

cis- and *trans*-Azoalkanes: Force Field Determination of Molecular Structures, Heats of Formation, and Strain Energies

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Received August 21, 1979

cis- und *trans*- Azoalkane:

Kraftfeld-Berechnungen von Molekülstrukturen, Bildungswärmen und Spannungsenergien

Rechnungen mit dem Kraftfeld von Allinger (MMI), das mit geänderten Parametern für *cis*- und *trans*-Azoalkane versehen wurde, liefern Molekülgeometrien und Bildungswärmen in vorzüglicher Übereinstimmung mit experimentellen Werten.

Azoalkanes are a class of compounds which have served extensively as novel synthetic intermediates¹⁾, mechanistic substrates^{1,2)}, and spectroscopically informative entities³⁾. Certain labile *cis*-derivatives decompose thermally as low as -100 to -120°C ⁴⁾. In order to provide a rapid and inexpensive evaluation of structure and energy content for this functionality, we have parameterized Allinger's MMI force field⁵⁾ to give molecular geometries, heats of formation, and strain energies for both *cis*- and *trans*-isomers.

Table 1. Parameters for calculations of azoalkane molecular geometries^{a)}

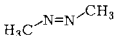
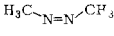

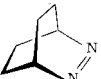



Bond	Bond stretching		angle	Torsional		
	l_0 (Å)	k (mdyn/Å ²)		V_1	V_2	V_3
N=N	1.236	9.20	$\text{C}_{\text{sp}^3}-\text{N}=\text{N}-\text{C}_{\text{sp}^3}$	-0.25	40.0	0.0
$\text{C}_{\text{sp}^3}-\text{N}$	1.467	3.50	$\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^3}-\text{N}=\text{N}$	0.0	0.0	-1.2
			$\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^3}-\text{N}$	0.0	0.0	0.53
			$\text{N}-\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^3}-\text{N}$	0.0	0.0	0.0
			$\text{H}-\text{C}_{\text{sp}^3}-\text{N}=\text{N}$	0.0	0.0	-1.8
			$\text{H}-\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^3}-\text{N}$	0.0	0.0	0.53
	Angle bending					
angle	θ_0	k (mdyn/rad ²)				
$\text{C}_{\text{sp}^3}-\text{N}=\text{N}$	110.3	1.35				
$\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^3}-\text{N}$	110.74	0.38				
$\text{H}-\text{C}_{\text{sp}^3}-\text{N}$	108.5	0.48				
	van der Waals ^{b)}			Bond moment		
atom	r^*	ϵ	bond	μ (Debye)		
N	1.70	0.039	C-N	1.95		

a) The force field equations are those found in MMI, QCPE no. 318, Ref. 5. – b) MMI/QCPE no. 318, Ref. 5).

Structural parameters⁶⁾ are given in table 1, while table 2 compares the experimental and the calculated values for both cyclic and acyclic species. On the average, N=N and C-N bond lengths are reproduced to within 0.002 and 0.006 Å, respectively, and bond angles to within

0.3 °). To assure ourselves that the derived parameters are capable of reliable conformational analysis for acyclic structures, the *trans*-RN=NR (R = CH₃, Et, *i*-Pr and *t*-Bu) potential energy surfaces for rotation about the C–N bond were generated by MMI. The resulting fully-optimized azoalkane rotamers were re-evaluated with the 4-31 G *ab initio* scheme⁸⁾ (R = CH₃) and PRDDO¹⁰⁾ (R = CH₃), Et, *i*-Pr and *t*-Bu). In all cases a qualitative correspondence was obtained. The relative conformational differences between MMI and 4-31 G or PRDDO amount to no more than 0.5 kcal/mol.

Table 2. Comparison of force field calculated and observed or PRDDO-optimized molecular geometries (bond lengths, Å; bond angles, deg)

compound		calcd.	obsd.	
	N=N	1.247	ED ^{a)}	ED ^{b)}
	N–C	1.482	1.247 ± 0.003	1.254 ± 0.003
	∗ N=N–C	112.3	1.482 ± 0.002	1.474 ± 0.003
			112.3 ± 0.3	111.9 ± 0.5
	N=N	1.254	MW ^{c)}	PRDDO-opt ^{d)}
	N–C	1.484	1.254	1.291
	∗ N=N–C	119.5	1.485	1.475
			119.4	119.5
	N=N	1.253	MW ^{e)}	
	N–C	1.492	1.253 ± 0.004	
	∗ N=N–C	108.5	1.512 ± 0.003	
			108.3 ± 0.3	
	N=N	1.252	X-ray ^{f)}	
	N–C	1.486	1.260 ± 0.004	
	∗ N=N–C	114.1	1.487 ± 0.003	
			114.7 ± 0.1	
	N=N	1.254	X-ray ^{f)}	
	N–C	1.492	1.259 ± 0.002	
	∗ N=N–C	114.1	1.497 ± 0.001	
			114.9 ± 0.1	
	N=N	1.251	X-ray ^{f)}	
	N–C	1.472	1.251 ± 0.004	
	∗ N=N–C	116.0	1.466 ± 0.004	
			115.7 ± 0.2	
	N=N	1.262	PRDDO-opt ^{g)}	
	N–C	1.491	1.267	
	∗ N=N–C	96.5	1.495	
			94.5	

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




Energy parameters are given in table 3; heats of formation and strain energies in table 4. The average deviation of the $\Delta H_f^\circ(\text{calc})$'s from experiment is 0.28 kcal/mol⁹⁾, well within experimental error. The heat of formation of the four-membered ring compound, tetramethyldiazetene¹¹⁾, is seriously overestimated by the present parameters. This can be attributed largely to MMI's inability to properly evaluate the energy contribution of interacting dipoles¹²⁾ and to the fact that the

C–C–N angles of the four-ring are deformed by 27–28° from normal tetravalent carbon values. This condition coupled to our choice of CNN bending force constant brings the present force field's angle bending functions to the limit of their applicability¹³).

Table 3. Azoalkane heat of formation parameters; kcal/mol

	$C_{sp^3-N=N-C_{sp^3}}$ <i>trans</i>	$C_{sp^3-N=N-C_{sp^3}}$ <i>cis</i>	CH_3-N	$C_{sec}-N$	$C_{tert}-N$
normal	52.39	46.64	1.35	-2.02	-5.07
"strainless"	57.80	57.40	1.15	-3.25	-8.05

Table 4. Heat of formation and strain energy data; kcal/mol

compound		$\Delta H_f^\circ(\text{exp})$	^{tor +} conf	$\Delta H_f^\circ(\text{calc})$	ΔH_f° (exp - calc)	Strain Energy calc	Strain Energy Engel ^{c)}
$R-N=N-R'$	<i>R</i>						
	<i>R'</i>						
	CH ₃	CH ₃	32.14 ± 0.90 ^{a)}	0.0	32.07	0.07	(0.0) ^{d)}
	CH ₃	Et	27.21 ± 0.90 ^{a)}	0.3	27.19	0.02	0.0
	Et	Et	22.29 ± 0.90 ^{a)}	0.8	22.40	-0.11	0.0
	<i>n</i> -Pr	<i>n</i> -Pr	12.27 ± 0.84 ^{b)}	1.8	12.21	0.06	1.0
<i>i</i> -Pr	<i>i</i> -Pr	8.51 ± 0.85 ^{b)}	0.8	8.50	0.01	(0.0) ^{d)}	(0.0) ^{d)}
<i>t</i> -Bu	<i>t</i> -Bu	-8.51 ± 0.87 ^{b)}	0.0	-8.50	-0.01	(0.0) ^{d)}	(0.0) ^{d)}
		9.39 ± 0.85 ^{b)}	0.0	10.32	-0.93	2.7	2.7
		10.0 ± 1.1 ^{b)}	0.0	9.81	0.19	7.8	8.3
		49.56 ± 0.64 ^{b)}	0.0	49.38	0.18	13.9	15.4
		22.1 ± 1.1 ^{b)}	0.0	20.86	1.24	7.9	10.1
		—	0.0	38.11	—	6.5	—

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Strain energies have been calculated by assuming *trans*-azomethane, -azoisopropane and -azo-*tert*-butane to be strain-free and by adopting a strainless *cis*-azo increment so as to reproduce Engel's experimentally based strain value for the five-membered tetramethylpyrrolidine¹⁴). A strain energy of 6.5 kcal/mol is thereby predicted for *cis*-azomethane.

An analysis of molecular structure, conformational properties, and thermochemical stability as it pertains to the thermal and photochemical decomposition of azoalkanes will be presented in a forthcoming discussion.

We are indebted to C. Jørgensen (H. C. Ørsted Institute) for some preliminary calculations and technical assistance. We are likewise grateful to F. Jørgensen and O. Manscher (H. C. Ørsted Institute) for useful advice and to Prof. P. Engel (Rice University), who engaged in stimulating discussion and provided the experimental data for *cis*-azomethane prior to publication.

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- 5) ^{5a)} N. L. Allinger, *Adv. Phys. Org. Chem.* **13**, 1 (1976). – ^{5b)} N. L. Allinger et al., *Quantum Chemistry Program Exchange* **11**, 318 (1976).
- 6) The C–N–C torsional parameter was obtained by carrying out PRDDO⁷⁾ and 4-31G⁸⁾ calculations on MMI optimized geometries of *cis*-azomethane with $\theta(\text{CNNC})$ fixed at various values from 0–30°. The resulting energy dependence was fitted to the three term torsional expression⁵⁾ by solution of the corresponding simultaneous equations.
- 7) T. A. Halgren and W. N. Lipscomb, *J. Chem. Phys.* **58**, 1569 (1973); Ref. ^{d)}, Table 2.
- 8) Gaussian 70: W. J. Hehre et al., *Quantum Chemistry Program Exchange* **11**, 236 (1973).
- 9) Standard deviations for the experimentally determined values are as follows: $r_{\text{N}=\text{N}} = 0.003 \text{ \AA}$; $r_{\text{N}-\text{C}} = 0.009 \text{ \AA}$; $\angle \text{N}=\text{N}-\text{C} = 0.5^\circ$; $\Delta H_f^\circ = 0.52 \text{ kcal/mol}$.
- 10) The PRDDO MO method⁷⁾ has been demonstrated to be equivalent in accuracy to the STO-3G *ab initio* minimum basis set: T. A. Halgren, D. A. Kleier, J. H. Hall, Jr., L. D. Brown, and W. N. Lipscomb, *J. Am. Chem. Soc.* **100**, 6595 (1978).
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Verantwortlich für den Inhalt: Prof. Dr. Hans Musso, Karlsruhe. Redaktion: Dr. Hermann Zahn, München.

Anzeigenleitung: H. Both, verantwortlich für den Anzeigenteil: R. J. Roth, Weinheim.

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