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MM2/MOMM Force-Field Parameters for Azoalkanes[†]

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Abstract: An improved force field for calculating structures and energies of azoalkanes is presented. Ab initio calculations have been performed to confirm and guide reparametrization. Both the structural and energetic results are superior to those previously reported. For a list of 13 azoalkanes, the mean deviation between the calculated and experimental heats of formation is 0.46 kcal/mol, compared with an average reported experimental error for the same group of molecules of 1.05 kcal/mol.

Azoalkanes, also known as alkyldiazenes, are characterized by the $-N{=}N-$functional group. Azoalkanes have attracted considerable attention in literature because of their importance in synthetic chemistry and chemical kinetics.[1] Thermochemical and structural data are desirable in order to have a better understanding of azo chemistry.

The molecular mechanics (MM) or force-field method has been shown to be a very reliable, fast, and efficient way of determining molecular properties.[2] There are several force fields for which extensive usages have been reported and they are currently in use worldwide. However, it appears that Allinger's MM2 is most popular for localized systems at this time.[2,3] Previously, force-field studies of azoalkanes have been reported, in some detail, by two independent groups.[4] However, these force-field calculations were based on somewhat less reliable (hydrocarbon) force fields, and many important experimental data were unavailable at that time. Because of interest in aroma compounds, we have recently proposed the molecular-orbital-based molecular mechanics (MOMM) method, which effectively combines molecular orbital (MO) and molecular mechanics (MM) calculations for conjugated hydrocarbons.[5] Extension of the MM2/MOMM algorithm to azoalkanes is a prerequisite to conjugated systems containing $C{=}N$ and $N{=}N$ fragments.[6,7] Reexamination of the azoalkanes using the MM2/MOMM algorithm is thus necessary in order to provide a *universal*, *consistent*, and *unique* force field method for hetero systems.

Theoretical Approaches

Geometries and Energies. The MM2 force-field equations and parameters developed previously for hydrocarbons[8] are carried over here. Only localized systems will be considered in this paper and, thus, no quantum mechanics calculations are necessary.[5] Some additional parameters, which pertain to bond lengths, bond angles, dihedral angles, and dipoles involving the $N{=}N$ functional group, are needed to deal with azoalkanes. These parameters have to be derived from existing experimental and theoretical data. Lack of accurate experimental and theoretical data have prompted us to perform ab initio calculations using the extensive 6-31G and 6-31G* basis sets[9] at the MM2/MOMM optimized geometries, which are designated as 6-31G//MOMM and 6-31G*//MOMM, respectively, to guide and confirm MM2/MOMM calculations.

The van der Waals parameters for the N_{sp2} atom (type 9 in MM2 program), the hydrogen atom attached to the N_{sp2} atom (type 5), and the electron lone pair (type 20) were taken from the appropriate values for amines.[10] The stretching force constants for bonds 9–9, 1–9, and 5–9 were taken from experimental estimates.[11] The natural bond length, the stretching constant, and the bond dipole moment for the 9–20 type were taken directly from the previous work,[4] and these values are very close to those used in amines. The dipole moments obtained from ab initio calculations are known for *cis*-diimine (STO-3G, 2.9 D; 4-31G, 3.8 D) and *cis*-azomethane (STO-3G, 3.1 D).[4] However, it is expected that the STO-3G basis set underestimates dipole moments, while the 4-31G basis set overestimates dipole moments.[4] Indeed, dipole moments obtained from 6-31G*//MOMM are 3.3 and 3.4 D respectively for *cis*-diimine and *cis*-azomethane, which are somewhere between STO-3G and 4-31G values. The dipole moment of *cis*-azomethane has been determined by the microwave technique to be 3.3 ± 0.1 D.[12] Thus, the 5–9 and 1–9 bonds were assigned bond moments of 1.20 and 1.30 D, respectively, with the N_{sp2} atom negative, to give a moment of 3.1 D for diimine and a moment of 3.2 D for *cis*-azomethane. The best theoretical estimates for disruption of the $N{=}N$ bond are in the range of 50–60 kcal/mol.[13] In the force-field 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 to the V_2 term for each of them. A similar value is used in $C{=}C$ bonds.[5]

Although it is difficult to develop a reliable force field solely on the basis of the existing experimental data, we were able to obtain the remaining necessary values by augmenting the available ab initio results. The force-field parameters developed previously for azoalkanes[4] were used as a starting point to extend MM2/MOMM calculations to a study of azoalkanes. These parameters were varied several times, through trial and error, until a reasonable overall agreement was reached. The values settled upon are given in Table I. One notes that the parameter values derived here are also consistent with those for conjugated systems containing $N{=}N$ fragments.[6]

Heats of Formation. According to the previously described model,[4,8] the heat of formation ($\Delta H_f°$) is expressed as

$$\Delta H_f° = \Delta H_{bond} + \Delta H_{struct} + \Delta H_{steric} + \Delta H_{thermo}$$

where ΔH_{bond} is the sum of the bond energy contributions, ΔH_{struct} is the sum of the structural energy contributions, ΔH_{steric} is the steric energy of the molecule calculated by the program, and ΔH_{thermo} is the partition function contribution. As for alkanes,

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Table I. Force-Field Parameters[a]

Natural Bond Lengths and Stretching Force Constants

bond	l_0, Å	k_l, mdyn Å^{-1}	dipole, D
1-9	1.475	4.23	1.30
5-9	1.010	5.24	1.20
9-9	1.242	10.72	0.00
9-20	0.500	4.60	0.60

Natural Bond Angles and Bending Force Constants[b]

angle	θ_0, deg	k_θ, mdyn Å rad^{-2}
1-1-9	109.50	0.45
5-1-9	108.50	0.36
9-1-9	110.00	0.95
1-9-9	108.00	0.60
1-9-20	115.00	0.36
5-9-9	106.00	0.60
5-9-20	115.00	0.36
9-9-20	135.00	0.24

Torsional Parameters (kcal/mol)

dihedral angle	V_1	V_2	V_3
1-1-1-9	0.40	0.20	0.52
5-1-1-9	0.00	0.00	0.52
9-1-1-9	3.50	0.20	0.00
1-1-9-9	-0.10	0.00	0.15
1-1-9-20	0.00	0.00	0.52
5-1-9-9	0.00	0.00	-0.20
5-1-9-20	0.00	0.00	0.52
9-1-9-9	-0.50	0.20	0.00
9-1-9-20	0.00	0.00	-0.40
1-9-9-1	-2.60	14.00	0.00
1-9-9-5	-1.50	14.00	0.00
1-9-9-20	0.00	14.00	0.00
5-9-9-5	-0.40	14.00	0.00
5-9-9-20	0.00	14.00	0.00
20-9-9-20	0.00	14.00	0.00

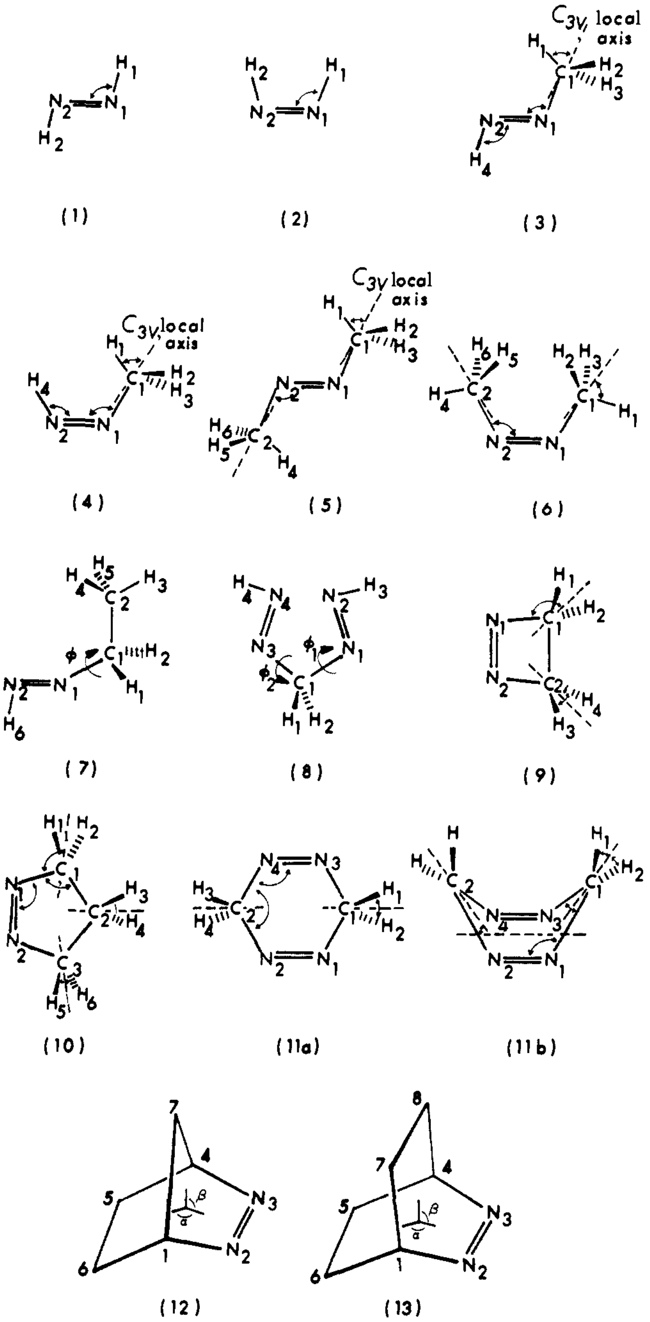
Heat of Formation Parameters (kcal/mol)

9-9	44.540	9 - Me	-0.330
5-9	-5.054	9 -1(1) (5)-1	-0.160
1-9	3.615	9 -1(1) (1)-1	-2.200

[a] MM2 atom types are used, 1 = C_{sp3}; 5 = H; 9 = N_{sp2}; 20 = lone pair. [b] In analogy with hydrocarbons, the bending constants for four-membered rings are reduced by 80%. Out-of-plane bending constant for 9-9-X angles = 0.05.

ΔH_{thermo} is assumed to be 2.4 kcal/mol (to account for translation, rotation, and a correction to constant volume) plus torsional terms, 0.36 kcal/mol for each bond about which there is a rotational barrier of less than 7 kcal/mol.[8] Heat of formation parameters developed for alkanes were carried over here. In this work, the bond energy for type 9-5 was taken directly from the previous work.[4] The additional five parameters (two bond energy terms and three structural energy terms) need to be fitted and their derived values are also shown in Table I.

Chart I



Discussion

Comparison between Experimental and Molecular Mechanics Structures. There is a very limited amount of experimental structural data available for azoalkanes. Of the 13 simple compounds shown in Chart I, there are only 4 molecules for which experimental structural data are available. Experimental data[14] for these four molecules are presented in Table II (supplementary material) along with the theoretical structures. Reported experimental standard errors are usually small, but results on the same compounds from different laboratories often differ greatly (Table I). 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 in Table II, experimental bond lengths are all reasonably reproduced by the force-field method. The mean deviation between the calculated and experimental bond lengths is less than 0.01 Å, if one is free to choose any experimental values for comparison. Experimental bond angles are also reasonably reproduced by the same method; all experimental values are reproduced to be within 4°, with the exception of the HC_1C_7 angle of 2,3-diazabicyclo[2.2.1]hept-2-ene, and the HC_1C_6 and HC_6H angles of 2,3-diazabicyclo[2.2.2]oct-2-ene. However, these discrepancies may come from experimental errors, since the theoretical values are more in line with those found in the related hydrocarbons.[4]

Although the previous force-field method (MM1)[4] gave similar results for these four molecules, there are differences between these two methods which need to be mentioned. Both the C—N and N═N bond lengths obtained from MM2/MOMM are consistently shorter (ca. 0.01 Å) than those obtained from MM1; furthermore, the MM2/MOMM results appear to be in better

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Table IV. Conformational and Isomerization Energies (kcal/mol)

transformations	ab initio reported[a]	ab initio this work	MM1	MOMM	exptl[a]
	Trans–Cis Isomerization				
diimine					
trans → cis	~5.8–7.4	8.8,[b] 7.5[c]	6.00	5.87	
methyldiazene					
trans → cis	5.27	7.2,[b] 6.7[c]	3.08	4.77	
azomethane					
trans → cis	8.88	11.9,[b] 11.7[c]	5.92	7.96	~7–8
di-*tert*-butyldiazene					
trans → cis			20.92	24.22	>22
azo-1-bicyclo[2.1.1]hexane				12.61	12.7
azo-1-bicyclo[2.2.1]heptane				18.22	16.2
azo-1-bicyclo[2.2.2]octane				23.36	25.9
	Conformational Transformation				
trans-methyldiazene					
ecl → stag	1.33		1.37	1.70	1.7
cis-methyldiazene					
ecl → stag	1.27		1.04	0.96	
trans-azomethane					
ecl,ecl → ecl,stag	1.14		1.31	1.68	
ecl,stag → stag,stag	1.29		1.32	1.68	
cis-azomethane					
ecl,ecl → ecl,stag	-2.23		-1.54	-1.66	
ecl,stag → stag,stag	-1.53		0.20	0.22	
trans-ethyldiazene					
gauche → syn	0.78		0.79	0.76	
gauche → anti	1.34		1.38	1.43	
1,2,4,5-tetraazactclohexa-1,4-diene					
boat → planar	6.52	0.3[b]	2.39	2.22	
trans,trans-1,2,4,5-tetraaza-1,4-pentadiene					
C_2(g,g) → C_s (g,g′)	0.46		0.61	0.15	
C_2(g,g) → C_{2v}(syn,syn)	7.40		7.97	7.08	
C_2(g,g) → C_{2v}(anti,anti)	1.86		1.32	1.51	
C_2(g,g) → C_1 (g,syn)	0.23		0.80	0.36	
C_2(g,g) → C_s (anti,syn)	2.33		2.93	1.86	

[a] See text or ref 4 for references. [b] 6-31G//MOMM. [c] 6-31G*//MOMM.

agreement with the experimental data. Slight improvements over MM1 are also noticeable for certain bond angles.

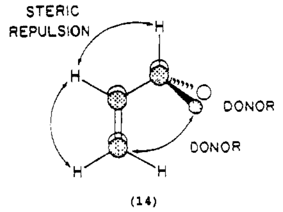
Comparison between ab Initio and MM2/MOMM Structures. MM2/MOMM structural parameters and conformational energies for the 13 model compounds are presented in Tables III (supplementary material) and IV along with respective ab initio STO-3G results. The difference between experimental and ab initio structural data requires comment, before making a comparison between the ab initio and MM2/MOMM results. Any possible systematic errors have to be considered for applying STO-3G structures to derive force-field parameters. Although the STO-3G structures are generally in good agreement with experimental results, there are notable systematic errors: (a) the N=N bond length obtained from the minimal basis set is too long by ca. 0.02 Å; (b) the STO-3G C_{sp3}–N_{sp2} bond length is probably too long by 0.03 Å; (c) the STO-3G N_{sp2}–H bond is too long by ca. 0.04 Å; (d) both the STO-3G N=N—C and N=N—H bond angles are probably too small by ca. 1°.

Agreement between STO-3G and MM2/MOMM structures is very good. This is particularly true if the possible systematic errors in STO-3G calculations are taken into account. The agreement between MM1 and MM2/MOMM structures is also very good. However, probable systematic errors in STO-3G results appear to be better corrected in the latter calculations.

Conformational Analysis. All compounds which were extensively studied in the MM1 work[4] are reexamined in this work, and notations for conformers used previously will be retained in the following discussion. Relevant STO-3G, MM1, and MM2/MOMM conformational energies for molecules depicted in Chart I are shown in Table IV. In general, there is a good agreement between MM1 and MM2/MOMM results. Thus, we shall concentrate on model studies and, in particular, on cases where there are significant differences between MM1 and MM2/MOMM results. Some bridgehead diazenes will also be examined, since their cis–trans isomerization reactions have recently been reported.[15] It will become clear after the following discussion that the MM2/MOMM results appear to be more reliable than MM1 calculations for conformational analysis.

The methyl groups of *trans*-methyldiazene (**3**) and *cis*-methyldiazene (**4**) are all predicted to exist in an eclipsed conformation (NN-CH = 0°) with a staggered form (NN-CH = 180°) being the rotational transition state. The conformational preference of an eclipsed form over a staggered conformation can be qualitatively rationalized in terms of the unfavorable donor–donor orbital interactions between π_{CH_3} and $\pi_{N=N'}$ as well as between the favorable donor–acceptor orbital interactions $\pi^*_{CH_3}$ and $\pi_{N=N}$ (or π_{CH_3} and $\pi^*_{N=N}$).[4,16,17]

The methyl rotational barrier for **3** is predicted to be 1.7 kcal/mol by MM2/MOMM, which can be compared with the experimental value of 1.7 kcal/mol obtained from the microwave spectrum measured by Steinmetz.[18] On the other hand, both MM1 and STO-3G[4] consistently underestimate these barriers by ca. 0.4 kcal/mol. The corresponding values for propene are 1.6 kcal/mol theoretically (by ab initio)[16] and 2.0 kcal/mol experimentally.[19] If orbital interaction **14** is the sole source for the



(14)

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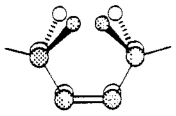
methyl rotation barrier, then the barrier for propene might be smaller than the one for **3**, because the N═N and C—N bonds of **3** are shorter than the C═C and C—C bonds of propene, respectively. However, this is certainly not the case. The higher barrier to internal rotation in propene is possibly related to the 1,4 H···H steric repulsions which exist in propene but are absent in **3**. These steric repulsions would prohibit the angle widening of C-C-C and C-C-H in propene, which is required to release the unfavorable secondary (donor–donor) interaction, and thus destabilize the staggered relative to the eclipsed form. A similar rationale has been proposed previously.[3,4] The methyl rotational barrier in **4** is smaller (ca. 0.7 kcal/mol) than that for **3**, presumably owing to the increased steric crowding in the eclipsed form of the former.

The distance between the two methyls in *trans*-azomethane (**5**) is large and no appreciable interaction between them would be expected. Indeed, all theoretical values for both methyl rotational barriers are very close to each other and similar to those found in **3**. One also notes that the methyl rotational barriers in propene and in *trans*-2-butene are experimentally and theoretically indistinguishable.[16,19] As expected, the MM2/MOMM results are consistently higher than those obtained from both MM1 and STO-3G by 0.4 kcal/mol.

For *cis*-azomethane (**6**), STO-3G results show different conformational aspects from those which might have been expected on the basis of *cis*-2-butene results.[20] The most stable structure is calculated to be the doubly staggered instead of the doubly eclipsed form. Nevertheless, the STO-3G results for **6** are very similar to those found in *cis*-dimethylazomethine.[6] These conformational differences appear to arise from the fact that the C═N and N═N bond lengths are shorter than the C═C bond, and the C—N═N and C—N═C bond angles are smaller than the C—C═C angle. A shorter bond length and a smaller bond angle would bring the methyl groups closer, increase the steric repulsions, and thus destabilize the doubly eclipsed form.

The preference of a singly eclipsed form over a doubly eclipsed form may be attributed to the unfavorable steric crowding in the latter. Nevertheless, the stability of a doubly staggered form over a singly eclipsed one may be ascribed to the presence of a 6π-electron stabilizing effect (**15**) or a stabilizing two-electron interaction (**16**).[16,21]



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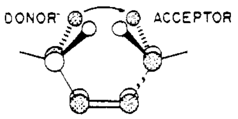


(16)

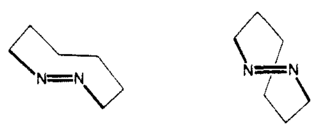
It is not surprising that the force-field calculations do not predict the doubly staggered conformation as the most stable structure for **6**, since interactions of the type shown in **15** and **16** are not explicitly included in calculating the steric energy. However, we regard the situation as providing us with an excellent opportunity to estimate the magnitude of interaction **15** or **16**. The energy changes for a single eclipsed form to a doubly staggered form are ca. −1.5 kcal/mol for STO-3G and ca. 0.5 kcal/mol for MM2/MOMM, which does not account for the stabilizing effect of **15** or **16**. Thus, the energy contribution from interaction **15** or **16** is probably around ~1.5–2.0 kcal/mol. It is interesting to note, that although there are differences in MM1 and MM2/MOMM results, the estimate for this stabilization is about the same.

The conformational characteristics of *trans*-ethyldiazene (**7**) are quite similar to those of 1-butene, where there are two stable conformations, gauche (NN-CC ~ 120°) and syn (NN-CC ~ 0°). The rotational potential functions about the N-C bond are very similar for all theoretical calculations (Table IV) and the gauche form is more stable than the syn by 0.7 kcal/mol.

The conformational problem becomes more complex in *trans,trans*-1,2,4,5-tetraaza-1,4-pentadiene (**8**) because of the two azo groups, and two independent axes of rotation must be considered. MM2/MOMM predicts that this molecule has three stable conformations belonging to point groups C_2, C_s, and C_1, with C_2 having the lowest energy. The results from MM2/MOMM seem to agree well with the results obtained from MM1 and ab initio calculations.

1,2,4,5-Tetraaza-1,4-cyclohexadiene (**11a** and **11b**) favors the boat conformation over the planar according to MM1, MM2/MOMM, and STO-3G calculations. The puckering angle, defined as the angle between NNC and NCN planes, was found to be 35° from MM2/MOMM, compared with the angles 33° and 41° from MM1 and ab initio, respectively. The planar-boat energy difference obtained from MM2/MOMM (2.2 kcal/mol) is slightly smaller than the MM1 value (2.4 kcal/mol). However, a larger difference (6.5 kcal/mol) was predicted by STO-3G calculations. Experimentally and theoretically, 1,4-cyclohexadiene and its hetero analogues such 1,4-dioxin and 1,4-dithiin are shown to have flat butterfly-flapping potential functions.[5] Thus, the STO-3G value is certainly too large mainly due to its overestimation of the angle strain.[4] Indeed, a much smaller value (0.3 kcal/mol) was obtained from 6-31G//MOMM calculations.

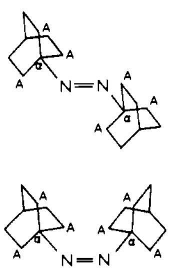
Two conformations were studied for *trans*-hexamethylenediazene (**17**), the C_{2v} chair and C_2 twist, and the calculations from both MM1 and MM2/MOMM predicted the twist to be the most stable form. The chair–twist energy differences are 6.9 and 5.8 kcal/mol according to MM2/MOMM and MM1, respectively. An X-ray diffraction study[22] of 3,8-diphenyl-1,2-diaza-1-cyclooctene revealed that the ring exists in the twist form with a dihedral angle across the NN double bond of 156°; the same angle was calculated to be 150° from MM2/MOMM, compared to 154° from MM1. Phenyl substitutions at positions 3 and 8 of the parent ring are expected to further increase the CN-NC torsional angle, due to steric interactions.



chair twist

(17)

Stereoisomerization and homolytic decomposition of bridgehead diazenes have recently been studied by Shmittel et al.[15] In this work, we report the conformational analysis for three bridgehead diazenes (**18**–**20**). For the trans isomers, the C_α–C bonds are found to prefer eclipsing the N═N bonds. Furthermore, the short chain (path) connecting bridge atoms is energetically more favorable to eclipse the N═N bond than the long chain. This is



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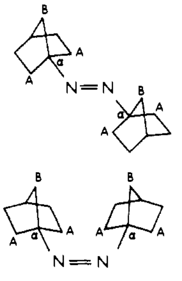
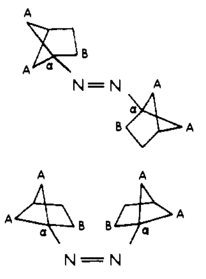


(19)



(20)

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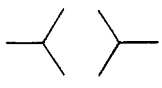
Table V. Comparison between Theoretical and Experimental $\Delta H_f°$ (kcal/mol)

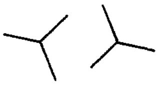
	$\Delta H_f°$(g)			calcd − exptl	
	MM1[a]	MOMM	exptl[b]	MM1	MOMM
trans-diimine	36.40	36.00	36 (2.0)	0.40	0.00
trans-methyl-*n*-butyldiazene		18.86	18.86 (0.53)		0.00
trans-di-*n*-propyldiazene	11.74	12.54	12.27 (0.84)	-0.53	0.27
trans-diisopropyldiazene	8.56	8.56	8.51 (0.85)	0.05	0.05
trans-di-*n*-butyldiazene		1.72	2.19 (0.90)		-0.47
trans-di-*tert*-butyldiazene	-7.71	-8.32	-8.70 (0.66)	0.99	0.38
trans-*tert*-butyl(1,1,3,3-tetramethylbutyl)diazene	-29.66	-28.27	-28.5 (1.3)	-1.16	0.23
trans-di(1,1,3,3-tetramethylbutyl)diazene	-50.02	-49.37	-47.0 (2.2)	-3.02	-2.37
3,3,4,4-tetramethyldiazetine		36.32	35.92 (0.69)		0.40
3,3,5,5-tetramethylpyrazoline	10.89	9.87	9.39 (0.85)	1.50	0.48
3,3,6,6-tetramethyl-1,2-diazacyclohexene	8.60	9.32	10.0 (1.1)	-1.40	-0.68
2,3-diazabicyclo[2.2.1]hept-2-ene	49.65	49.46	49.56 (0.64)	0.09	-0.10
1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene	21.89	21.58	22.1 (1.1)	-0.21	-0.52
mean error			1.05 (1.15)[c]	(0.94)[c]	0.46 (0.51)[c]

[a] Reference 4. [b] Reference 23. [c] The value in parentheses is the mean for 10 compounds (excluding *trans*-methyl-*n*-butyldiazene, *trans*-di-*n*-butyldiazene, and 3,3,4,4-tetramethyldiazetine).

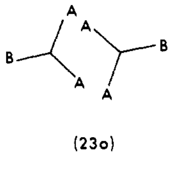
presumably due to the fact that the short chain has a larger CCN bond angle (lying back effect) and, thus, there is less steric congestion in the former conformation. The energy difference between the staggered and eclipsed form is 0.2 kcal/mol for *trans*-azo-1-bicyclo[2.2.2]octane, which is identical with the value found in *trans*-di-*tert*-butyldiazene. However, the energy difference between the staggered and eclipsed forms becomes much larger (>1.0 kcal/mol) for *trans*-azo-1-bicyclo[2.2.1]heptane and *trans*-azo-1-bicyclo[2.1.1]hexane due to the breakdown of symmetry and lying back effect.

It is important to look at simple and similar compounds before we discuss the conformations of the cis isomers of **18**–**20**. For *cis*-azomethane, the most stable conformation (C_{2v}) is schematically depicted in **21**, where the direction of viewing is from the α carbon atoms toward the nitrogen atoms in the plane of the heavy atoms. However, for *cis*-di-*tert*-butyldiazene, the C_{2v} conformation (**21**) must be reduced to the skew C_2 form (**22**) by

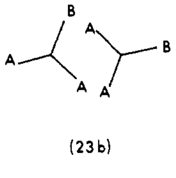

(21)


(22)

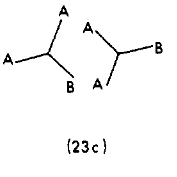
rotating away these four terminal methyls, in order to avoid the close contacts between these terminal groups. As for *cis*-di-*tert*-butyldiazene, *cis*-azo-1-bicyclo[2.2.2]octane (**18**) exists preferentially in the C_2 conformation rather than other forms due to steric crowding. For both *cis*-azo-1-bicyclo[2.1.1]hexane (**20**) and *cis*-azo-1-bicyclo[2.2.1]heptane (**19**), the conformation problem becomes more complex because there are six possible skew conformations (**23**). According to MM2/MOMM calculations,



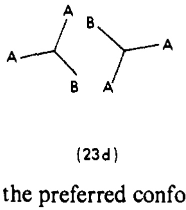
(23a)



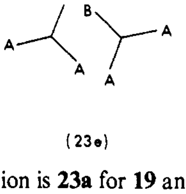
(23b)



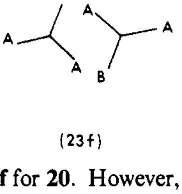
(23c)



(23d)



(23e)



(23f)

the preferred conformation is **23a** for **19** and **23f** for **20**. However, if the lying back effect is the dominant factor in determining the stable conformations for cis isomers, one would instead pick other conformations to be the most stable forms. The rationale for conformational preference can be found by investigating how these systems can effectively reduce steric crowding. According to a detailed analysis, the key parameter in determining how well these systems can reduce steric crowding is the bond angles associated with the α carbons (AαA and AαB angles). The larger the bond angles between terminal methyls facing each other, the less crowded the system is. Indeed, the AαA and AαB angles of the most stable conformations are, respectively, 109 and 102° for **19** and 88 and 102° for **20**.

Heats of Formation. All appropriate systems for which the $\Delta H_f°$ (g) are reported[23] were examined in the present work. Table V lists the experimental and calculated $\Delta H_f°$ (g), differences between experimental and MM2/MOMM values, as well as the quoted probable experimental errors. The previous MM1 results are also included in Table V for comparison. As can be seen in Table V, the calculated MM2/MOMM results are in fair to excellent agreement with the experimental values. In particular, there is no compound for which the calculated value differs from the experimental one by more than twice the reported error. The average difference between the experimental and MM2/MOMM values is 0.46 kcal/mol for 13 compounds and 0.51 kcal/mol for 10 compounds. These values may be compared with the average estimated experimental error of 1.05 kcal/mol for 13 compounds and of 1.15 kcal/mol for 10 compounds. A value of 0.94 kcal/mol for 10 compounds was obtained for the average deviation between the experimental and MM1 results. Thus, a significant improvement of ca. 30% is indeed accomplished for calculating heats of formation by using this new force field.

In addition to the above heats of formation, further calculations were done for MM2/MOMM, just as those done for MM1, for all of the related molecules. These predicted heats of formation are presented in Table VI (supplementary material) along with the previous predicted ones obtained from MM1. There are some notable differences between MM1 and MM2/MOMM results. However, the heats of formation obtained from MM2/MOMM are deemed to be more reliable, since the MM2/MOMM parameters are developed on a broader base of experimental data. Undoubtedly, the MM2/MOMM results can be further improved when more reliable data become available. This is particularly true for polyaza cases.

Many theoretical attempts have been made in trying to derive the heat of formation for azomethane, and the values span the range of ~32–44 kcal/mol.[4] MM2/MOMM predicted a value of 35.96 kcal/mol which is in good agreement with the most recent value, 35.54 ± 1.23, estimated by Rossini et al. using the group increment method.[24] On the other hand, the MM1 value, 32.18

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kcal/mol, is probably too low, because MM1 parametrization did not take into account the experimental value of *trans*-methyl-*n*-butyldiazene, which was unavailable at that time. The heats of formation of *trans*-methylethyldiazene and *trans*-diethyldiazene have also been estimated by Rossini et al.[24] to be 28.71 (0.54) and 21.89 (0.92) kcal/mol, respectively, which agree well with the MM2/MOMM values of 29.67 and 23.33 kcal/mol. However, for highly strained molecules, MM2/MOMM results are expected to be more reliable than the group increment method since strains of these molecules are explicitly calculated by the former method.

Isomerization Energies. Calculated isomerization energies for trans–cis geometrical transformations are presented in Table IV. The previous theoretical estimates for the trans–cis isomerization of diimine are in the range of 5.8–7.4 kcal/mol, for which the lower bound is the CEPA value,[13] while the higher bound refers to the STO-3G value. The CEPA value is deemed to be more reliable owing to its handling of electron correlation. The 6-31G//MOMM and 6-31G*//MOMM values are 8.8 and 7.5 kcal/mol, respectively, which are close to the STO-3G value. Similarly, the trans–cis isomerization energies for methyldiazene and azomethane appear to be consistently overestimated by STO-3G, 6-31G//MOMM, and 6-31G*//MOMM. Indeed, Engel et al. 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.[25]

As can be seen in Table IV, MM2/MOMM estimates for trans–cis isomerizations are consistently lower than the corresponding STO-3G, 6-31G//MOMM, and 6-31G*//MOMM values for methyldiazene and azomethane while its estimate reproduces the CEPA value for diimine. The cis–trans isomerization energies for several bridgehead diazenes have recently become known through the important work of Schmittel et al.,[15] and they provide a crucial test for MM2/MOMM parametrizations. The MM2/MOMM values shown in Table IV appear to agree well with all the experimental estimates.[15,25] We calculate the energy difference between *cis*- and *trans*-di-*tert*-butyldiazene to be 24.2 kcal/mol, a value much larger than that in the corresponding alkenes (10.3 kcal/mol). The MM2/MOMM value is also significantly larger than the MM1 value (20.9 kcal/mol). Although the MM1 value is more consistent with the observation[26] that the activation energy for thermolysis of *cis*-di-*tert*-butyldiazene is about 20 kcal/mol less than that of the trans isomer, the recent work of Schmittel[15] appears to favor a value of ca. 25 kcal/mol. Finally, it should be commented that, as far as cis–trans isomerization energy is concerned, MM2/MOMM is more reliable than MM1, since the latter consistently underestimates the steric energy of the cis form.

Conclusions

We have systematically studied the molecular properties of more than 50 azoalkanes. 6-31G//MOMM and 6-31G*//MOMM calculations have been performed to confirm and guide reparametrization. MM2/MOMM parameters are reported for this class of compounds. MM2/MOMM results are generally superior to the previous theoretical results. This work provides an important step for developing a universal, consistent, and unique force field for nitrogen-containing systems.

Acknowledgment. We thank Mr. A. Lilly, Mr. W. Kuhn, Dr. R. Ferguson, and Dr. J. Seeman for their support and comments.

Supplementary Material Available: Experimental and MOMM equilibrium geometries for **1**, **5**, **12**, and **13** (Table II), comparison of theoretical structures for **1–11** (Table III), and predicted $\Delta H_f°$ (Table VI) (7 pages). Ordering information is given on any current masthead page.

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Empirical Potential Energy Surfaces Relating Structure and Activation Energy. 2. Determination of Transition-State Structure for the Spontaneous Hydrolysis of Axial Tetrahydropyranyl Acetals

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Contribution from the Laboratory for Chemical and Mineralogical Crystallography, University of Berne, CH-3012 Berne, Switzerland. *Received December 31, 1987*

Abstract: Experimental ground-state structural data and valence force constants are combined with activation energy estimates to obtain energy surfaces describing bond-breaking reactions. The model may be used to describe systematic variations in the structural and energetic behavior of families of related molecules undergoing the same type of reaction and provides estimates of transition-state structure. For spontaneous acetal hydrolysis, which is discussed as an example, changes in ground-state structure are related to changes in free energy of activation in a quantitative way, and the calculated transition-state structures are shown to be compatible with available experimental and theoretical evidence on related systems.

Recently, we have developed models relating free energy of activation with ground-state structure for series of related molecules undergoing the same type of reaction.[1,2] The basic idea is to parametrize a simplified potential energy surface with the help of structural, vibrational, and kinetic data pertaining to an arbitrarily chosen reference molecule and its reaction intermediate. Energy surfaces for the remaining molecules in the series are obtained by applying a simple perturbation to the reference surface. As a test of the model, perturbed ground-state structure and free energy of activation are calculated and compared to experimental quantities. This procedure provides insight into a sometimes dramatic dependence of reaction rate on small struc-

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