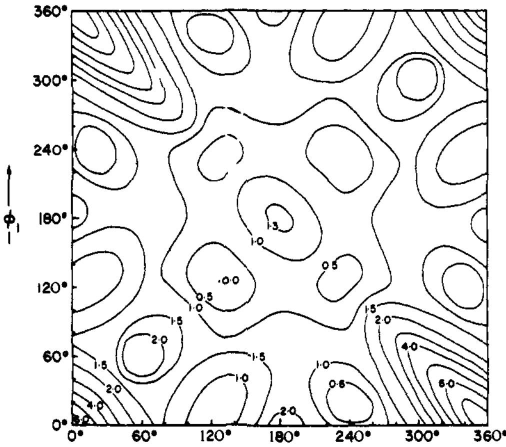


Figure 2. The theoretical (STO-3G) rotational potential surface for *trans,trans*-1,2,4,5-tetraaza-1,4-pentadiene (see text for discussion).

Table III. Force-Field Parameters[a]

van der Waals Parameters for the Hill Equation

atom	γ^*, Å	ϵ, kcal mol^{-1}
N_{sp^2}	1.700	0.039
H	1.200	0.040
Lp	1.200	0.025

Natural Bond Lengths and Stretching Force Constants

bond	l_0, Å	k_l, mdyn Å^{-1}	dipole, D[b]
$N_{sp^2}{=}N_{sp^2}$	1.250	10.72	0.00
$N_{sp^2}—C_{sp^3}$	1.480	3.95	−1.75
$N_{sp^2}—H$	1.029	5.23	−1.50
$N_{sp^2}—Lp$	0.500	4.60	0.60

Natural Bond Angles and Bending Force Constants

angle	type[c]	θ_0, deg	k_θ, mdyn Å rad^{-2}
$N_{sp^2}—N_{sp^2}—C_{sp^3}$		107.00	0.38
$N_{sp^2}—N_{sp^2}—H$		108.30	0.36
$N_{sp^2}—N_{sp^2}—Lp$		126.70	0.36
$C_{sp^3}—N_{sp^2}—Lp$		126.30	0.36
$H—N_{sp^2}—Lp$		125.00	0.36
$N_{sp^2}—C_{sp^3}—N_{sp^2}$	0	108.27	0.38
	1	109.31	0.38
	2	109.00	0.38
$N_{sp^2}—C_{sp^3}—C_{sp^3}$	0	109.47	0.38
	1	110.51	0.38
	2	110.20	0.38
$N_{sp^2}—C_{sp^3}—H$	0	108.50	0.24
	1	108.51	0.24
	2	107.90	0.24

out-of-plane bending constant for $N_{sp^2}—N_{sp^2}—X$ bonds = 0.05 mydn Å rad^{-2}

Stretch-Bend Constants

angle	$k_{l\theta}$, mdyn rad^{-1}
$N_{sp^2}—N_{sp^2}—C_{sp^3}$	0.12
$N_{sp^2}—C_{sp^3}—C_{sp^3}$	0.12
$N_{sp^2}—N_{sp^2}—H$	0.04
$N_{sp^2}—C_{sp^3}—H$	0.04
$N_{sp^2}—N_{sp^2}—Lp$	0.00
$C_{sp^3}—N_{sp^2}—Lp$	0.00
$H—N_{sp^2}—Lp$	0.00

Torsional Parameters (kcal mol^{-1})

dihedral angle	V_1	V_2	V_3
$C_{sp^3}—N_{sp^2}—N_{sp^2}—C_{sp^3}$	−6.60	14.00	0.00
$C_{sp^3}—N_{sp^2}—N_{sp^2}—Lp$	0.00	14.00	0.00
$C_{sp^3}—N_{sp^2}—N_{sp^2}—H$	−4.99	14.00	0.00
$Lp—N_{sp^2}—N_{sp^2}—Lp$	0.00	14.00	0.00
$H—N_{sp^2}—N_{sp^2}—Lp$	0.00	14.00	0.00
$H—N_{sp^2}—N_{sp^2}—H$	−3.38	14.00	0.00
$C_{sp^3}—C_{sp^3}—N_{sp^2}—Lp$	0.00	0.00	1.95
$H—C_{sp^3}—N_{sp^2}—Lp$	0.00	0.00	1.95
$N_{sp^2}—C_{sp^3}—N_{sp^2}—Lp$	0.00	0.00	1.95
$H—C_{sp^3}—N_{sp^2}—N_{sp^2}$	0.00	0.00	0.00
$C_{sp^3}—C_{sp^3}—N_{sp^2}—N_{sp^2}$	0.00	0.00	0.70
$N_{sp^2}—C_{sp^3}—N_{sp^2}—N_{sp^2}$	0.00	−0.20	1.20
$C_{sp^3}—C_{sp^3}\text{- -}C_{sp^3}—N_{sp^2}$	0.00	0.00	0.53
$N_{sp^2}—C_{sp^3}—C_{sp^3}—N_{sp^2}$	0.00	0.00	0.53
$H—C_{sp^3}—C_{sp^3}—N_{sp^2}$	0.00	0.00	0.53

Heat of Formation Parameters[d] (kcal mol^{-1})

$N_{sp^2}{=}N_{sp^2}$	46.758		
		$N_{sp^2}—CH<$	−1.700
$N_{sp^2}—H$	−5.054		
$N_{sp^2}—C$	4.071	$N_{sp^3}—C\lessdot$	−4.827
$N_{sp^2}—CH_3$	1.299		

[a] For hydrocarbon parameters see ref 34. Lp represents the electron lone pair of the N_{sp^2} atom. [b] The positive sign is defined as having the atom to the left at the positive end of the dipole and vice versa. [c] The type refers to the number of hydrogens attached to the central atoms. [d] See text for derivation and reliability.

worldwide.[35] The force-field parameters developed previously[34] for hydrocarbons are carried over here. Some additional parameters, which pertain to bond lengths, bond angles, dihedral angles, energetics, and dipoles involving the N=N functional group, are needed to deal with azo compounds and their values settled upon are given in Table III.

The van der Waals parameters for the N_{sp^2} atom, the hydrogen atom attached to the N_{sp^2} atom, and the electron lone pair (Lp) of the N_{sp^2} atom were taken from the appropriate values in amines and oxa compounds.[11] In principle, one may or may not introduce the lone pair of the N_{sp^2} atom into the force-field calculation as long as experimental facts are reproduced. However, we have chosen to parametrize the force field by including explicitly the lone-pair electrons owing to the following two reasons. First, it has been shown that consideration of electron pairs is required for amines and oxa compounds, at least, for the 1973 Allinger force field.[11,36] Secondly, we wish to develop a model analogous to the one used in alkenes[37] that simulates a rehybridization rather than simple twisting of the N=N double bond for highly distorted compounds (vide infra).

We have carried out 4-31G calculations on *trans*-diimine and *trans*-azomethane in order to assess theoretically the force constants for the $N_{sp^2}—C_{sp^3}$, the N=N, and the $N_{sp^2}—H$ stretching. The theoretical stretching constants obtained for the N=N, $N_{sp^2}—H$, and $N_{sp^2}—C_{sp^3}$ bonds are respectively 13.95, 6.80, and 5.14 mdyn Å^{-1}.[39] Thus, the theoretical values for the N=N, $N_{sp^2}—H$, and $N_{sp^2}—C_{sp^3}$ stretching are apparently too large, compared with the experimental estimates (10.72, 5.24, and 4.23 mdyn Å^{-1}), although one might have expected that a better agreement would be obtained on the basis of previous results.[40] The stretching force constants employed in this work are hence the scaled-down values (by 23%). The natural bond length, the stretching constant, and the bond dipole moment for N_{sp^2}-Lp were all directly taken from the oxa compounds. No experimental values are currently available for the dipole moments of *cis*-diimine and *cis*-azomethane. The STO-3G values[17] obtained for *cis*-diimine and *cis*-azomethane are respectively 2.9 and 3.1 D while the 4-31G basis set predicts a higher value (3.8 D) for *cis*-diimine. The 4-31G set probably gives more reliable results than the minimal STO-3G basis set. To fit the theoretical (4-31G) dipole moments of both molecules (the 4-31G dipole moment for *cis*-azomethane is estimated to be 4.1 D by adding the difference in STO-3G dipole moments between *cis*-diimine and *cis*-azomethane to the calculated 4-31G dipole moment of the former), the N_{sp^2}-H and N_{sp^2}-C_{sp^3} bonds were assigned bond moments of 1.50 and 1.75 D, respectively, with the N_{sp^2} atom negative.

The best theoretical estimates for disruption of the N=N bond are in the range of 50-60 kcal mol^{-1}.[19,20] In the molecular mechanics framework, there are four torsional energies to be summed across the N=N double bond. We have arbitrarily assigned a value of 14.0 kcal mol^{-1} to the V_2 term for each of them.

Both *cis*- and *trans*-diimine have been identified experimentally.[41] The theoretical estimates[17-20] for the cis-trans isomerization energy are in the range of 5.8-7.4 kcal mol^{-1}, for which the lower bound is the CEPA value[20] while the higher bound refers to the STO-3G value (Table IV). A value of −3.88 kcal mol^{-1} was assigned for the V_1 term of HNNH torsion, this resulting in an isomerization energy of 6.0 kcal mol^{-1} for diimine. The V_1 term of CNNC torsion was, on the other hand, adjusted to fit observed heats of formation for various cis and trans compounds. The chosen value is −6.60 kcal mol^{-1}, which would give an isomerization energy of 5.9 kcal mol^{-1} for azomethane while the STO-3G value is 8.9 kcal mol^{-1}. The V_1 term of HNNC was taken as the arithmetic mean of V_1 terms of CNNC and CNNH. The calculated

Table IV. Comparison of Theoretical Conformational and Isomerization Energies (kcal mol^{-1})

transformations	ab initio	molecular mechanics
diimine		
trans → cis	~5.8-7.4[a]	6.00
methyldiazene		
trans → cis	5.27[b]	3.08
azomethane		
trans → cis	8.88[c]	5.92
trans-methyldiazene		
ecl → stag	1.33[b]	1.37
cis-methyldiazene		
ecl → stag	1.27[b]	1.04
trans-azomethane		
ecl,ecl → ecl,stag	1.14[c]	1.31
ecl,stag → stag,stag	1.29[c]	1.32
cis-azomethane		
ecl,ecl → ecl,stag	−2.23[c]	−1.54
ecl,stag → stag,stag	−1.53[c]	0.20
trans-ethyldiazene		
gauche → syn	0.78[b]	0.79
gauche → anti	1.34[b]	1.38
1,2,4,5-tetraaza-cyclohexa-1,4-diene		
boat → planar	6.52[b]	2.39
trans,trans-1,2,4,5-tetraaza-1,4-pentadiene		
$C_2 \rightarrow C_s$ (gauche,gauche)	0.46[b]	0.61
$C_2 \rightarrow C_{2v}$ (syn,syn)	7.40[b]	7.97
$C_2 \rightarrow C_{2v}$ (anti,anti)	1.86[b]	1.32
$C_2 \rightarrow C_1$	0.23[b]	0.80
$C_2 \rightarrow C_s$ (anti,syn)	2.33[b]	2.93

[a] From ref 17-20. The lower bound is the CEPA value (ref 20) while the higher bound corresponds to the HF STO-3G value. [b] STO-3G level, from this work. [c] STO-3G level, from ref 18.

cis-trans isomerization energy is 3.1 kcal mol^{-1}, which is smaller than the STO-3G value by about 2.2 kcal mol^{-1}.

Although the available experimental structural and energetic data are scarce, we are able to obtain the numerical values for the rest of the necessary parameters by augmenting the ab initio results. These parameters were initially given the values from the appropriate analogous alkenes and had been varied several times, through trial and error, until a reasonable overall agreement was reached. Comparison of structural parameters between ab initio and molecular mechanics calculations is made in Table VI while comparison of conformational and isomerization energies is shown in Table IV.

The difference between experimental and ab initio structural data requires comment here (Table V). There are only two simple molecules, *trans*-diimine and *trans*-azomethane, for which experimental structures[42-45] are available. Comparison between available experimental and theoretical STO-3G data seems to suggest that (a) the N—H and N—C bond lengths obtained from the minimal basis set are comparatively too short by respectively 0.03 and 0.01-0.02 Å while the N═N bond length is too long by 0.01-0.02 Å; (b) the STO-3G NNH and NNC bond angles are about 1° larger than the experimental counterparts. For other compounds, similar trends would be expected. One also notes that, for the N═N bond length and the NNH and NNC bond angles, the STO-3G structures are probably more accurate than the 4-31G results but the latter basis set seems to give better bond lengths for the N-C and N-H bonds.

Heats of Formation. One of our major objectives is to calculate the enthalpies of formation for azo compounds for which experimental information is lacking. According to the molecular mechanics model described previously,[10] the heat of formation [$\Delta H_f°(g)$] is calculated by the equation

Table V. Comparison of Experimental and ab Initio Structural Parameters

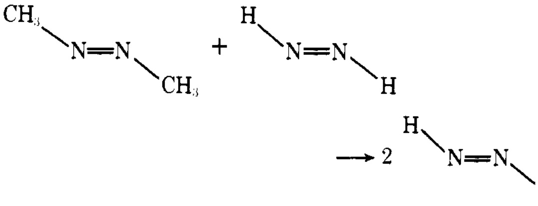
molecule	structural parameter	exptl	ab initio STO-3G	ab initio 4-31G
diimine (**7**)	N_1-N_2	1.252,[a] 1.23[b]	1.267[c]	1.225[c]
	N_1-H_1	1.028, 1.014	1.061	1.011
	$N_2N_1H_1$	106.9, 100	105.3	110.5
trans-azomethane (**9**)	N_1-N_2	1.247,[d] 1.254[e]	1.268[c]	1.222
	N_1-C_1	1.482, 1.474	1.509	1.460
	$(C\text{-}H)_{av}$	1.105, 1.107	1.089	[1.081][f]
	$N_2N_1C_1$	112.3, 111.9	110.2	115.7
	$(NCH)_{av}$	107.5, 109.4	109.4	[109.5][f]
	$N_1C_1H_{1,2,3}$	4.1	2.4	2.4

[a] From ref 42. [b] From ref 43. [c] From ref 17 and 18. [d] From ref 44. [e] From ref 45. [f] Assumed values in brackets; see text.

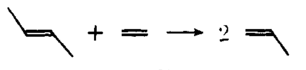
$$\Delta H_f°(g) = \Delta H_{steric} + \Delta H_{bond} + \Delta H_{stru} + \Delta H_{thermo} \quad (1)$$

where ΔH_{steric} is the steric energy of the molecule calculated by the program, ΔH_{bond} is the sum of the bond enthalpy contributions, ΔH_{stru} is the sum of the structural enthalpy contributions, and, finally, ΔH_{thermo} refers to the additional enthalpy resulting from torsional, translational, rotational, and conformational contributions.

Heat of formation parameters for hydrocarbons from the 1973 force field are used without any change. The additional enthalpy parameters for calculation for the heats of formation of azo compounds are also included in Table I. The values for these additional structural enthalpy terms are taken directly from the alkene analogues which, in turn, are from the alkane work. One also notes that even for thiaalkanes[46] the structural enthalpy parameters are very similar to those of alkanes. The good agreement between calculated and experimental heats of formation (vide infra) gives a direct support for this approach. We are also able to assign the bond enthalpy contributions on the basis of the calculated $\Delta H_f°$ for azomethane and the less accurate experimental $\Delta H_f°$ for diimine.[47] Thus the accuracy of the calculated $\Delta H_f°$ for alkyldiazenes seems to rely on the experimental error of the reported $\Delta H_f°$ of diimine, which is as high as 2 kcal mol^{-1}.[50] However, considerations of the reaction heat for eq 2 suggest that our results are very consistent. The heat of reaction calculated from force field heats of formation is 0.2 kcal mol^{-1}, which can be compared with that (−0.6 kcal mol^{-1}) obtained from STO-3G total energies. The corresponding reaction heats for the alkene analogue (eq 3) are −0.3 and −0.1 kcal mol^{-1}, respectively, for



(2)



(3)

STO-3G and MM calculations[51] while the experimental value is 0.3 kcal mol^{-1}.

Table VIII lists all of the compounds for which experimental[50,53] heats of formation are available while Table IX lists the predicted heats of formation for several interesting molecules.

An additional energetic property of interest is the strain energy. This measures the energy cost in deforming a molecule from an idealized model structure in terms of bond stretching, bond angle bending, torsion, and compression of nonbonded atoms.[10,54] Here, we have used our calculated heats of for-

Table VII. Equilibrium Geometries of 2,3-Diazabicyclo[2.2.1]-hept-2-ene and 2,3-Diazabicyclo[2.2.2]oct-2-ene

molecule	parameter	exptl		calcd
2,3-diazabicyclo[2.2.1]-hept-2-ene (**13a**)	C_1–N_2	1.503[a]	1.445[b]	1.501
	C_1–C_6	1.542	1.538	1.535
	C_1–C_7	1.534	1.547	1.532
	C_5–C_6	1.552	1.530	1.542
	N_2–N_3	1.246	1.221	1.261
	C_1–H	1.087	1.112	1.101
	$(C_5\text{–H})_{av}$	1.089		1.100
	$(C_7\text{–H})_{av}$	1.095		1.100
	$C_1C_7C_4$	91.3	108.0	89.9
	α	108.9	118.2	111.8
	β	128.3	103.5	125.1
	$C_1C_6C_5$	102.0	108.6	101.7
	$C_1N_2N_3$	108.4	116.3	107.6
	HC_1N_2	111.0	103.1	112.9
	HC_1C_7	119.7	178.6	112.9
	HC_1C_6	116.8	78.8	118.8
	HC_6H	108.2	116.5	108.7
	HC_7H	111.4	100.4	110.9
2,3-diazabicyclo[2.2.2]-oct-2-ene (**13b**)	C_1–N_2	1.473[b]		1.497
	C_1–C_6	1.550		1.532
	C_5–C_6	1.516		1.535
	N_2–N_3	1.243		1.258
	C_1–H	1.119		1.105
	$(C_6\text{–H})_{av}$			1.100
	$C_1C_6C_5$	108.4		107.9
	$C_1N_2N_3$	115.1		114.0
	α	122.5		119.9
	HC_1C_6	121.8		110.7
	HC_1N_2	108.5		108.2
	HC_6H	114.2		106.8

[a] From ref 59. [b] From ref 60.

mation for azo compounds as well as experimental data[55] for the reference molecules to evaluate strain energies for all azo compounds in this study as the negative of the enthalpy changes in homodesmotic reactions.[56-58] Some typical reactions for the evaluation of strain energies are described in eq 4-8.

open-chain series

$$\begin{aligned} &CH_3(CH_2)_nN{=}N(CH_2)_mCH_3 + HN{=}NH\ (\textit{trans}\text{-diimine}) + (n+m)C_2H_6\ (\text{ethane}) \\ &\rightarrow 2CH_3N{=}NH\ (\textit{trans}\text{-methyldiazene}) + (n+m)C_3H_8\ (\text{propane}) \end{aligned} \tag{4}$$

$$\begin{aligned} &(HN{=}N)_2CH_2 + 2C_2H_6\ (\text{ethane}) \\ &\rightarrow 2CH_3N{=}NH\ (\textit{trans}\text{-methyldiazene}) + C_3H_8\ (\text{propane}) \end{aligned} \tag{5}$$

cyclo compounds

$$\begin{aligned} &\overline{(CH_2)_nN{=}N} + HN{=}NH\ (\textit{trans}\text{-diimine}) + (n+1)C_2H_6 \\ &(\text{ethane}) \rightarrow 2CH_3N{=}NH\ (\textit{trans}\text{-methyldiazene}) + nC_3H_8\ (\text{propane}) \end{aligned} \tag{6}$$

$$\begin{aligned} &\overline{CH_2(N{=}N)CH_2(N{=}N)} + 2HN{=}NH\ (\textit{trans}\text{-diimine}) \\ &+ 4C_2H_6\ (\text{ethane}) \rightarrow 4CH_3N{=}NH\ (\textit{trans}\text{-methyldiazene}) + 2C_3H_8\ (\text{propane}) \end{aligned} \tag{7}$$

bicyclo[*l.m.n*] compounds

$$\begin{aligned} &C_{l+m+n+2}H_{2(l+m+n+1)}N_2 + HN{=}NH\ (\textit{trans}\text{-diimine}) \\ &+ (l+m+n+4)C_2H_6\ (\text{ethane}) \rightarrow 2C_4H_{10}\ (\text{isobutane}) \\ &+ 2CH_3N{=}NH\ (\textit{trans}\text{-methyldiazene}) + (l+m+n)C_3H_8\ (\text{propane}) \end{aligned} \tag{8}$$

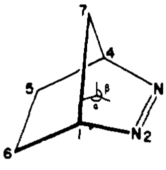
Strain energies obtained in this manner are all presented in Table X. Strain energies will be further discussed later in this paper.

Discussion

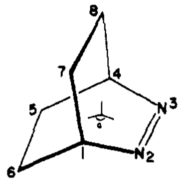
Structures. Comparison between Experimental and Molecular Mechanics Structures. There is a very limited amount of experimental structural data available for azoalkanes. In addition, one might note that, while reported standard errors in experimental structures are usually small, results on the same compounds from different laboratories often differ greatly. Thus the accuracy of the current experimental data is probably no better than 0.02 Å for bond lengths and 2° for bond angles.

As can be seen from Tables V and VI,[105] experimental structures for *trans*-diimine and *trans*-azomethane are reasonably reproduced by the force-field method. Recently, the molecular structure of 2,3-diazabicyclo[2.2.1]hept-2-ene (**13a**) has been studied by the electron-diffraction[60] technique as well as the microwave method.[59] Both results differ significantly except for certain bond lengths (Table VII). The structural parameters obtained from the molecular mechanics calculations are generally in good agreement with the microwave values (Table VII). The major discrepancies, for which no immediate answers can be afforded, between the microwave and the force-field structures are the angle (β) between $C_1N_2N_3$ and $C_1C_7C_4$ planes, the angle (α) between $C_1N_2N_3$ and $C_1C_6C_5$ planes, and the HC_1C_7 bond angle. The corresponding experimental α angle reported by different research groups spans quite a range for norbornane (111–116°) as well as norbornadiene (108–113°).[61] The experimental HC_1C_7 bond angle (119.7°) seems rather large compared with the observed value in norbornane (109.5°).[62] On the other hand, the theoretical HC_1C_7 angle (112.9°) appears to be more in line with that expected on the basis of the experimental data for norbornane.

The gas-phase molecular structure of 2,3-diazabicyclo[2.2.2]oct-2-ene (**13b**) has also recently been reported.[60] One might have expected that the reported structure would probably be very poor in light of the determined structure of 2,3-diazabicyclo[2.2.1]hept-2-ene which was reported in the same paper. Interestingly, agreement between experimental and theoretical parameters is good except for the HC_1C_6 and HC_6H bond angles and the angle (α) between $C_1N_2N_3$ and $C_1C_6C_5$ planes. The experimental HC_6H bond angle (114.2°) is significantly larger than the observed values[63] in bicyclo[2.2.2]octane (110.1°), bicyclo[2.2.2]octene (109.2°), and bicyclo[2.2.2]octadiene (111.3°). Again the experimental HC_1C_7 bond angle (121.8°) is surprisingly large compared with its counterpart in norbornane. The theoretical values, on the other hand, are more in line with those found in related molecules.



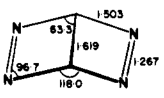
(13a)



(13b)

Comparison between ab Initio and Molecular Mechanics Structures. Agreement between STO-3G and MM structures is generally good (see Table VI). Most importantly, probable systematic errors in the STO-3G results have been corrected in the molecular mechanics calculations. For bond angles, the largest difference (5.4°) occurs for the $H_1C_1H_2$ angle of diazetine, which is probably overestimated by the molecular mechanics method.[64] Agreement in torsional angles and certain bond angles of *trans,trans*-1,2,4,5-tetraaza-1,4-pentadiene is less satisfactory. However, the situation here is more complex indeed since firstly only partial optimization and a minimal basis set have been used in the ab initio calculations and sec-

Chart II. Equilibrium Geometries Predicted by the Molecular Mechanics Method



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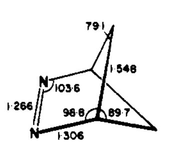

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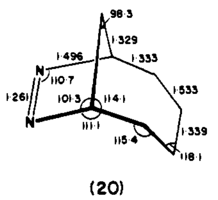

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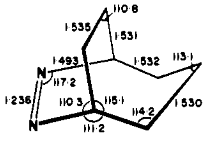

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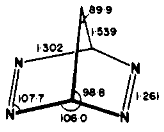

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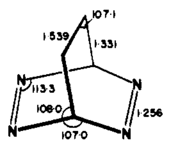

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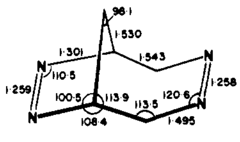

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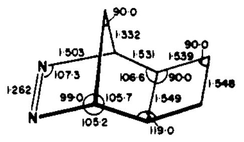

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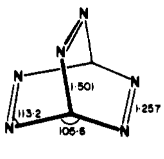

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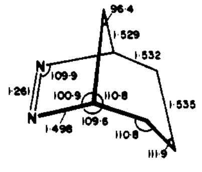

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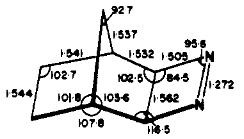

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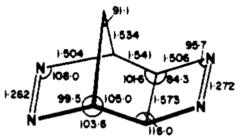

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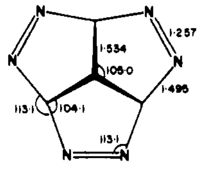

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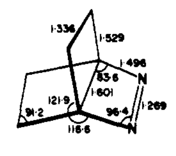


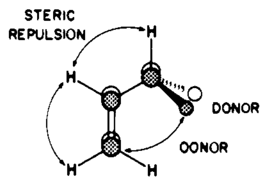
(27)

ondly the strained rotational transition states ($\phi_1 = 0°$, $\phi_2 = 0°$ and $\phi_1 = 0°$, $\phi_2 = 180°$) are certainly less well described by the theoretical calculations.

Finally, Chart II depicts the additional structures for which no experimental data are currently available. These structures are of chemical interest as for their hydrocarbon counterparts and they are presented here for later comparison (not only to show the extensive calculations which have been carried out). There is no doubt that some molecules presented here may lose nitrogen with great celerity. However, we present our calculations in hope that their derivatives may be stabilized to a great extent by substitution.

Conformational Analysis. A. Alkyldiazenes. Alkyldiazenes are of great chemical interest.[67] Several trans isomers of alkyldiazenes have been synthesized and their properties have been studied.[67-69]

According to ab initio STO-3G results, *trans*-methyldiazene exists in an eclipsed conformation and has a barrier of 1.3 kcal mol^{-1}, which is smaller than that for propene (1.6 kcal mol^{-1} theoretically[70] and 2.0 kcal mol^{-1} experimentally[71]). A barrier of 1.7 kcal mol^{-1} was obtained from the microwave spectrum measured by Steinmetz.[69] The conformational preference in *trans*-methyldiazene may be rationalized, as analogous to propene,[70,72] in terms of orbital interactions between π_{CH_3} and $\pi_{N=N}$ as well as $\pi^*_{CH_3}$ and $\pi_{N=N}$ (or π_{CH_3} and $\pi^*_{N=N}$). The higher barrier to internal rotation in propene than in *trans*-methyldiazene is possibly related to the 1,4 H···H steric repulsions (**28**) which exist in the former molecule but are absent in the latter. These steric repulsions would prohibit the angle widening of $C_1C_2C_3$ and $C_2C_1H_{1,2,3}$ in propene, which is required to release the unfavorable secondary interaction[73] between the filled $\pi_{C=C}$ and π_{CH_3} orbitals, and thus destabilize the staggered relative to the eclipsed form. A similar rationale has been proposed for vinyl alcohol and vinyl mercaptan.[74]



(28)

cis-Methyldiazene is also predicted to assume an eclipsed conformation. However, the methyl rotational barrier here is slightly smaller than that for *trans*-methyldiazene, presumably owing to the increased steric crowding in the eclipsed form of the former.

The gauche conformer of *trans*-ethyldiazene was calculated to be more stable than the syn by 0.8 kcal mol^{-1}. The calculated rotational barriers (Figure 2) for the gauche → gauche and gauche → syn transformations are respectively 1.5 and 1.3 kcal mol^{-1} for STO-3G and 1.4 and 1.4 kcal mol^{-1} for MM. The conformational characteristics of *trans*-ethyldiazene are hence quite similar to those of 1-butene.[37,70,75]

For *cis*-ethyldiazene, a detailed scan of the rotational potential function along the N-C bond (cf. Figure 2) reveals that there are also two stable conformations, the syn and a gauche (NNCC = 116°). However, the syn-gauche energy difference here is much larger than that in the trans isomer. This may be attributed to the shorter N=N bond and the smaller NNC angle, which increase the van der Waals repulsions in the syn conformation of the cis isomer.

For *n*-propyldiazenes, there are two aspects of the rotational potential surface that are of chemical interest, namely, the rotation about the C-N and C-C bonds. Shown in Figure 3 are the five possible conformations, GA, GG, GG′, SA, and SG, where the first notation refers to a gauche (G) or syn (S) conformation about the C-N bond and the second notation to

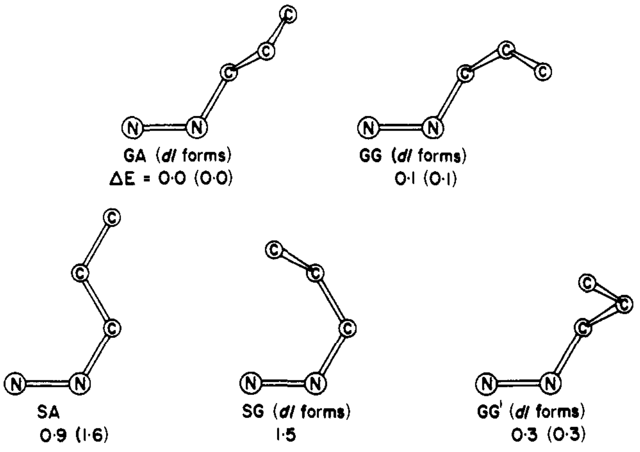


Figure 3. Conformations and relative energies (kcal mol^{-1}) for *trans*- and *cis*-*n*-propyldiazene (in parentheses). For clarity, hydrogens are not shown.

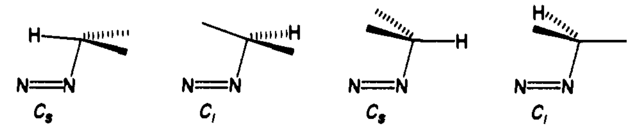


Figure 4. Conformations and relative energies (kcal mol^{-1}) for *trans*- and *cis*-isopropyldiazene (in parentheses). For clarity, hydrogens are usually not shown.

the rotational isomerism about the C–C bond. G and G′ represent two nonequivalent gauche conformations. Also shown in Figure 3 are their relative energies calculated by the force-field method.

For both *trans*- and *cis*-*n*-propyldiazene, GA, GG, and GG′ forms are very close in energy (within 0.3 kcal mol^{-1}) and the GA form is the most stable one. Both SA and distorted SG conformations of *trans*-*n*-propyldiazene are local minima in the potential well and they are less stable than the GA form by 0.9 and 1.5 kcal mol^{-1}. Note that distortion from planarity in the SG form is as high as 30°. For *cis*-*n*-propyldiazene, the SA form is also a stable form with an energy of 1.6 kcal mol^{-1} higher than the GA form. However, in contrast to its trans isomer, the SG form of *cis*-*n*-propyldiazene is no longer a minimum but a point on the potential well. (We initially optimized the SG form under appropriate restricted motions. Then, we placed no restrictions on the molecule and we found the SG form minimized to the GG′ conformation.) The energy differences between SA and GA forms for both *trans*- and *cis*-*n*-propyldiazene are similar to those for the corresponding ethyldiazenes and may be attributed to the same reason.

In Figure 4 are shown the four distinct conformations of *trans*- and *cis*-isopropyldiazene, two of which are with C_s symmetry. We calculate the C_s form with the NNCH syn frame to be the most stable for both *trans*- and *cis*-isopropyldiazene. The C_1 form with the NNCC syn frame is higher in energy than the NNCH syn conformation by 0.8 kcal mol^{-1} for the trans isomer and 1.5 kcal mol^{-1} for the cis isomer. The unfavorable N-H···CH$_3$ steric interaction in the NNCC syn conformation of *cis*-isopropyldiazene also manifests itself in a large distortion from planarity (about 19° as measured by the NNCC dihedral angle). Staggered conformations are rotational transition states and they have much higher energies than the stable C_s forms.

The eclipsed conformation ($\phi = 2°$) of *trans*-*tert*-butyldiazene is the most stable form with an energy of 0.4 kcal mol^{-1} lower than the staggered while the planar eclipsed form of *cis*-*tert*-butyldiazene is highly unstable, which corresponds to a rotational transition state due to the unfavorable N-H···CH$_3$ steric interaction. The preferred conformation for *cis*-*tert*-butyldiazene is instead a staggered structure with C_s symmetry, which is more stable than the distorted eclipsed form ($\phi = 25°$) by about 0.3 kcal mol^{-1}.

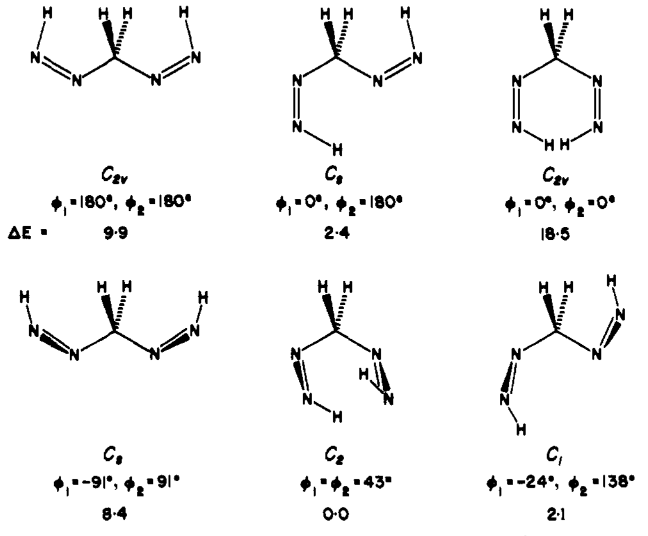


Figure 5. Conformations and relative energies (kcal mol^{-1}) for *cis,cis*-1,2,4,5-tetraaza-1,4-pentadiene.

For higher alkyldiazenes, the conformation problem becomes more complex. However, one should be able to make reasonable predictions on the basis of results presented above. We now look at 1,2,4,5-tetraaza-1,4-pentadienes as representatives of open-chain series with two azo groups. Conformational analysis of the 1,2,4,5-tetraaza-1,4-pentadiene system is of chemical interest owing to the existence of two independent axes of hindered internal rotation.[76]

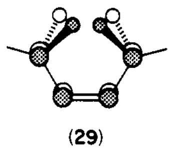
Ab initio STO-3G calculations indicate that *trans,trans*-1,2,4,5-tetraaza-1,4-pentadiene has three stable conformations (belonging to point groups C_2, C_s, and C_1) for which the C_2 form has the lowest energy. The detailed calculated results are dipicted in Table II and Figure 2. Similar results are also obtained from the molecular mechanics calculations. Conformational energies calculated from the ab initio and molecular mechanics methods are compared in Table V. The agreement is acceptable in view of the partial optimization and the limited basis set employed for ab initio calculations as well as the known limitations of the current force-field method.

The results for *cis,cis*-1,2,4,5-tetraaza-1,4-pentadiene obtained from the molecular mechanics calculations are displayed in Figure 5. Since the C_2 form is much lower in energy than any other conformations (at least by 2.1 kcal mol^{-1}), one may conclude that *cis,cis*-1,2,4,5-tetraaza-1,4-pentadiene exists exclusively in the C_2 structure in the gas phase. The dipolar interactions are mainly responsible for the distinct conformational difference between *cis,cis*- and *trans,trans*-1,2,4,5-tetraaza-1,4-pentadiene.

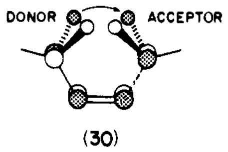
B. Dialkyldiazenes. The distance between the two methyls in *trans*-azomethane is large and no appreciable interaction between them would be expected. Indeed theoretical values for both (ecl,ecl) → (ecl,stag) and (ecl,stag) → (stag,stag) transformations are very close to each other and similar to that found in *trans*-methyldiazene (Table IV). One also notes that methyl rotational barriers in propene and in *trans*-2-butene are experimentally and theoretically indistinguishable.[70,71]

For *cis*-azomethane, STO-3G results[18] show several conformational aspects which are different to those which might have been expected on the basis of *cis*-2-butene results.[70,77] The most stable conformation is calculated to be the doubly staggered instead of the doubly eclipsed. The doubly eclipsed form is in fact a rotational transition state. The recent spectroscopic study[78] has suggested that *cis*-azomethane probably has C_{2v} symmetry, which seems to indicate that the most stable conformation is the doubly staggered since the C_{2v} doubly eclipsed structure is highly strained and should be rotated from planarity and tilted as in *cis*-2-butene.[37,73] The (ecl,ecl) → (ecl,stag) and (ecl,stag) → (stag,stag) transformations of *cis*-azomethane all have negative values (−2.23 and −1.53 kcal mol^{-1}, respectively) as opposed to positive values in *cis*-2-butene (0.42 and 0.47 kcal mol^{-1}, respectively). Again, these differences appear to arise from the fact that the N=N bond is shorter than the C=C bond and the N=N—C angle is smaller than the C=C—C angle. Of course, contributions from the lower methyl rotational barrier around the N_{sp^2}-C_{sp^3} bond compared to the C_{sp^2}-C_{sp^3} bond cannot be neglected.

The preference of (ecl,stag) over (ecl,ecl) may be ascribed to the unfavorable steric crowding in the latter. Nevertheless, the negative value for (ecl,stag) → (stag,stag) may be visualized as due to the presence of a 6π-electron stabilizing effect (**29**), or a stabilizing two-electron interaction between propene and methyl fragments (**30**).[70,78]



(**29**)



(**30**)

It is not surprising that our force-field calculations do not predict the doubly staggered conformation as the most stable structure for *cis*-azomethane since interactions of the type as shown in **29** and **30** are not included in the current force-field model. However, we regard the situation here as providing us with an excellent opportunity to estimate the magnitude of interaction **29** or **30**. The energy changes for (ecl,stag) → (stag,stag) are −1.5 kcal mol^{-1} for STO-3G and +0.2 for MM, which does not account for the stabilizing effect (**29** or **30**). Therefore, the energy contribution from interaction **29** or **30** is probably in the range of 1.5–2.0 kcal mol^{-1}.

As for *cis*-di-*tert*-butylethylene, *cis*-di-*tert*-butyldiazene exists preferentially in a C_2 symmetric conformation rather than a C_{2v} or a C_s form (Figure 6) owing to steric crowding. The calculated torsional angles for the lowest energy (C_2) conformation are 1 and 50°, respectively, for CNNC and CCNN.

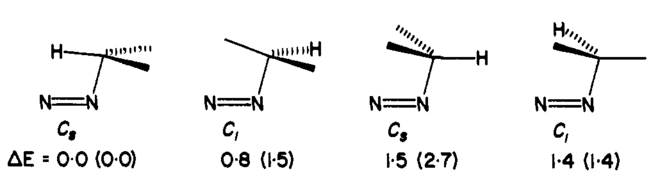
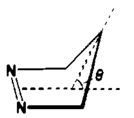


Figure 6. Conformations and relative energies for *cis*-di-*tert*-butyldiazene. Hydrogens are not shown and all methyl groups are approximately staggered.

As in *trans*-azomethane, the two *tert*-butyl groups of di-*tert*-butyldiazene are removed from each other and no appreciable interaction between them would be expected. The C_{2h} conformation with terminal methyls eclipsing to the NN double bond is found favored over the NNCC doubly eclipsed form (C_{2h}) by 0.6 kcal mol^{-1}, which is about two times the energy difference between the staggered and eclipsed conformations of *trans*-*tert*-butyldiazene.

C. Cycloazo Compounds. Pyrazoline itself and a wide range of its derivatives have been known for a long time.[4a,79] We predicted that pyrazoline would exist preferentially in the envelope conformation (**31**) with the planar form being 1.1 kcal mol^{-1} higher in energy mainly owing to torsion. The calculated puckering angle (θ) is 31°. For cyclopentene, a puckering angle of 23° and a barrier of 0.7 kcal mol^{-1} were obtained from the infrared spectrum.[80] The planar-envelope energy difference is much smaller in 3,3,5,5-tetramethylpyrazoline than in pyrazoline itself (0.1 vs. 1.1 kcal mol^{-1}), as can be expected from steric effects. The calculated puckering angle for 3,3,5,5-tetramethylpyrazoline is only 11°, a value much smaller than that for pyrazoline.



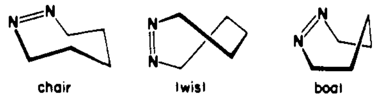
(**31**)

As for cyclohexene, tetramethylenediazene favors a chair conformation (C_2) over the boat (C_s), the boat form being the saddle point in the pseudorotation from one chair form to another. However, the energy difference between the chair and boat conformations is about half of that for cyclohexene (5.3–7.0 kcal mol^{-1}).[36,81] As expected, the introduction of four methyls to tetramethylenediazene leads to a highly unfavorable 1,4-diaxial interaction in the boat form and the boat–chair energy difference increases from 3.2 to 8.2 kcal mol^{-1}.

The boat form (**4**) of 1,2,4,5-tetraaza-1,4-cyclohexadiene is calculated to be more stable than the planar structure by both ab initio and molecular mechanics calculations. However, both the puckering angle (33°) and the planar-boat energy difference (2.4 kcal mol^{-1}) obtained from molecular mechanics calculations are smaller than those (41° and 6.5 kcal mol^{-1}) predicted by the STO-3G method. The STO-3G values are certainly too large since the planar form is highly bent and it is commonly known that the STO-3G basis overestimates the angle strain.[82,83]

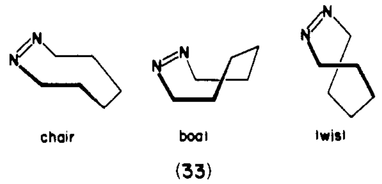
The conformational preference of 1,4-cyclohexadiene has been the subject of much controversy.[37,84,85] It seems clear now that the planar form (D_{2h}) is the ground state. Therefore, the favored conformation of 1,4-cyclohexadiene is in striking contrast to that of 1,2,4,5-tetraaza-1,4-cyclohexadiene. Again, this may be attributed to the smaller NNC angle and the shorter N=N double bond, which greatly increases the angle strain in the planar form.

Three possible conformations of *cis*-pentamethylenediazene (**32**) have been examined. The chair form is found favored over the twist and the boat, respectively, by 3.3 and 3.0 kcal mol^{-1}. The chair form has the lowest bending and van der Waals energies among these three conformations. The twist–chair and boat–chair energy differences in cycloheptene were calculated to be 0.6 and 3.4 kcal mol^{-1}, respectively.[37]

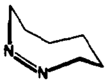


(**32**)

The cis and trans isomers of hexamethylenediazene and its 3,8-dimethyl and 3,8-diphenyl derivatives are experimentally known.[86,87] For *cis*-hexamethylenediazene, an examination of models shows that there are three possible symmetric forms (**33**, C_s chair, C_s boat, and C_2 twist) but they all suffer from ethane-type H/H eclipsing interactions and other nonbonded H···H repulsions. Our lowest energy conformation (**34**) is favored over the chair, boat, and twist forms, respectively, by 6.1, 7.1, and 11.1 kcal mol^{-1}. The results described here are very similar to those for *cis*-cyclooctene.[37]

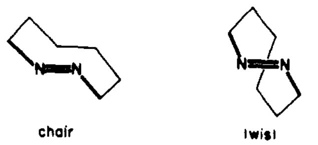


(**33**)

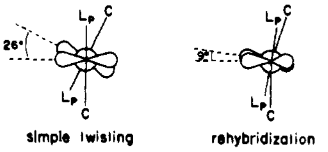


(34)

We have also investigated the conformations of *trans*-hexamethylenediazene. By analogy with *trans*-cyclooctene, two distinct conformations (**35**, C_{2v} chair and C_2 twist) were studied. Our calculations indicate that the twist is lower in energy than the chair by 5.8 kcal mol^{-1}, a value much larger than that found in *trans*-cyclooctene (2.4 kcal mol^{-1}).[36] A recent X-ray diffraction study[76] of 3,8-diphenyl-1,2-diaza-1-cyclooctene has revealed that the ring exists in the twist form with a dihedral angle across the NN double bond of 156°. Our calculated CNNC dihedral angle is 154°, which is in good agreement with the experimental value. Other calculated torsional angles are also in good agreement with the experimental results. As for previous work on cycloalkenes,[37] our model simulates a rehybridization rather than simple twisting of the double bond (cf. **36**); a simple twisting of the NN double bond to yield a 154° torsional angle would give a 26° dihedral angle between the two pπ atomic orbitals while the calculated angle is approximately 9°.

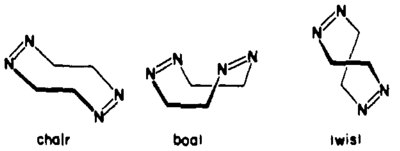


(35)



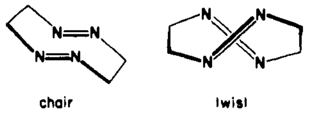
(36)

The chair conformation (C_{2h}) of *cis,cis*-1,2,5,6-tetraaza-1,5-cyclooctadiene was calculated to be the most stable of several possible conformations (**37**), boat (C_{2v}) and twist (D_2) forms being respectively 8.7 and 6.9 kcal mol^{-1} less stable. The energy difference between boat and chair is mainly due to the dipolar interactions. It is interesting to note that the twist-boat form of 1,5-cyclooctene, for which the dipolar interactions are less important, is preferred over the chair by 1.5 kcal mol^{-1}.[34b]



(37)

For *trans,trans*-1,2,5,6-tetraaza-1,5-cyclooctadiene (**38**) the twist form (D_2) is found favored over the chair (C_{2h}) by 4.8 kcal mol^{-1}. The calculated CNNC dihedral angle is close to 144° for both the twist and the chair. The major contribution to the chair–twist energy difference arises from the torsional interactions, about 81% of which comes from the ethane-type H/H eclipsing and the butane-type N/N eclipsing. For *trans,trans*-1,5-cyclooctadiene, the chair was calculated to be more stable than the twist by 5.4 kcal mol^{-1} and the calculated C—C=C—C dihedral angles were close to those found here.



(38)

D. Polycyclic Series. We have extended our studies to a number of polycyclic compounds..These compounds are of current interest.[88-93] A knowledge of their structures and conformations would be beneficial to the understanding of correlations between the CNN bond angle and other molecular properties such as ionization potentials, the σ_I of the alkyl substituents, and $n_+ \rightarrow \pi^*$ transition energies. We first considered 2,3,5,6-tetraazabicyclo[2.2.0]hexa-2,5-diene (**14**), which is an analogue of bicyclo[2.2.0]hexa-2,5-diene[94] (commonly referred to as Dewar benzene). According to our calculations, the nitrogen atoms lie in two planes and the angle between the planes is 119°, which is compared with a theoretical value[95] of 118° for Dewar benzene and experimental values[96] of 115–124° for Dewar benzene derivatives.

For 6,7-diazabicyclo[3.2.1]oct-6-ene, we calculate the structure (**19**) containing a chair conformation of the cyclohexane ring to be more stable than the one involving the boat form by 3.9 kcal mol^{-1}. The conformational preference here is mainly determined by van der Waals repulsions and torsional energies as in cyclohexane.

For 7,8-diazabicyclo[4.2.1]non-7-ene, we find that the endo form (**20**, the conformation having a chair form of the cycloheptane ring) is more stable than the exo form by 2.4 kcal mol^{-1}. The exo–endo energy difference is mainly due to the higher bending and torsional energies in the exo form.

We calculate the exo conformation of 6,7-diazabicyclo[3.2.2]non-6-ene (**21**) to be 1.8 kcal mol^{-1} lower in energy than the endo form. The main difference in steric energy between the two forms occurs in van der Waals and torsional energies.

In 3,4,7,8-tetraazabicyclo[4.2.1]nona-3,7-diene, the exo (**22**) is calculated to be of lower energy than the endo by 2.7 kcal mol^{-1}. The favoring of the exo form is as expected from considerations of conformational preferences of component rings. The exo conformation (**25**) of 3,4,7,8-tetraazatricyclo[4.2.1.0^{2,5}]nona-3,7-diene is also predicted to be more stable than the endo form (by 8.4 kcal mol^{-1}) owing largely to the increased unfavorable dipolar interactions in the endo.

The exo conformation (**23**) of 7,8-diazatricyclo[4.2.1.0^{2,5}]non-7-ene is calculated to be more stable than the endo conformer by 0.6 kcal mol^{-1}. Similarly, 3,4-diazatricyclo[4.2.1.0^{2,5}]non-3-ene is predicted to assume the exo structure (**24**), the endo form being 1.8 kcal mol^{-1} higher in energy.

Finally, we looked at 2,3,5,6,8,9-hexaazatricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (**26**), which is of interest due to its structural resemblance to triquinacene.[97] The molecule is calculated to have C_{3v} symmetry. The obtained $C_1C_{10}C_4$ bond angle is 105° compared with a value of 107° in triquinacene.[98]

Heats of Formation. Despite the importance in understanding the reactivity of azoalkanes,[99] very little experimental thermochemical data was known until Rossini and Engel et al.[53] reported their excellent work. Comparison between the available experimental and our calculated values is made in Table VIII. The average difference between experimental and calculated results for ten compounds is 0.9 kcal mol^{-1}, compared with the average experimental standard error of 1.2 kcal mol^{-1}. For five compounds with reported possible errors of less than 1.0 kcal mol^{-1}, the mean deviation is reduced to 0.6 kcal mol^{-1} while the mean of the reported probable errors is decreased to 0.8 kcal mol^{-1}. We may conclude that our theoretical model is reasonably good for heats of formation.

The predicted heats of formation are shown in Table X.[105] Several previous predictions[99,100] have been reported, but they are based on less accurate information available at that time and/or on limited correlation schemes. On the other hand, the

Table VIII. Comparison between the Calculated and Observed Heats of Formation (kcal mol^{-1})

molecule	steric energy	torsion energy	conf energy	$\Delta H_f°$(g) calcd	$\Delta H_f°$(g) exptl[a,b]	calcd − exptl
trans-diimine	−2.65	0.0	0.0	36.40	36 (2.0)	0.40
trans-di-*n*-propyldiazene	8.72	0.6	0.4	11.74	12.27 (0.84)	−0.53
trans-diisopropyldiazene	7.14	0.0	0.2	8.56	8.51 (0.85)	0.05
trans-di-*tert*-butyldiazene	8.50	0.0	0.0	−7.71	−8.70 (0.66)	0.99
trans-*tert*-butyl(1,1,3,3-tetramethylbutyl)diazene	16.53	0.0	0.0	−29.66	−28.5 (1.3)	−1.16
trans-di(1,1,3,3-tetramethylbutyl)diazene	25.75	0.0	0.0	−50.02	−47.0 (2.2)	−3.02
3,3,5,5-tetramethylpyrazoline	9.48	0.0	0.0	10.89	9.39 (0.85)	1.50
3,3,6,6-tetramethyl-1,2-diazacyclohexene	14.08	0.0	0.0	8.60	10.0 (1.1)	−1.40
2,3-diazabicyclo[2.2.1]hept-2-ene	20.08	0.0	0.0	49.65	49.56 (0.64)	0.09
1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene	16.64	0.0	0.0	21.89	22.1 (1.1)	−0.21

[a] Experimental $\Delta H_f°$(g) are taken from ref 50 or 53. [b] The figures given in parentheses are reported standard deviations.

present enthalpy parameters are derived from the new data and steric energies are systematically accounted for in the force-field approach. Thus, we feel that heats of formation presented here are probably more reliable than any previous calculations.

Several numbers are worthy of comment. The measurement of $\Delta H_f°$ for azomethane is of interest[99,101] since it would provide important information for energy correlation schemes for azoalkanes. However, no results have been reported yet apparently owing to its explosive nature. Our predicted $\Delta H_f°$ for *trans*-azomethane is 32.2 kcal mol^{-1}, which can be compared with other theoretical estimates, 32.1,[99] 35.6,[99] 43.8,[100] and 34.0[101] kcal mol^{-1}.

cis-Diisopropyldiazene is also experimentally known,[102] and its heat of formation was estimated to be at least 1.9 kcal mol^{-1} higher than that of the trans isomer.[99] We calculate the cis-trans energy difference to be as high as 8.0 kcal mol^{-1}. The discrepancy may be attributed to the fact that *cis*-diisopropyldiazene is easy to tautomerize and hard to purify.[99] Note that Engel et al.[103] have concluded, from studies of thermolysis of cis and trans azoalkanes, that the ground-state energy difference between cis and trans azoalkanes is about 7–8 kcal mol^{-1}.

We calculate the energy difference between *cis*- and *trans*-di-*tert*-butyldiazene to be 20.9 kcal mol^{-1}, a value much larger than that in the corresponding alkenes (10.3 kcal mol^{-1}). However, our value is consistent with the observation[104] that the activation energy for thermolysis of *cis*-di-*tert*-butyldiazene is about 20 kcal mol^{-1} less than that of the trans isomer.

Strain Energies. Throughout this work, strain energies of azoalkanes are defined in terms of homodesmotic reactions,[56-58] and they are obtained from theoretical heats of formation. Strain energy numbers obtained in this manner are listed in Table X.[105] As one would expect, trans noncyclic compounds usually have low strain energies while the corresponding cis isomers have strain energies consistently higher (by about 3.0 kcal mol^{-1} for alkyldiazene and about 6.0 kcal mol^{-1} for dialkyldiazenes). The strain energy increases for congested molecules and becomes very large for strained cyclic or polycyclic compounds.

Table X also includes the strain energies for the analogous alkenes, which are again defined in terms of homodesmotic reactions, and the strain energy differences between azoalkanes and the appropriate alkenes. These strain-energy differences are of particular interest since they indicate the strain-energy changes as the C=C double bonds are replaced by the corresponding N=N linkages. Several points of interest are described below.

cis-Azomethane is more strained than *cis*-2-butene by 4.9 kcal mol^{-1} while *trans*-azomethane has almost the same strain energy as *trans*-2-butene. The strain in *trans*-di-*tert*-butyldiazene is quite similar to that of *trans*-di-*tert*-butylethylene. However, the strain-energy difference between *cis*-di-*tert*-butyldiazene and *cis*-di-*tert*-butylethylene becomes very large, an effect which may be ascribed to the increased steric crowding in the former due to the shorter N=N bond and smaller NNC bond angles.

It is perhaps worth pointing out here that for monocyclic alkenes the strain minimum occurs at the six-membered ring. A similar situation is also found in monocyclic alkanes. However, pyrazoline has the smallest strain in the monocyclodiazene series. The difference in behavior is apparently caused by the inherent structural differences between azo compounds and alkenes.

One expects that the structural differences between azo compounds and alkenes would also result in, for small ring systems, the azoalkane being less strained, while for moderate rings the reverse situation is true. In fact, diazetine, pyrazoline, 2,3-diazabicyclo[2.2.1]hept-2-ene, and 2,3,5,6-tetraazabicyclo[2.2.1]hepta-2,5-diene all have smaller strain energies than their alkene counterparts. Similarly, it may be anticipated that 2,3,5,6-tetraazabicyclo[2.2.0]hexa-2,5-diene, 2,3-diazabicyclo[2.1.1]hex-2-ene, 7,8-diazatricyclo[4.2.1.$0^{2,5}$]non-7-ene, 3,4-diazatricyclo[4.2.1.$0^{2,5}$]non-3-ene, 2,3,5,6,8,9-hexaazatricyclo[5.2.1.$0^{4,10}$]deca-2,5,8-triene, and 2,3-diazatricyclo[2.2.2.$0^{1,4}$]oct-2-ene would contain less strain energies than their alkene analogues. Note that 2,3,5,6-tetraazabicyclo[2.2.0]hexa-2,5-diene and 2,3-diazatricyclo[2.2.2.$0^{1,4}$]oct-2-ene are highly strained and they present a challenge to synthetic chemists.

According to our calculations, *trans*-hexamethylenediazene is nearly as stable as the cis isomer and has a moderate amount of strain (11.3 kcal mol^{-1}). This is in striking contrast to the case in cyclooctene, for which the strain in the trans isomer is 16.6 kcal mol^{-1} while that in the cis isomer is only 6.1 kcal mol^{-1}. *trans*-Cyclooctene may therefore isomerize to the cis isomer in order to relieve its strain. This explains why *trans*-hexamethylenediazene and several derivatives are isolable and stable while *trans*-cyclooctene is highly reactive.

An examination of calculated steric energies indicates that, although the cis isomer of hexamethylenediazene is greatly favored by torsional interactions, the trans isomer is strongly preferred by bending and dipolar energies. The difference in bending and dipolar energy contributions between cyclooctene and hexamethylenediazene may be ascribed to their inherent structural and bond-moment differences. Nonetheless, it cannot be neglected that there is a greater preference for the trans isomer in azenes than in alkenes (for example, the energy difference between *trans*- and *cis*-2-butene is only 1.1 kcal mol^{-1} while that for azomethane is probably as high as 7.4 kcal mol^{-1}).

6,7-Diazabicyclo[3.2.1]oct-6-ene and 2,3-diazabicyclo[2.2.2]oct-2-ene are structural isomers. 6,7-Diazabicyclo[3.2.1]oct-6-ene is less strained than 2,3-diazabicyclo[2.2.2]oct-2-ene (by 3.4 kcal mol^{-1}), because the former has a chair conformation of the cyclohexane ring while the latter contains the boat form.

7,8-Diazabicyclo[4.2.1]non-7-ene and 6,7-diazabicyclo[3.2.2]non-6-ene are also two isomeric structures. We find that 6,7-diazabicyclo[3.2.2]non-6-ene is less strained than 7,8-diazabicyclo[4.2.1]non-7-ene by 2.3 kcal mol^{-1}. This may be attributed to the fact that the former contains a seven- and a six-membered ring while the latter has an eight- and five-membered ring. Moreover, the strain difference between six- and five-membered rings (0.8 kcal mol^{-1}) is negligible as compared with that between eight- and seven-membered rings (2.9 kcal mol^{-1}), and 6,7-diazabicyclo[3.2.2]non-6-ene is hence favored over 7,8-diazabicyclo[4.2.1]non-7-ene.

Finally, we predict that 7,8-diazatricyclo[$4.2.1.0^{2,5}$]non-7-ene is more stable than its isomer, 3,4-diazatricyclo-[$4.2.1.0^{2,5}$]non-3-ene, by 1.0 kcal mol^{-1}.

Conclusions

We have described the potential of the combined application of ab initio and molecular mechanics methods to study structures, enthalpies of formation, strain energies, and conformations of large molecules, for which such experimental data are lacking. Calculations on 54 molecules are reported in this work. Comparison with experimental data is made in all cases where such data exist, and reasonable agreement is usually found. Extensive comparison is made with analogous alkenes and it is found that both groups differ significantly in some respects. Undoubtedly, the results presented here can be improved to a certain extent when more reliable (theoretical or experimental) data becomes available. Nevertheless, we do expect that results presented are at least qualitatively correct. It is our hope that this work will stimulate further theoretical and experimental research in this area and various predictions made here can be verified in the near future.

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Supplementary Material Available: Calculated structural and energetic data for ethyldiazene (Table I) and 1,2,4,5-tetraaza-1,4-pentadiene (Table II), comparison of theoretical structures (Table VI), predicted heats of formation (Table IX), and strain energies (Table X) (13 pages). Ordering information is given on any current masthead page.

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(28) All bond lengths in this paper are in ångstroms, bond angles in degrees.

(29) The symbol $H_{i,j,k}$ denotes a point on the C_{3v} local axis of C–H_i, C–H_j, and C–H_k bonds.

(30) The obtained total energies are respectively −147.142 21 and −147.133 91 au for the staggered forms of *trans*- and *cis*-methyldiazene. The optimized structural parameters for the N_1–C_1 bond and $N_2N_1C_1$ and $N_1C_1H_{1,2,3}$ angles are respectively 1.515 Å, 110.1°, and 178.6° for *trans*-methyldiazene and 1.516 Å, 115.8°, and 179.1° for *cis*-methyldiazene.

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