

amounts of only one chair conformation. In VII, however, the vicinal coupling constants spanning from 3.1 to 8.4 Hz, appear to be time-averaged values resulting from an equilibrium between B and C in which C predominates.

Again the axial methyl proton signals appear at lower field than the corresponding equatorial methyl signals. The methyl signal of V (Fig. 1) clearly demonstrates that axial and equatorial methoxy substituents at arsenic give rise to different stereo-specific substituent effects.

**Experimental.** The 60 MHz NMR spectra of the eight compounds were examined in benzene solutions (ca. 50 % v/v for the liquid compounds). A small amount of TMS was added and used as internal standard and lock signal source. The spectra were run at ambient probe temperature (ca. 30 °C) on a JEOL-C-60H spectrometer.

1. Aksnes, D. W. and Vikane, O. *Acta Chem. Scand.* 26 (1972) 4170.
2. Aksnes, D. W. *Acta Chem. Scand. A* 28 (1974) 1175.
3. Samitov, Y. Y., Taceeva, N. K., Chadaeva, N. A. and Kamai, G. H. *Chem. Heterocycl. Compounds (USSR)* (1973) 457.
4. Aksnes, D. W. and Bjorøy, M. *Acta Chem. Scand. A* 29 (1975). *In press.*
5. Aksnes, D. W. and Vikane, O. *Acta Chem. Scand.* 27 (1973) 2135, and references therein.
6. Denney, D. Z. and Denney, D. B. *J. Amer. Chem. Soc.* 88 (1966) 1830.
7. Aksnes, G., Eriksen, R. and Mellingen, K. *Acta Chem. Scand.* 21 (1967) 1028.
8. Haemer, M., Ottinger, R., Zimmermann, D. and Reisse, J. *Tetrahedron* 29 (1973) 3539.
9. Kamai, G. and Chadaeva, N. A. *Chem. Abstr.* 47 (1953) 3792c-f, 10470c-h.
10. White, D. W., Bertrand, R. D., McEwen, G. K. and Verkade, J. G. *J. Amer. Chem. Soc.* 92 (1970) 7125.
11. Bentrude, W. G. and Hargis, J. H. *J. Amer. Chem. Soc.* 92 (1970) 7136.
12. Albriksen, P. *Acta Chem. Scand.* 26 (1972) 1783.
13. Buchanan, G. W., Stothers, J. B. and Wood, G. *Can. J. Chem.* 51 (1973) 3746.
14. Bergesen, K. and Albriksen, P. *Acta Chem. Scand.* 26 (1972) 1680.
15. Maroni, P. and Gorrichon, J.-P. *Bull. Soc. Chim. Fr.* (1972) 785.

Received January 13, 1975.

## Conformational Energies and Conversion Barriers for Cyclononane

STEINAR RUSTAD and HANS M. SEIP

Department of Chemistry, University of Oslo, Oslo 3, Norway

A novel approach to semiquantitative calculations of conformational energies of  $C_9$ - $C_{16}$  cycloalkanes has been suggested by Dale.<sup>1</sup> The method is based on the reasonable assumptions that the bonding energies are of minor importance and that the main part of the non-bonded interactions can be included in the torsional potentials. According to Dale, cyclononane has three conformations which he denoted [333] ( $D_3$  symmetry), [234] ( $C_1$ ) and [12222] ( $C_2$ ) cf. Fig. 1). He found [333] to be the most stable form, [234] and [12222] were found to be 1.4 and 2.8 kcal mol<sup>-1</sup> less stable, respectively. We used these results as a starting point for the present, more accurate calculation. Results for an additional conformation with  $C_3$  symmetry considered by Bixon and Lifson,<sup>2</sup> are also included.

The conformational energies were calculated according to the method first applied by Westheimer,<sup>3</sup> and later used by many others in various versions.<sup>4-8</sup> A combination of the steepest-descent and the Newton-Raphson method was used to obtain the energy minima. The computer program was written by one of us (S.R.) in FORTRAN EXTENDED for CYBER 74. A subroutine for calculating the dependent structural parameters for the molecule must be provided.

For cyclononane we used the cartesian coordinates for the carbon atoms as independent parameters. The van der Waals energy was calculated as described by Eliel *et al.*<sup>4</sup> with the necessary constants from their book (p. 452). The intrinsic barrier to torsion about a CC bond was given the value 2.65 kcal mol<sup>-1</sup>.<sup>9</sup> The CCC angle was assigned the normal value 112° and the bending force constant 1.086 mdyne Å rad<sup>-2</sup>.<sup>10</sup> The normal value and the stretching force constant for a CC bond were taken as 1.535 Å and 4.534 mdyne Å<sup>-1</sup>.<sup>10</sup> The CH bond lengths and the HCH angles were kept at the fixed values 1.113 Å and 112°. The planes through HCH were assumed perpendicular to the planes through CCC, bisecting the CCC angles. No symmetry restrictions were imposed on the models during the minimalization. The iteration procedure was terminated when the absolute value of the shifts in the independent parameters were less than 10<sup>-3</sup> Å.

Table I gives the calculated conformational energies and the corresponding torsional angles and bond angles. Results obtained by Dale and by Bixon and Lifson are also included. The agreement is quite good. As in previous calcula-

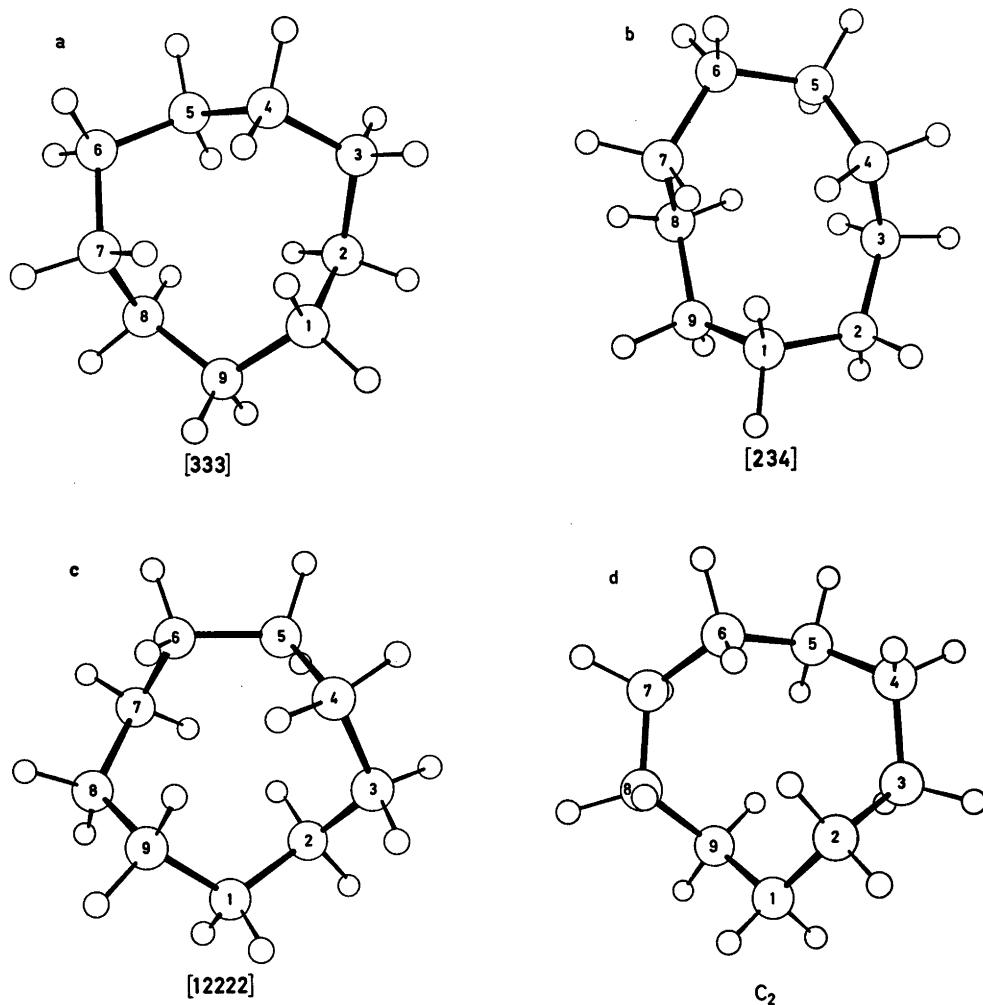


Fig. 1. The conformations found for cyclononane.<sup>14</sup>

tions<sup>1,2,5</sup> we get the lowest energy for the [333] form. Our results indicate that the [12222] form is slightly more stable than the [234] form, while Dale obtained a lower energy for the [234] form. The <sup>13</sup>C NMR spectrum of cyclononane is consistent with  $D_3$  symmetry for the most stable form,<sup>11</sup> and evidence for small amounts of other conformers has also been obtained.<sup>12</sup>

In a second paper<sup>13</sup> Dale has dealt with interconversions in cycloalkanes. The reasonable path for the interconversion of [333] forms is [333]→[234]→[234] (mirror image)→[333].

The corresponding energy profile was computed. The path linking [333] and [234] was obtained by letting the torsional angle  $\phi_{2-3}$  pass through zero. Similarly, going from [234] to its mirror image implies that  $\phi_{5-8}$  passes through zero. The energies and structural parameters corresponding to the transition states [1233] and [1323] are included in Table 1. The energies are seen to be in good agreement with those calculated by Dale, though there are considerable differences in torsional angles and bond angles.

Table 1. Conformational energies (kcal mol<sup>-1</sup>) and corresponding torsional and CCC bond angles (degrees) in cyclononane. The CC bond lengths obtained were in the range 1.538–1.554 Å.

	[333]	Ref. 1	[234]	Ref. 1	[12222]	Ref. 1	C <sub>2</sub>	Ref. 2	[1233]	Ref. 1	[1323]	Ref. 1
1-2 <sup>a</sup>	128	135	58	65	68	75	-65	-63	92	110	64	80
2-3	-57	-55	51	50	-73	-85	120	121	0	0	52	45
3-4	-57	-55	-131	-140	-48	-45	-74	-77	102	-95	-137	-150
4-5	128	135	110	115	105	110	87	86	122	145	82	95
5-6	-57	-55	-41	-40	-92	-100	-123	-120	-47	-65	0	0
6-7	-57	-55	-50	-55	105	110	87	86	-48	-40	-82	-95
7-8	128	135	137	160	-48	-45	-74	-74	140	130	137	150
8-9	-57	-55	-52	-45	-43	-85	120	121	-67	-55	-52	-45
9-1	-57	-55	-70	-85	68	75	-65	-67	-60	-60	-64	-80
9-1-2 <sup>b</sup>	113.7	<sup>c</sup>	116.9	<sup>c</sup>	118.2	<sup>c</sup>	113.8	113	120.8	<sup>c</sup>	117.5	<sup>c</sup>
1-2-3	113.7		117.3		116.1		113.0	113	120.4		115.0	
2-3-4	114.9		115.1		117.6		114.8	114	113.4		113.3	
3-4-5	113.7		113.1		115.2		114.6	115	114.6		118.2	
4-5-6	113.7		114.7		115.4		114.6	115	114.3		118.2	
5-6-7	114.9		115.4		115.4		114.6	116	113.6		113.3	
6-7-8	113.7		113.9		115.2		114.6	115	112.2		114.9	
7-8-9	113.7		114.3		117.6		114.8	115	114.2		117.5	
8-9-1	114.9		117.4		116.1		113.0	113	114.1		116.7	
E <sub>r</sub> <sup>d</sup>	0.15		0.22		0.17		0.08		0.28		0.26	
E <sub>θ</sub> <sup>e</sup>	1.06		2.85		4.24		1.15		4.16		4.26	
E <sub>φ</sub> <sup>f</sup>	7.72		8.32		7.29		10.91		11.46		8.81	
E <sub>v</sub> <sup>g</sup>	-5.49		-4.57		-5.38		-6.29		-4.76		-4.46	
E <sub>tot</sub> <sup>h</sup>	3.43		6.82		6.31		5.85		11.14		8.87	
ΔE <sup>i</sup>	0.0	0.0	3.39	1.4	2.89	2.8	2.42	3.11	7.71	8.6	5.44	5.6

<sup>a</sup> Torsional angles. <sup>b</sup> CCC bond angles. <sup>c</sup> Dale assumed tetrahedral bond angles. <sup>d</sup> Bond stretching energies. <sup>e</sup> Bond angle strain energies. <sup>f</sup> Torsional strain energies. <sup>g</sup> Van der Waals energies. <sup>h</sup> Total energies. <sup>i</sup> Conformational energies above the value for the [333] form.

- Dale, J. *Acta Chem. Scand.* 27 (1973) 1115.
- Bixon, M. and Lifson, S. *Tetrahedron* 23 (1967) 769.
- Westheimer, F. H. In Newman, M. S., Ed., *Steric Effects in Organic Chemistry*, Wiley, New York 1956.
- Eliel, E. L., Allinger, N. L., Angyal, S. J. and Morrison, G. A. *Conformational Analysis*, Interscience, New York 1965.
- Hendrickson, J. B. *J. Amer. Chem. Soc.* 83 (1961) 4537; 84 (1962) 3355; 86 (1964) 4854.
- Allinger, N. L., Miller, M. A., Van-Catledge, F. A. and Hirsch, J. A. *J. Amer. Chem. Soc.* 89 (1967) 4345.
- Allinger, N. L., Hirsch, J. A., Miller, M. A., Tyminski, I. J. and Van-Catledge, F. A. *J. Amer. Chem. Soc.* 90 (1968) 1199.
- Boyd, R. H. *J. Chem. Phys.* 49 (1968) 2574.
- Abraham, R. J. and Parry, K. J. *J. Chem. Soc. B* (1970) 539.
- Schachtschneider, J. H. and Snyder, R. G. *Vibrational Analysis of Polyatomic Molecules IV* (Force Constants for the Haloparaffins) Project No. 31450, Technical Report No. 122-63 of Shell Development Company.
- Anet, F. A. L. and Wagner, J. J. *J. Amer. Chem. Soc.* 93 (1971) 5266.
- Anet, F. A. L. and Krane, J. *Unpublished results*.
- Dale, J. *Acta Chem. Scand.* 27 (1973) 1130.
- Johnson, C. K. (1965) *ORTEP*, Report ORNL-3795, Oak Ridge National Laboratory, Oak Ridge.

Received December 9, 1975.