

nuclei perpendicular to the *c* axis. The 3-dimethylamino-2-methylpropyl side chains lie between these layers in a relatively empty environment, and do not seem to be subject to any severe conformational restraints.

None of the intermolecular contact distances are shorter than the sum of the appropriate van der Waals radii.

Levomepromazine sulphoxide was kindly supplied by Leo AB, Helsingborg, Sweden. We would also like to thank Dr B. Klewe at the Institute of Chemistry, University of Oslo, for collection of the low-temperature data.

#### References

- BYLUND, D. B. (1981). *J. Pharmacol. Exp. Ther.* **217**, 81–86.
- CHU, S. S. C. (1975). *Acta Cryst.* **B31**, 1082–1087.
- CHU, S. S. C. & VAN DER HELM, D. (1975). *Acta Cryst.* **B31**, 1179–1183.
- DAHL, S. G. (1976). *Clin. Pharmacol. Ther.* **19**, 435–442.
- DAHL, S. G. (1981). In *Clinical Pharmacology in Psychiatry: Neuroleptic and Antidepressant Research*, p. 125. London: Macmillan.
- DAHL, S. G. & GARLE, M. (1977). *J. Pharm. Sci.* **66**, 190–193.
- DAHL, S. G. & HALL, H. (1981). *Psychopharmacology*, **74**, 101–104.
- DAHL, S. G., JOHNSEN, H. & LEE, C. R. (1982). *Biomed. Mass Spectrom.* In the press.
- DAHL, S. G. & REFSUM, H. (1976). *Eur. J. Pharmacol.* **37**, 241–248.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *MULTAN. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England.
- HORN, A. S., POST, M. L. & KENNARD, O. (1975). *J. Pharm. Pharmacol.* **27**, 553–563.
- JACOBS, J. & SUNDARALINGAM, M. (1969). *Acta Cryst.* **B25**, 2487–2496.
- JOHNSEN, H. & DAHL, S. G. (1982). *Drug Metab. Dispos.* **10**, 63–67.
- JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- MCDOWELL, J. J. H. (1969). *Acta Cryst.* **B25**, 2175–2181.
- MARSAU, P. & GAUTHIER, J. (1973). *Acta Cryst.* **B29**, 992–998.
- PEROUTKA, S. J. & SNYDER, S. H. (1980). *Am. J. Psychiatry*, **137**, 1518–1522.
- TOLLENAERE, J. P., MOEREELS, H. & KOCH, M. H. (1977). *Eur. J. Med. Chem.—Chim. Ther.* **12**, 199–211.

*Acta Cryst.* (1982). **B38**, 2428–2435

## Structure of and Energy Calculations for 1,2,9,10,17,18-Hexadehydro[2.2.2]paracyclophane

BY KENNETH TRUEBLOOD, KIRA MIRSKY, EMILY MAVERICK, CAROLYN KNOBLER AND LINDA GROSSENBACHER

*Department of Chemistry, University of California, Los Angeles, CA 90024, USA*

(Received 23 November 1981; accepted 3 March 1982)

#### Abstract

The crystal structure of 1,2,9,10,17,18-hexadehydro-[2.2.2]paracyclophane,  $C_{24}H_{18}$ ,  $M_r = 306.41$ , has been determined at 113 and 298 K. At low temperature, the space group is  $P2_1/n$ , with  $Z = 4$ ,  $a = 16.914$  (7),  $b = 10.066$  (4),  $c = 10.292$  (3) Å and  $\beta = 105.90$  (3)°,  $V = 1685$  Å<sup>3</sup>,  $D_x = 1.208$  g cm<sup>-3</sup>. At room temperature, the space group is  $C2/c$ , with  $Z = 4$ ,  $a = 17.111$  (8),  $b = 10.132$  (6),  $c = 10.581$  (4) Å and  $\beta = 106.95$  (3)°,  $V = 1755$  Å<sup>3</sup>,  $D_x = 1.160$  g cm<sup>-3</sup>. Intensity data were collected on a Syntex *P1* diffractometer with graphite-monochromatized Mo *K* $\alpha$  radiation. The low-temperature structure was determined with *MULTAN*; the room-temperature structure was deduced from that at low temperature. Each structure was refined by full-matrix least squares to

$R = 0.086$  (113 K) and  $R = 0.103$  (298 K), reflections with  $F \geq 2\sigma(F)$  being used in the refinements (2325 at 113 K and 886 at 298 K). In the room-temperature structure, the molecule lies on a twofold axis of the crystal; in the low-temperature structure it is rotated approximately 4° (chiefly about the  $c^*$  direction) from the room-temperature position, and has no symmetry, the individual rings having rotated an average of about 5° from their apparent positions at 298 K. Lattice-energy calculations with rigid molecules indicate that the room-temperature structure might be described by a 50:50 mixture of asymmetric molecules of the low-temperature geometry in two different positions; this hypothesis is supported by an examination of the Gaussian ellipsoids of the atoms at 298 K. Calculations suggest also that the apparent position found for the molecule at 298 K is not the most stable

position at *any* temperature. The minimum in energy corresponds to a rotation of asymmetric molecules about the  $c^*$  direction by about  $5^\circ$ , to a position close to that found in the low-temperature structure (or to one related to this by a twofold rotation about  $b$ ). There is evidence that even at 113 K there may be differing proportions of two molecules (related by the  $180^\circ$  rotation), the ratio depending on the exact conditions of cooling. Molecular-mechanics and packing calculations for the molecule are consistent with a dynamic disorder at room temperature, including rotations about the normal to the best plane of the entire molecule, and separate librations of the three aromatic rings.

### Introduction

Olefinic paracyclophanes, with general formula  $-(C_6H_4CH=CH)_n-$ , consist of  $-C_6H_4-$  rings linked through *para* positions by  $-CH=CH-$  groups. Crystal structures of molecules with  $n = 2$  (Coulter & Trueblood, 1963) and  $n = 4$  (Ljungström, Lindqvist & Wennerström, 1978) have been reported previously. The structures of these paracyclophanes can be discussed in terms of a least-squares plane determined by all the  $-C-C=C-C-$  groups. The aromatic rings are twisted out of this reference plane by amounts that depend upon the number of  $-(C_6H_4CH=CH)-$  units. In the  $[2_2]$ paracyclophanediene, the aromatic rings are normal to the reference plane and are significantly deformed; the  $[2_4]$ paracyclophanetetraene molecule in the crystal has nearly planar aromatic rings that are twisted out of the reference plane by  $27-40^\circ$ , and in solution the rings move freely even at  $-60^\circ$ . The present study of the title compound, also called  $[2_3]$ paracyclophanetriene, (I) (Cram & Dewhirst, 1959), was undertaken to provide information about the conformation of the molecule and the deformation of the aromatic rings. The structure of (I) is illustrated in Fig. 1.

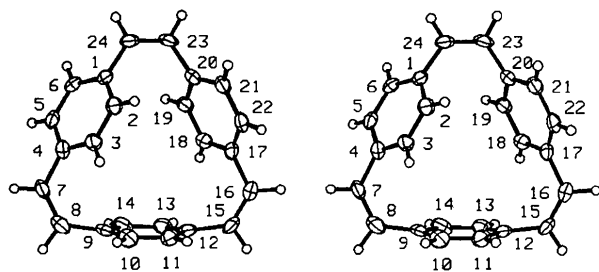


Fig. 1. ORTEP stereoview of the molecule at 113 K. C-atom numbers are shown; H atoms are numbered to correspond to the attached C atom. C-atom ellipsoids are drawn at 50% probability; H-atoms are represented as spheres of diameter  $0.1 \text{ \AA}$ .

### Experimental

Pale yellow-white monoclinic crystals of (I) were grown from 95% ethanol. Two different crystals were used for data collection, each measuring about  $0.15 \times 0.20 \times 0.35 \text{ mm}$ ; graphite-monochromatized  $Mo K\alpha$  radiation was used, with no absorption corrections ( $\mu = 0.63 \text{ cm}^{-1}$ ). First a low-temperature (113 K) data set was collected (set *L1*) (Strouse, 1976). Next, a room-temperature data set was collected (set *Rm*) with a second crystal, and then this crystal was cooled slowly (over a period of about 30 h) to 113 K while three reflections were monitored (Fig. 2). A second low-temperature data set (*L2*) was then collected with the second crystal. A malfunction of the diffractometer necessitated interrupting the data collection for nearly three weeks, during which time the crystal warmed to room temperature; when it was rapidly re-cooled and data collection was started again, the standards and duplicate reflections were essentially unchanged. However, relatively weak reflections that are systematically absent at room temperature (those with  $h + k$  odd) had *increased* in intensity significantly. (The increase for ten of the strongest of these duplicated reflections ranged from 5 to 40%; the corresponding e.s.d. of the intensity ranged from 1 to 6%.) Some of the details of the various data sets are given in Table 1. All intensity data were collected in the  $\theta:2\theta$  mode at a scan speed of  $2^\circ \text{ min}^{-1}$  in  $2\theta$ , with background measured at each end of the scan for a time equal to half the scan time.

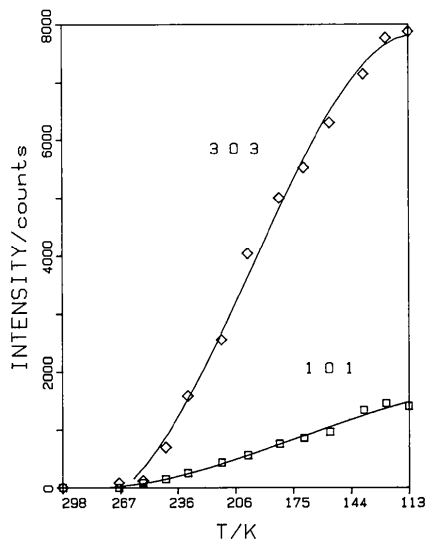


Fig. 2. Intensities of 101 and 303 as a function of temperature, measured as the first crystal was cooled over a period of about 30 h (see text). The crystal was recentered at each temperature and each measurement was repeated until it became steady; usually five replications (over a period of 20–30 min) sufficed. The intensity of 202 was also measured at each temperature to provide a normalizing factor.

Table 1. Refinement information

Data set	L1	L2	Rm
( $\sin \theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.60*	0.65	0.60
Number of parameters	289	289	145
Unique $F_o$	3409	3905	1561
$R$ for all data	0.143	0.146	0.173
Unique $F_o \geq 2\sigma(F_o)$	2325	2783	886
$R$	0.086	0.100	0.103
$R_w$	0.068	0.084	0.060
Goodness of fit	2.26	1.91	2.57

\* In addition, 167 reflections with  $F_o \geq 2\sigma(F_o)$  were collected between 0.60 and 0.65 Å<sup>-1</sup>.

All the C atoms of the molecule were found with *MULTAN* (Germain, Main & Woolfson, 1971) with data set L1. Refinement of this structure was done with isotropic and then anisotropic vibration parameters by full-matrix least squares. All 18 H atoms of the molecule appeared in a difference map, with no other peak above 0.3 e Å<sup>-3</sup>. The final refinement stages included the positions and isotropic vibration parameters for the H atoms.

The room-temperature structure was deduced from that at low temperature, with account taken of the fact that the molecules in the low-temperature structure lie not far from the line 0,  $y$ , 0.75, which is a twofold axis of the room-temperature space group (see Fig. 3). The molecule must lie on a twofold axis at room temperature, while it has no required symmetry at 113 K. A reasonable set of trial positions for the C atom was derived by rotating the molecule found in the low-temperature structure 180° about the line 0,  $y$ , 0.75 and averaging the positions of corresponding C atoms in half the molecule. These 12 C-atom positions were then refined by full-matrix least squares, first isotropically and then anisotropically. All nine unique H atoms were found in a difference map and refinement was continued to convergence. There is a large proportion of weak intensities in both the low-temperature and room-temperature data sets (for example,

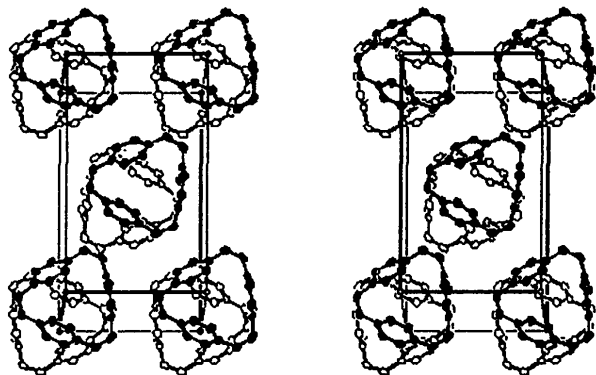


Fig. 3. ORTEP stereoview of the 113 K unit cell along  $c^*$ , with  $b$  horizontal. The molecules nearer the viewer are distinguished by shaded ellipsoids.

only about one-fourth of the intensities are larger than five times their e.s.d. in set Rm, and fewer than one-third meet this criterion in set L1 or L2); all data with  $F$  greater than or equal to twice the e.s.d. of  $F$  were

Table 2. Positional and isotropic thermal parameters for [2<sub>3</sub>]paracyclophanetriene

Units of each e.s.d., in parentheses, are those of the least significant digit of the corresponding parameter. If  $B$  has no e.s.d., it is the equivalent isotropic  $B$  for an atom refined anisotropically.

$$B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$B_{eq}$ or $B$ (Å <sup>2</sup> )
(a) At 113 K, L1				
C(1)	0.1004 (2)	0.1713 (3)	0.7857 (3)	2.3
C(2)	0.0703 (2)	0.0819 (3)	0.6813 (4)	2.6
C(3)	0.1025 (2)	-0.0435 (3)	0.6829 (4)	2.6
C(4)	0.1675 (2)	-0.0862 (3)	0.7894 (3)	2.5
C(5)	0.2013 (2)	0.0058 (4)	0.8896 (4)	2.6
C(6)	0.1683 (2)	0.1322 (3)	0.8882 (4)	2.5
C(7)	0.1983 (2)	-0.2242 (4)	0.7935 (4)	3.1
C(8)	0.1522 (2)	-0.3340 (4)	0.7710 (4)	3.7
C(9)	0.0610 (2)	-0.3344 (3)	0.7463 (4)	2.8
C(10)	0.0076 (2)	-0.3409 (4)	0.6190 (4)	3.2
C(11)	-0.0765 (2)	-0.3221 (3)	0.5981 (4)	3.1
C(12)	-0.1093 (2)	-0.3023 (3)	0.7066 (3)	2.5
C(13)	-0.0565 (2)	-0.3105 (4)	0.8344 (4)	3.1
C(14)	0.0276 (2)	-0.3239 (4)	0.8555 (4)	3.3
C(15)	-0.1983 (2)	-0.2681 (4)	0.6805 (4)	3.1
C(16)	-0.2285 (2)	-0.1458 (4)	0.6672 (4)	3.2
C(17)	-0.1794 (2)	-0.0212 (3)	0.6916 (3)	2.6
C(18)	-0.1187 (2)	-0.0029 (3)	0.8129 (3)	2.5
C(19)	-0.0705 (2)	0.1098 (3)	0.8352 (4)	2.5
C(20)	-0.0803 (2)	0.2078 (3)	0.7374 (3)	2.5
C(21)	-0.1443 (2)	0.1945 (4)	0.6202 (4)	2.8
C(22)	-0.1924 (2)	0.0815 (4)	0.5972 (4)	2.7
C(23)	-0.0207 (2)	0.3197 (3)	0.7573 (4)	3.1
C(24)	0.0598 (2)	0.3015 (3)	0.7871 (4)	2.9
H(2)	0.028 (2)	0.106 (3)	0.607 (3)	1.5 (6)
H(3)	0.083 (2)	-0.101 (3)	0.603 (3)	2.2 (7)
H(5)	0.246 (2)	-0.017 (3)	0.962 (3)	3.8 (9)
H(6)	0.189 (2)	0.189 (2)	0.959 (3)	1.4 (6)
H(7)	0.257 (2)	-0.235 (3)	0.819 (3)	3.1 (8)
H(8)	0.181 (2)	-0.422 (4)	0.770 (4)	5.2 (11)
H(10)	0.026 (2)	-0.351 (3)	0.538 (3)	2.5 (8)
H(11)	-0.113 (2)	-0.321 (3)	0.502 (4)	4.9 (9)
H(13)	-0.075 (2)	-0.300 (3)	0.914 (3)	2.6 (8)
H(14)	0.062 (2)	-0.328 (3)	0.944 (3)	2.8 (8)
H(15)	-0.236 (2)	-0.341 (4)	0.667 (3)	4.6 (9)
H(16)	-0.291 (2)	-0.128 (4)	0.635 (4)	5.8 (11)
H(18)	-0.114 (2)	-0.065 (3)	0.882 (3)	1.5 (7)
H(19)	-0.025 (2)	0.119 (3)	0.921 (3)	3.6 (8)
H(21)	-0.150 (2)	0.261 (3)	0.548 (3)	2.6 (7)
H(22)	-0.233 (2)	0.068 (3)	0.513 (3)	2.6 (7)
H(23)	-0.041 (2)	0.409 (3)	0.753 (3)	3.2 (8)
H(24)	0.095 (2)	0.376 (3)	0.808 (3)	3.0 (8)
(b) At 298 K, Rm				
C(1)	0.0896 (5)	0.1838 (8)	0.7731 (7)	7.4
C(2)	0.0711 (4)	0.0921 (7)	0.6733 (7)	6.7
C(3)	0.1113 (4)	-0.0255 (7)	0.6822 (6)	6.4
C(4)	0.1729 (4)	-0.0580 (8)	0.7957 (7)	7.0
C(5)	0.1963 (5)	0.0344 (13)	0.8951 (9)	9.9
C(6)	0.1553 (6)	0.1562 (10)	0.8818 (8)	8.3
C(7)	0.2128 (7)	-0.1900 (17)	0.8136 (9)	11.6
C(8)	0.1746 (9)	-0.3003 (14)	0.7907 (11)	12.3
C(9)	0.0863 (7)	-0.3182 (6)	0.7698 (10)	9.2
C(10)	0.0287 (9)	-0.3252 (9)	0.6448 (10)	11.0
C(14)	-0.0530 (9)	-0.3224 (8)	0.6262 (10)	10.5
C(24)	0.0406 (6)	0.3073 (9)	0.7643 (9)	10.1
H(2)	0.027 (3)	0.107 (5)	0.595 (5)	6.6 (14)
H(3)	0.087 (4)	-0.130 (8)	0.607 (6)	14.9 (22)
H(5)	0.251 (4)	0.023 (6)	0.977 (7)	12.5 (20)
H(6)	0.178 (3)	0.195 (4)	0.960 (5)	5.9 (14)
H(7)	0.272 (4)	-0.179 (5)	0.839 (5)	8.5 (17)
H(8)	0.208 (4)	-0.373 (8)	0.811 (6)	12.0 (22)
H(10)	0.047 (4)	-0.317 (8)	0.576 (7)	12.7 (27)
H(14)	-0.084 (4)	-0.323 (7)	0.538 (8)	12.9 (28)
H(24)	-0.086 (6)	0.355 (11)	0.713 (11)	21.6 (48)

used in refinement. The room-temperature structure is not a precise one, as will be evident from the discussion below; however, the precision indicated for the low-temperature structure by the values of the e.s.d.'s of the parameters is supported by the self-consistency of the molecular geometry. All computer programs were local programs except for *ORTEP* (Johnson, 1965), *PCK6* (Williams, 1972), and *PACKRB* (Shmueli & Goldberg, 1973). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

The final positional parameters and isotropic vibration parameters (equivalent values for atoms refined anisotropically) are given in Table 2(a) and (b).\*

## Results and discussion

### Low-temperature structure

Refinement of the structure was carried out with both data sets, *L1* and *L2*, and for *L1* was performed using weighting inversely proportional to the variance and also with the weighting scheme proposed by Dunitz & Seiler (1973);  $r$  was  $3.25 \text{ \AA}^2$ . The weighting scheme made no significant difference in either the final position parameters or the results of the analysis of rigid-body motion and internal motion of the molecule (see below). (Some significant differences were observed for individual atomic vibration parameters.) The results reported here are from the refinement with conventional weights.

There were significant differences in the molecular geometry resulting from refinement of data sets *L1* and *L2*, with the latter giving poorer internal consistency. The poor internal consistency of the parameters from set *L2* may be due to the effects of warming and (rapidly) recooling the crystal during data collection, noted above. A difference map calculated with the final parameters from the refinement of set *L2* showed small but significant positive peaks,  $0.3$  to  $0.6 \text{ e \AA}^{-3}$  in height, at the position expected for every C atom of a hypothetical molecule related to the refined positions by a twofold axis along  $0, y, 0.75$ . A similar difference map for the structure resulting from set *L1* showed no peaks above  $0.3 \text{ e \AA}^{-3}$ . We interpreted this finding as implying the presence of a small proportion of disorder in the structure based on set *L2* and carried out further refinements with varying occupancy for the two molecules, with the constraint that the sum of the

occupancies was unity. In these refinements anisotropic vibration parameters were used for the C atoms of the predominant molecule, isotropic ones for those of the minor molecule; H-atom positions were fixed. The results were consistent with relative occupancies of about  $0.85$  and  $0.15$  for the two molecules in the structure derived from data set *L2*. Constrained refinements were also tried, with each of these molecules described in various ways: three rigid  $-\text{CHC}_6\text{H}_4\text{CH}-$  groups; a single rigid group containing  $24$  C atoms; or three rigid groups containing  $\text{C}_6\text{H}_4$  and six freely moving bridging C atoms. Neither the relative occupancies of  $85:15$  nor the atomic positions were greatly changed.

Similar experiments with the structure resulting from data set *L1* indicated that the occupancy of any second (disordered) molecule was less than  $0.05$ . In this connection, it is noteworthy that for the ten reflections with  $h + k$  odd mentioned above as having increased in intensity when the crystal warmed and was re-cooled during collection of data set *L2*, the scaled intensities averaged  $25\%$  higher in set *L1* than they did in set *L2* after data collection was resumed. Apparently, rapid cooling to  $113 \text{ K}$  (as before set *L1* or at the end of set *L2*) led to a more ordered structure in space group  $P2_1/n$ , while slow cooling (as at the beginning of set *L2*) produced a less ordered structure, with lower (but still significant) intensities for reflections with  $h + k$  odd. The implication that the degree of disorder may depend in part on the exact conditions of cooling, and may vary from crystal to crystal, is not surprising, and is consistent with the packing-energy and molecular-mechanics calculations reported below. We confine our discussion of the details of the low-temperature structure to that derived from data set *L1*.

The molecule as found at  $113 \text{ K}$  is depicted in Fig. 1 (Johnson, 1965) and aspects of its molecular geometry are summarized in Tables 3 and 4. The results of analysis of its rigid-body motion (Schomaker & Trueblood, 1968) and of libration of the aromatic rings about the bonds connecting them to the olefinic bonds (Trueblood, 1978) are summarized in Table 5. The bond distances and angles (Table 3) are quite normal; although short olefinic double bonds and pairs of short aromatic C—C bonds were reported for  $[2_4]$ paracyclophanetetraene (Ljungström *et al.*, 1978) there are no such abnormalities here. The aromatic rings are bent to a small extent into a boat shape (Table 4), considerably less than in the corresponding diolefin (Coulter & Trueblood, 1963) but more than in the tetraene (Ljungström *et al.*, 1978). There is a significant twist of the olefinic double bonds, the torsion angles about these bonds averaging nearly  $7^\circ$  in the present molecule, as compared with only about  $1^\circ$  in the diolefin and  $5.5^\circ$  in the tetraene. The aromatic rings are twisted out of the reference plane determined by the three  $-\text{C}-\text{C}=\text{C}-\text{C}-$  groups by an average of  $64^\circ$  in

\* Lists of structure factors, anisotropic vibration parameters for both the room-temperature and low-temperature structures, and distances, angles and torsion angles for the room-temperature structure have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36887 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Distances (Å), angles (°) and torsion angles (°) (113 K, L1)

E.s.d.'s in parentheses are in units of the least significant digit of the corresponding value. No corrections for libration are included.

1	2	3	4	Distance 1-2	Angle 1-2-3	Torsion angle 1-2-3-4
C(20)	C(23)	C(24)	C(1)	1.488 (5)	122.8 (3)	9.0 (6)
C(23)	C(24)	C(1)	C(2)	1.324 (5)	124.8 (3)	43.2 (5)
C(24)	C(1)	C(2)	C(3)	1.482 (5)	120.6 (3)	-174.6 (3)
C(24)	C(1)	C(6)	C(5)		122.2 (3)	175.0 (3)
C(1)	C(2)	C(3)	C(4)	1.387 (5)	121.8 (3)	-0.5 (5)
C(2)	C(3)	C(4)	C(5)	1.373 (5)	121.3 (3)	-3.6 (5)
C(3)	C(4)	C(5)	C(6)	1.391 (5)	117.1 (3)	4.1 (5)
C(4)	C(5)	C(6)	C(1)	1.387 (5)	121.4 (3)	-0.4 (5)
C(5)	C(6)	C(1)	C(2)	1.388 (5)	121.0 (3)	-3.8 (5)
C(6)	C(1)	C(2)	C(3)	1.387 (5)	117.2 (3)	4.2 (5)
C(3)	C(4)	C(7)	C(8)		120.6 (3)	-46.7 (6)
C(5)	C(4)	C(7)	C(8)		122.4 (3)	133.3 (4)
C(4)	C(7)	C(8)	C(9)	1.480 (5)	126.0 (3)	-4.1 (6)
C(7)	C(8)	C(9)	C(10)	1.336 (5)	124.0 (4)	98.4 (5)
C(8)	C(9)	C(14)	C(13)	1.493 (5)	119.4 (3)	173.4 (4)
C(8)	C(9)	C(10)	C(11)		122.8 (3)	-170.7 (4)
C(9)	C(10)	C(11)	C(12)	1.374 (5)	121.2 (3)	-3.0 (6)
C(10)	C(11)	C(12)	C(13)	1.392 (5)	120.7 (3)	-4.0 (5)
C(11)	C(12)	C(13)	C(14)	1.391 (5)	117.5 (3)	6.7 (5)
C(12)	C(13)	C(14)	C(9)	1.375 (5)	121.7 (3)	-2.4 (6)
C(13)	C(14)	C(9)	C(10)	1.385 (5)	120.4 (3)	-4.7 (5)
C(14)	C(9)	C(10)	C(11)	1.393 (5)	117.8 (3)	7.4 (5)
C(11)	C(12)	C(15)	C(16)		119.5 (3)	-89.6 (5)
C(13)	C(12)	C(15)	C(16)		122.9 (3)	87.8 (5)
C(12)	C(15)	C(16)	C(17)	1.495 (5)	125.0 (3)	-7.7 (6)
C(15)	C(16)	C(17)	C(18)	1.326 (6)	125.8 (3)	-52.0 (5)
C(16)	C(17)	C(18)	C(19)	1.487 (5)	120.2 (3)	177.5 (3)
C(16)	C(17)	C(22)	C(21)		122.2 (3)	-177.9 (4)
C(17)	C(18)	C(19)	C(20)	1.394 (5)	121.0 (3)	-0.6 (5)
C(18)	C(19)	C(20)	C(21)	1.379 (5)	121.1 (3)	4.9 (5)
C(19)	C(20)	C(21)	C(22)	1.387 (5)	118.1 (3)	-5.3 (5)
C(20)	C(21)	C(22)	C(17)	1.389 (5)	120.7 (3)	1.3 (5)
C(21)	C(22)	C(17)	C(18)	1.381 (5)	121.2 (3)	3.0 (5)
C(22)	C(17)	C(18)	C(19)	1.394 (5)	117.6 (3)	-3.4 (5)
C(19)	C(20)	C(23)	C(24)		119.8 (3)	52.2 (5)
C(21)	C(20)	C(23)	C(24)		122.0 (3)	-124.9 (4)

C-H distances		
C(2)	H(2)	0.93 (3)
C(3)	H(3)	0.99 (3)
C(5)	H(5)	0.93 (3)
C(6)	H(6)	0.92 (3)
C(10)	H(10)	0.97 (3)
C(11)	H(11)	1.01 (4)
C(13)	H(13)	0.96 (3)
C(14)	H(14)	0.94 (3)
C(18)	H(18)	0.93 (3)
C(19)	H(19)	1.00 (3)
C(21)	H(21)	0.99 (3)
C(22)	H(22)	0.96 (3)
C(7)	H(7)	0.96 (3)
C(8)	H(8)	1.01 (4)
C(15)	H(15)	0.96 (4)
C(16)	H(16)	1.03 (4)
C(23)	H(23)	0.96 (3)
C(24)	H(24)	0.94 (3)

the present structure, with individual values varying from 49 to 83°; these variations are apparent in Fig. 1. As discussed below, the amplitudes of libration of the rings about these bonds are significant even at low temperature and our calculations indicate that the potential wells for rotation are relatively shallow. In the diolefin, the rings are nearly normal to its reference plane, and are presumably quite rigidly constrained in this position, while in the tetraene the twists average only 33°.

The vibration parameters of the molecules found in the low-temperature structure with data set L1 using

Table 4. Comparison of some features of the molecular geometry of  $[2_n]$ paracyclophane(n)enes

<i>n</i>	<i>D</i> *	Average twist around C=C	Average twist of aromatic rings†
2	0.17 Å	1.0°	89°
3	0.05	6.9	64
4	0.02	5.5	33

\* *D* is the average distance of the aromatic C atoms that are attached to the olefinic atoms from the plane of the other four aromatic atoms in each ring.

† The twist of an aromatic ring is the angle between the normal to its least-squares plane and the normal to the least-squares plane of all the olefinic C atoms and their adjacent aromatic C atoms.

Table 5. Some results of the thermal-motion analysis at 113 K

The e.s.d. of each amplitude is given in parentheses, in degrees. The reference axes are parallel to **a**, **b** and **c**\*

	r.m.s. libration amplitude (°)	Direction cosines
Overall motion		
$L_{11}^{1/2}$	2.6 (0.1)	0.061, 0.100, 0.993
$L_{22}^{1/2}$	2.0 (0.2)	0.728, 0.676, -0.112
$L_{33}^{1/2}$	1.6 (0.2)	0.683, -0.730, 0.032
Internal motion†		
Ring 1	2.7 (1.4)	
Ring 2	5.8 (0.5)	
Ring 3	3.0 (1.3)	

† Ring 1 contains atoms 1 to 6, ring 2 atoms 9 to 14, and ring 3 atoms 17 to 22. The libration amplitude of each ring is that measured about the exocyclic bond to the adjacent lower-numbered olefinic atom.

both conventional weights and Dunitz-Seiler weights were subjected to thermal-motion analysis (Schomaker & Trueblood, 1968), including analysis of possible libration of the rings about the exocyclic bonds (Trueblood, 1978). The results were nearly the same for each parameter set; those for the analysis of the data from the refinement using weights inversely proportional to the variances are summarized in Table 5. They show that each of the aromatic rings is librating significantly even at 113 K, with the ring containing atoms 9 through 14 having an r.m.s. amplitude of about 6°, twice as great as that of either of the other rings. The entire molecule is also librating with an amplitude of about 2.6° about an axis that is not far (about 18°) from being parallel to the normal to the molecular least-squares plane (the approximate viewing direction in Fig. 1). The generalization of Hirshfeld's (1976) rigid-bond test proposed by Rosenfield, Trueblood & Dunitz (1978) was applied to the vibration parameters to test their self-consistency; the average difference in the mean-square vibration amplitude for pairs of bonded atoms was 0.0030 Å<sup>2</sup>, comparable to

the average e.s.d. expected for this difference (calculated from the average e.s.d. of the  $U^{ij}$ ),  $0.0027 \text{ \AA}^2$ . Furthermore, the differences in mean-square vibration amplitudes for non-bonded pairs of atoms within each ring were the same as those for bonded pairs of atoms, even in the ring (ring 2, Table 5) with the largest libration amplitude, a finding consistent with the expected rigidity of an aromatic ring. In contrast, the differences in mean-square vibration amplitudes for pairs of atoms involving the unsubstituted atoms on a given ring (these are the atoms with highest vibration amplitude) and atoms in other parts of the molecule averaged more than three times greater, consistent with a picture of significant internal motion. These differences were especially large for atoms C(10), C(11), C(13) and C(14).

#### Room-temperature structure

The molecule as found in the crystal at 298 K is depicted in Fig. 4. It is apparent that there is a great deal of dynamic or static disorder at this temperature. The average e.s.d. of the position parameters is more than twice that at low temperature, and the thermal-motion analysis suggests that the individual aromatic rings are librating about their exocyclic bonds with r.m.s. amplitudes of about  $5^\circ$  and nearly  $13^\circ$  (the latter for the ring normal to the molecular twofold axis), about twice the values found at 113 K. The molecule as a whole is librating with an amplitude of  $7^\circ$  around an axis that lies just  $5^\circ$  from the normal to the molecular least-squares plane.

Constrained refinement for a twofold disordered structure, based on the *L1* molecule, did not improve the fit of the room-temperature reflection data, perhaps because the position and vibration parameters for the two half-molecules are strongly correlated. The molecular geometry at room temperature is sufficiently imprecise that we will not discuss it here; however, within the estimated precision, it is normal. A table of distances, bond angles and torsion angles comparable to Table 3 has been deposited. Potential-energy

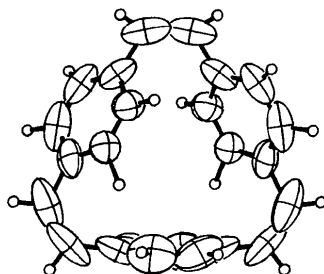


Fig. 4. ORTEP drawing of the molecule as found at 298 K. The atoms in an asymmetric unit (1–10, 14, and 24) are numbered as in Fig. 1, and ellipsoids are represented as in Fig. 1.

calculations described in the next section suggest possible models of disordering at room temperature.

#### Energy calculations

For the packing-energy (lattice-energy) calculations, the atom-atom potential method was used (Kitai-gorodsky, 1973), with the same C and H non-bonded potential parameters as for [2.2]paracyclophane, [3.3]-paracyclophane and other hydrocarbon crystals (Mirsky, 1976). The C-atom coordinates in Table 2(a) (*L1*) and (b) (*Rm*) were used; the C–H bond lengths were adjusted to 1.08 Å. The calculations were performed with the computer program *PCK6* (Williams, 1972). The results for the *L1* and *Rm* structures are given in Table 6.

The lattice energy at the temperature of the experiment (the second line of Table 6) corresponds to the minimum of the crystal packing energy with respect to molecular rotations and translations in the observed unit cell. The lattice energy and the volume per molecule at 0 K (Table 6) were obtained by successive minimization of the lattice energy with respect to the unit-cell parameters, rotations and translations. The final deviations of the calculated molecular positions from those observed at 113 K and 298 K are shown in the last two lines of the table.

Comparing the 0 K lattice energies and volumes corresponding to parameter sets *Rm* and *L1*, we notice that the molecules with the geometry found at 298 K occupy larger volumes and are packed together with higher energy than are those with the geometry found at 113 K. Thus they are less favorable energetically and their apparent twofold symmetry might be due to disorder rather than to any real change in the molecular geometry over the observed temperature interval. With this assumption in mind, we tested other models for the room-temperature structure. The results of these additional calculations follow.

Table 6. Results of packing-energy calculations

	<i>L1</i>	<i>Rm</i>
Temperature (K) at which structure was determined	113	298
Lattice energy ( $\text{kJ mol}^{-1}$ ) at the temperature at which the structure was determined	-120.6	-112.9
Observed volume ( $\text{\AA}^3$ ) per molecule	421.3	438.7
Lattice energy ( $\text{kJ mol}^{-1}$ ) at 0 K	-124.4	-120.5
Calculated volume ( $\text{\AA}^3$ ) per molecule at 0 K	405.5*	411.6
Rotations ( $^\circ$ ) from observed positions	2.7	2.2
Translations ( $\text{\AA}$ ) of the center of mass	0.030	0.015

\* Corresponding unit-cell parameters are  $a = 16.550$ ,  $b = 9.976$ ,  $c = 10.224 \text{ \AA}$ ,  $\beta = 106.09^\circ$ .

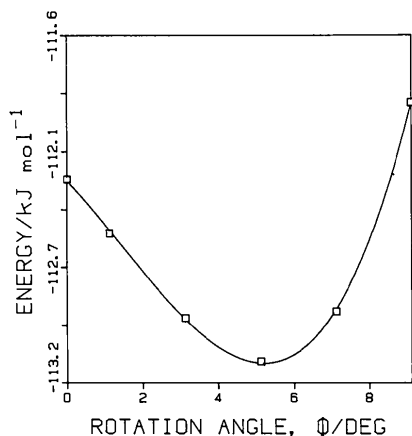


Fig. 5. Rotation of the *L1* molecule in the room-temperature unit cell ( $P2_1/n$ ). At the starting point ( $\Phi = 0$ ), the approximate molecular twofold axis is oriented along the twofold axis of the crystal. For each value of  $\Phi$ , the lattice energy is minimized with respect to molecular translations.

(1) If the molecules of the 113 K (*L1*) geometry are placed in a unit cell with the dimensions of the Rm cell (in space group  $P2_1/n$ ), the minimum lattice energy with respect to rotations and translations ( $-113.5$  kJ mol $^{-1}$ ) is lower than for the Rm molecule ( $-112.9$  kJ mol $^{-1}$ , see Table 6).

(2) Rotation of the *L1* molecule in the Rm cell indicates that the apparent position found for the molecule in the Rm structure is not the most stable one (Fig. 5). The minimum in energy corresponds to a rotation of about  $5^\circ$  around a vector through the center of mass and parallel to  $\mathbf{c}^*$ . The minimum-energy position is close to that found in the *L1* structure (or to one related to this position by a twofold rotation parallel to  $\mathbf{b}$ ).

(3) If each Rm molecule in the Rm unit cell is replaced by two half-occupancy *L1* molecules related by the twofold rotation parallel to  $\mathbf{b}$ , the calculated lattice-energy loss is small ( $1.9$  kJ mol $^{-1}$ ) and is almost compensated by the entropy contribution to the free energy at 298 K ( $-1.7$  kJ mol $^{-1}$ ) for the two-molecule case ( $RT \ln 2$ ). [The technique of calculations for crystals with various degrees of disorder has been described by Bernstein & Mirsky (1978).] Fig. 6 illustrates that the Gaussian ellipsoids for the Rm data set fit well with a model of static or dynamic disorder. The positions found for the individual atoms at 298 K are just intermediate between those for the two-fold-related positions derived from the low-temperature structure.

Molecular-mechanics calculations (Maverick, Smith, Kozerski, Anet & Trueblood, 1975) indicate that the most important intramolecular 'strains' are of the type  $\text{H}(2)\cdots\text{H}(19)$  and  $\text{H}(3)\cdots\text{H}(10)$ , and that the strain energy decreases as the torsion angles around the exocyclic bonds approach  $90^\circ$ . The barrier to rotation

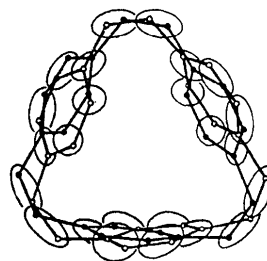


Fig. 6. Superposition of the ellipsoids for the C atoms in the room-temperature structure (Fig. 4) and the positions of two molecules: the molecule found in the low-temperature structure and one related to that molecule by a twofold rotation about the line  $0, y, 0.75$ .

about these bonds is expected to be low, in keeping with the observation that all aromatic H atoms are chemically equivalent in solution. In addition, a sort of cooperativity is apparent; the more nearly perpendicular one ring is to the reference plane (see *Introduction*), the greater the rotational freedom of the other two rings.

In the crystal at 113 K, however, the torsion angles around the exocyclic bonds may be strongly influenced by molecular packing. There are four  $\text{H}\cdots\text{H}$  distances shorter than  $2.40$  Å (separated by at least four bonds when intramolecular; C–H bond distances adjusted to  $1.08$  Å):

$\text{H}(13)\cdots\text{H}(18)$		$2.33$ Å
$\text{H}(2)\cdots\text{H}(3)$	at $-x, -y, 1-z$	$2.22$
$\text{H}(5)\cdots\text{H}(15)$	$\frac{1}{2} + x, -y - \frac{1}{2}, \frac{1}{2} + z$	$2.34$
$\text{H}(7)\cdots\text{H}(11)$	$\frac{1}{2} + x, -y - \frac{1}{2}, \frac{1}{2} + z$	$2.38$

Of these, three are intermolecular contacts.

The lattice-energy calculations described above were therefore supplemented by exploring the environment around a single molecule in the crystal. The same non-bonded potential parameters for C and H (Mirsky, 1976) were used in four separate calculations. Parameters were those of the low-temperature molecule, and the low-temperature space group, in the room-temperature unit cell (corresponding to the minimum-energy position in Fig. 5). Each of the individual aromatic rings was rotated about the axes C(1)–C(4), C(9)–C(12), and C(20)–C(17) respectively, using the method of Shmueli & Goldberg (1973). In addition, the entire molecule was rotated about a vector through the center of mass, parallel to  $\mathbf{c}^*$ . The results are shown in Fig. 7.

The first ring, C(1)–C(6), and the third ring, C(17)–C(22), were found to be in shallow wells (half-width at  $RT$  for 298 K about  $7^\circ$ ; see Fig. 7), asymmetric with respect to their non-bonded contacts. These two rings can achieve a lower potential energy (by about  $3$  kJ mol $^{-1}$ ) by rotating  $8$  or  $9^\circ$ , so that the rings are more nearly perpendicular to the plane of the entire molecule. The second ring, C(9)–C(14), lies in a symmetric and even more shallow well (half-width at

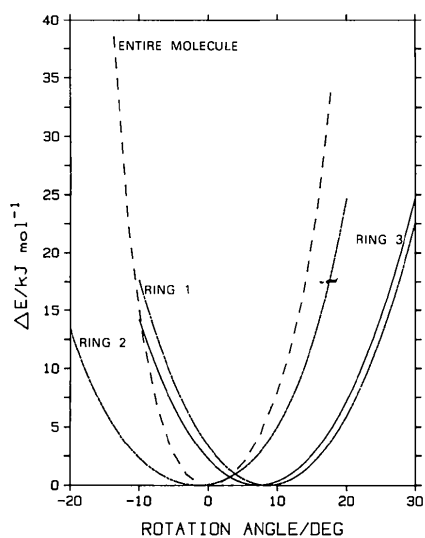


Fig. 7. Potential wells for the *L1* molecule and the individual aromatic rings with respect to rotation (see text) in the room-temperature unit cell. The zero of rotation corresponds to the minimum-energy structure in Fig. 5. The half-widths of the wells at  $2.5 \text{ kJ mol}^{-1}$  (which equals  $RT$  at 298 K) are about  $5^\circ$  for the entire molecule, about  $7^\circ$  for rings 1 and 3, and about  $9^\circ$  for ring 2. These values may be compared with the amplitudes of libration in the room-temperature structure,  $7^\circ$ ,  $5^\circ$  and  $13^\circ$ , respectively (see text).

$RT$  for 298 K about  $9^\circ$ ). Rotation of the entire molecule shows that a  $5^\circ$  rotation (to the average position found at room temperature) costs about  $3 \text{ kJ mol}^{-1}$ ; this value can be thought of as a maximum, since the rotation of other molecules and of the individual rings at the same time would reduce the barrier to rotation.

In conclusion, our crystallographic data and the potential-energy calculations are consistent with an ordered structure at 113 K in which individual rings are librating; the entire molecule librates as well. At 298 K, molecular motion has increased, and the cal-

culations suggest that the observed structure is a dynamic average of two equivalent molecules related by a twofold axis. The space group changes from  $P2_1/n$  to  $C2/c$ .

We are indebted to Drs Dewhirst and Cram for a sample of the title compound and to the staffs of the UCLA Office of Academic Computing and of the departmental VAX computer for facilitating this work.

#### References

- BERNSTEIN, J. & MIRSKY, K. (1978). *Acta Cryst.* **A34**, 161–165.
- COULTER, C. L. & TRUEBLOOD, K. N. (1963). *Acta Cryst.* **16**, 667–676.
- CRAM, D. J. & DEWHIRST, K. C. (1959). *J. Am. Chem. Soc.* **81**, 5963–5971.
- DUNITZ, J. D. & SEILER, P. (1973). *Acta Cryst.* **B29**, 589–595.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HIRSHFELD, F. L. (1976). *Acta Cryst.* **A32**, 239–244.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 73, 102. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KITAIGORODSKY, A. I. (1973). *Molecular Crystals and Molecules*. New York: Academic Press.
- LJUNGSTRÖM, E., LINDQVIST, O. & WENNERSTRÖM, O. (1978). *Acta Cryst.* **B34**, 1889–1893.
- MAVERICK, E., SMITH, S., KOZERSKI, L., ANET, F. A. L. & TRUEBLOOD, K. N. (1975). *Acta Cryst.* **B31**, 805–815.
- MIRSKY, K. (1976). *Acta Cryst.* **A32**, 199–207.
- ROSENFELD, R. E., TRUEBLOOD, K. N. & DUNITZ, J. D. (1978). *Acta Cryst.* **A34**, 828–829.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **A24**, 68–76.
- SHMUELI, U. & GOLDBERG, I. (1973). *Acta Cryst.* **B29**, 2466–2471.
- STROUSE, C. E. (1976). *Rev. Sci. Instrum.* **47**, 871–876.
- TRUEBLOOD, K. N. (1978). *Acta Cryst.* **A34**, 950–954.
- WILLIAMS, D. E. (1972). *Acta Cryst.* **A28**, 629–635.