

## 145. Crystal and Molecular Structure of 2,3,5,6,7,8-Hexamethylidenebicyclo[2.2.2]octane ('[2.2.2]hericene')<sup>1)</sup>

by A. Alan Pinkerton and Dieter Schwarzenbach

Institut de Cristallographie, Bâtiment des Sciences Physiques de l'Université,  
CH-1015 Lausanne-Dorigny

and Olivier Pilet<sup>2)</sup> and Pierre Vogel<sup>3)</sup>

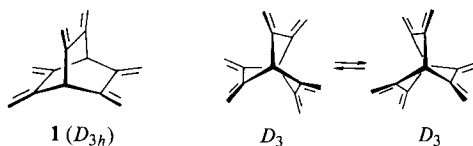
Institut de chimie organique de l'Université, 2, rue de la Barre, CH-1005 Lausanne

(3. VIII. 82)

### Summary

The title molecule **1** has virtual  $D_{3h}$ -symmetry in the crystalline state.

The [2.2.2]hericene (**1**) occupies a place between barrelene (= bicyclo[2.2.2]octa-2,5,7-triene) [2] and triptycene (= 9,10-dihydro-9,10[1',2']-benzoanthracene) [3]. Theoretical calculations [4] and experimental results [5] [6] indicated that the underlying bicyclo[2.2.2]octane skeleton possesses a broad energy minimum for twisting around the C(1)–C(4) axis. Dunitz & Ermer [6] analyzed the thermal vibration parameters from X-ray diffraction data of the crystalline bicyclo[2.2.2]octane-1,4-dicarboxylic acid in terms of rigid-body translation and libration tensors. The r.m.s. amplitude for rotation about the threefold axis indicates an upper limit for the twist angle of molecules with  $D_3$ -symmetry of  $11.8 \pm 0.4^\circ$ , the estimate for the energy barrier between enantiomeric forms being only 0.1 kcal/mol.



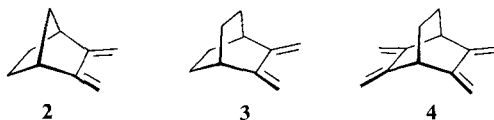
While triptycene has a  $D_{3h}$ -structure in the crystalline state [3b], its perhydro derivatives can be twisted up to *ca.* 30° for *trans*-junction of the cyclohexane rings [7] (see also the <sup>1</sup>H-NMR data of the all-*trans*-hexamethyl bicyclo[2.2.2]octane-2,3,5,6,7,8-hexacarboxylate [1]). From PES [8] and <sup>13</sup>C-NMR [9] data, Klessinger *et al.* proposed an eclipsed structure for 2,3-dimethylidenebicyclo[2.2.1]heptane (**2**)

<sup>1)</sup> Interaction between non-conjugated chromophores, Part 19; Part 18, see [1].

<sup>2)</sup> Present address: Stanford University, Department of Chemistry, Stanford, CA 94305.

<sup>3)</sup> Author to whom correspondence should be addressed.

and a twisted one for 2,3-dimethylidenebicyclo[2.2.2]octane (**3**), the latter being more flexible than the former diene. However, force-field MMPII calculations predicted an eclipsed conformation for **1** (**3** and **4**) with planar *s-cis*-butadiene moieties [1]. We report now the X-ray crystal structure of this compound which is in agreement with the predictions made by molecular mechanics calculations for molecules in the gas phase.



Crystals of **1** [1] grown from solution were invariably hexagonal plates. X-ray precession photographs indicated a disordered structure with stacking faults along the plate normal. Suitable crystals for structure determination were obtained as optically uniaxial hexagonal plates by rapid sublimation *in vacuo*. They are rhombohedral,  $a = 7.0966(5)$ ,  $c = 38.211(2)$  Å, space group  $R\bar{3}c$ , (hexagonal setting),  $Z = 6$ . Observed and calculated densities are 1.10 and 1.09  $\text{g} \cdot \text{cm}^{-3}$ , respectively. Intensity measurements were made with a *Syntex-P2<sub>1</sub>* diffractometer using Nb-filtered *MoK $\alpha$*  radiation ( $\lambda = 0.71069$  Å) for  $\sin \theta / \lambda \leq 0.60$  Å<sup>-1</sup>. Backgrounds were estimated from the scan profile [10]. Crystal dimensions [11] were  $0.26 \times 0.25 \times 0.08$  mm. A numerical absorption correction was applied ( $\mu = 0.7$  cm<sup>-1</sup>). The number of unique reflections was 374, of which 192 had  $I > 3\sigma(I)$ .

Data reduction and structure analysis were made with the 'XRAY-72' program system [12]. The scattering factor for C-atoms was taken from *Cromer & Mann* [13] and for H-atoms from *Stewart et al.* [14].

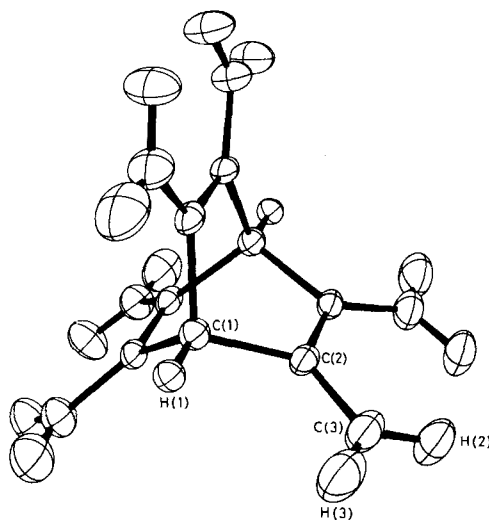


Figure. ORTEP Perspective View of **1** with 20% Probability Ellipsoids. For practical reasons, the numbering of the C- and H-atoms differs from that recommended by IUPAC.

Table 1. Positional and Thermal Parameters for **1** with Standard Deviations in Parentheses. The temperature factors have the form  $e^{-T}$  with  $T = 2\pi^2 \sum h_i^2 U_{ij} a_i^* a_j^*$ . For C(1) and H(1),  $U_{11} = U_{22} = 2U_{12}$ ,  $U_{13} = U_{23} = 0$  (point symmetry  $C_3$ )

Atoms	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	0	0	0.28357(8)	0.0479(10)	0.0479(10)	0.070(2)	0.0239(5)	0	0
C(2)	0.1995(2)	0.0008(2)	0.26929(4)	0.0404(9)	0.0418(8)	0.093(1)	0.0207(7)	-0.0063(9)	0.0006(9)
C(3)	0.3506(5)	0.0036(5)	0.29011(9)	0.069(2)	0.095(2)	0.118(3)	0.051(1)	-0.013(2)	-0.002(2)
H(1)	0	0	0.3094(5)	0.05(1)	0.05(1)	0.05(1)	0.025(5)	0	0
H(2)	0.473(2)	0.002(3)	0.2782(4)	0.09(1)	0.15(1)	0.11(1)	0.09(1)	0.00(1)	0.00(1)
H(3)	0.339(3)	0.003(4)	0.3156(8)	0.09(1)	0.12(1)	0.20(3)	0.06(1)	-0.04(2)	0.00(2)

Table 2. Bonds Lengths ( $\text{\AA}$ ) and Angles ( $^\circ$ ) in **1** with Estimated Standard Deviations in Parentheses. See the Figure for numbering of the atoms.

C(1)-C(2)	1.515(2)	C(2)-C(1)-C(2')	107.8(1)
C(2)-C(2')	1.474(2)	C(2)-C(1)-H(1)	111.1(1)
C(2)-C(3)	1.327(4)	C(1)-C(2)-C(2')	111.1(2)
C(1)-H(1)	0.99(2)	C(1)-C(2)-C(3)	122.1(2)
C(3)-H(2)	0.99(2)	C(3)-C(2)-C(2')	126.8(2)
C(3)-H(3)	0.98(3)	C(2)-C(3)-H(2)	116(1)
H(2)...H(2')	2.16(2)	C(2)-C(3)-H(3)	122(2)
		H(2)-C(3)-H(3)	122(2)

The possible space groups are  $R3c$  and  $R\bar{3}c$ . In  $R\bar{3}c$ , the nearly spherical molecules 7 Å in diameter must occupy either the positions 0,0,1/4 or 0,0,0 with point symmetries  $D_3$  (32) and  $S_6$  ( $\bar{3}$ ), respectively. Only the former are compatible with the maximal symmetry  $D_{3h}$  ( $\bar{6}m2$ ) of the molecule. By unit-cell transformation, an  $F$ -centered lattice with  $a' = 10.4$  Å,  $\alpha = 86.3^\circ$ , and  $Z = 4$  can be obtained, indicating an approximate cubic close packing. Simple packing considerations applied to the hexagonal layers perpendicular to  $c$  lead to coordinates  $y \approx 0$  for the C-atoms in general positions, corresponding to a nearly or completely eclipsed molecular conformation. This arrangement is also compatible with the stacking faults observed for the crystals grown from solution. In  $R3c$ , the same packing is obtained as in  $R\bar{3}c$ , the molecules occupying the positions 0,0, $z$  with point symmetry  $C_3$  (3). The higher space group was therefore considered the more likely, and approximate coordinates were calculated for a C-skeleton staggered by about  $10^\circ$  and centered at 0,0,1/4. This starting model was refined to  $R = 0.12$ . H-positions were then obtained from a difference *Fourier* synthesis and refinement continued to  $R = 0.031$ . The anisotropic temperature parameters of the hydrogen atoms converged to reasonable values with the possible exception of H (3) (the *Figure*). The final atomic parameters are given in *Table 1* and bond lengths and angles in *Table 2*. A perspective drawing of the molecule, prepared by the program ORTEP [15] is shown in the *Figure*.

Although the molecules only have crystallographic  $D_3$  (32) site symmetry, the deviation from exact  $D_{3h}$  ( $\bar{6}m2$ )-symmetry is negligible: the twist angle around the triad axis is  $0.37^\circ$ ; the torsion angle in the butadiene unit is  $1.34^\circ$ ; the maximum deviation from the mean butadiene plane is 0.007 Å (including the bridgehead C-atoms 0.011 Å). The anisotropic temperature parameters of the C-atoms were analyzed in terms of rigid-body motions of the molecules<sup>4)</sup> [16]. The r.m.s. amplitudes for libration about the three-fold axis and perpendicular to it are, respectively,  $4.7 \pm 0.2^\circ$  and  $4.6 \pm 0.1^\circ$ . Although it is not possible to distinguish between 'in-phase' rigid-body motion and an 'out-of-phase' twisting motion around the three-fold axis, the nearly isotropic libration tensor indicates the former to be probably dominant. As in the analogous bicyclo[2.2.2]octane-1,4-dicarboxylic acid [6], the effective symmetry is  $D_{3h}$  ( $\bar{6}m2$ ). The r.m.s. amplitudes of the translational motion are  $0.276 \pm 0.003$  Å along and  $0.190 \pm 0.003$  Å perpendicular to the triad axis. The dominant contribution to the thermal motion is thus in the  $c$ -direction.

Inspection of the bond lengths (*Table 2*) reveals short terminal C–C bonds in the butadiene units, intermediate central bonds, and normal single bonds to the bridgeheads. The distance between the inner H-atoms is short (2.16 Å), but they do not deviate significantly from the plane of the diene system.

---

<sup>4)</sup> We thank Prof. J. D. Dunitz (Zürich) for the calculations and for helpful comments.

## REFERENCES

- [1] *O. Pilet, J. L. Birbaum & P. Vogel*, *Helv. Chim. Acta* 66, 19 (1983).
- [2] *H. E. Zimmerman & R. M. Paufler*, *J. Am. Chem. Soc.* 82, 1514 (1960); *H. E. Zimmerman, G. L. Grunewald, R. M. Paufler & M. A. Sherwin*, *ibid.* 91, 2330 (1969); see also: *W. G. Dauben, G. T. Rivers, R. J. Twieg & W. T. Zimmerman*, *J. Org. Chem.* 41, 887 (1976); *C. W. Jefford, T. W. Wallace & M. Acar*, *ibid.* 42, 1654 (1977).
- [3] a) *P. D. Bartlett & E. S. Lewis*, *J. Am. Chem. Soc.* 72, 1005 (1950); *C. F. Wilcox, jr. & A. C. Craig*, *J. Org. Chem.* 26, 2491 (1961); *G. Wittig & R. Ludwig*, *Angew. Chem.* 68, 40 (1956); see also: *H. Hart, S. Shamouilian & Y. Takehira*, *J. Org. Chem.* 46, 4427 (1981); b) *K. Anzenhofer & J. J. De Boer*, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* 131, 103 (1970).
- [4] *E. M. Engler, L. Chang & P. v. R. Schleyer*, *Tetrahedron Lett.* 1972, 2525; *N. L. Allinger*, *Adv. Phys. Org. Chem.* 13, 2 (1976); *J. Fournier & B. Waegell*, *Bull. Soc. Chim. Fr.* 1973, 436.
- [5] *Y. Morino, K. Kuchitsu & A. Yokozeki*, *Bull. Chem. Soc. Jpn.* 43, 2017 (1970); *J. J. McFarlan & I. G. Ross*, *J. Chem. Soc.* 1960, 4169; *A. H. Nethercot & A. J. Javan*, *Chem. Phys.* 21, 363 (1953).
- [6] *O. Ermer & J. D. Dunitz*, *Helv. Chim. Acta* 52, 1861 (1969).
- [7] *S. Brückner, G. Allegra, A. Albinati & M. Ferina*, *J. Chem. Soc. Perkin Trans. 2* 1980, 523, and lit. cit. therein.
- [8] *P. Amus & M. Klessinger*, *Tetrahedron* 30, 2477 (1974).
- [9] *H.-U. Pfeffer & M. Klessinger*, *Org. Magn. Reson.* 9, 121 (1977).
- [10] a) *H. Blessing, P. Coppens & P. Becker*, *J. Appl. Cryst.* 7, 488 (1972); b) *D. Schwarzenbach*, 'TWOHLEH', a *Syntex-P2* data collection program including scan profile interpretation, *Abs.*, Fourth European Crystallographic Meeting (1977) p. 134.
- [11] *A. A. Pinkerton, G. Chapuis, P. Vogel, U. Hänisch, Ph. Narbel, T. Boschi & R. Roulet*, *Inorg. Chim. Acta* 35, 197 (1979).
- [12] *J. M. Stewart, F. A. Kundell & J. C. Baldwin*, 'X-RAY-72', version of June 1972, Technical Report TR-192 of the Computing Science Center, University of Maryland (as modified by *D. Schwarzenbach*).
- [13] *D. T. Cromer & J. B. Mann*, *Acta Crystallogr.* A24, 321 (1968).
- [14] *R. F. Stewart, E. R. Davidson & W. T. Simpson*, *J. Phys. Chem.* 42, 3175 (1965).
- [15] *C. K. Johnson*, 'ORNL-3794', Oak Ridge National Laboratory 1971.
- [16] *V. Schomaker & K. N. Trueblood*, *Acta Crystallogr.* B24, 63 (1968).