

Structure of 4,7,12,15-Tetrahydro[2.2]paracyclophane;* a Molecule with Interdeck Through-Space Interaction

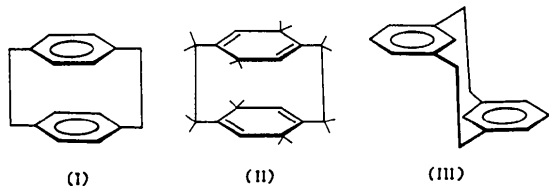
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Abstract. $C_{16}H_{20}$, $M_r = 212.33$, tetragonal, $P\bar{4}n2$, $a = b = 7.924$ (5), $c = 9.499$ (3) Å, $V = 596.44$ Å³, $Z = 2$, $D_x = 1.18$, $D_m = 1.24$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 3.2$ mm⁻¹, $F(000) = 232$, $T = 298$ K. Final $R = 0.025$ for 287 observed independent reflections. The structure consists of discrete chiral $C_{16}H_{20}$ molecules with ideal D_2 symmetry. The cyclohexadiene rings are distorted from a boat to a twist-like conformation, the double bonds being slightly non-planar. The shortest non-bonding distance between the two cyclohexadiene rings is 2.789 (3) Å, which is in the range that has been predicted on the basis of MINDO/3 and MINDO/1 calculations.

Introduction. [2.2]Paracyclophane (I) undergoes Birch reduction to give the tetrahydro product, 4,7,12,15-tetrahydro[2.2]paracyclophane (II) (Hopf, 1982). (II) was the subject of UV and CD spectroscopic investigations (Jenny & Reiner, 1970; Marshall & Folsom, 1971; Marshall & Hall, 1981); the photoelectron (PE) spectrum was also presented (Gleiter, Spanget-Larsen, Hopf & Mlynek, 1984). These efforts have been undertaken in order to learn more about the electronic structure of (II). The PE spectrum together with MINDO/3 and MINDO/1 calculations based on an essentially 'strain-free' Dreiding model of (II) showed that the interdeck through-space interaction is very sensitive to the C(1), C(1B) and C(1A), C(1AB) separations and that through-bond interaction *via* the ethano bridges seems to be relatively insignificant.



These results were contrary to those obtained by MINDO/2 calculations (Marshall & Hall, 1981), which implied that interaction between the two decks of (II)

contributes essentially nothing to the electronic transitions. By examination of a Dreiding model (Gleiter, Spanget-Larsen, Hopf & Mlynek, 1984) these non-bonding distances should be about 2.6 Å, whereas earlier MINDO/3 (Bingham, Dewar & Lo, 1975; Bischof, 1976, 1979) and MINDO/1 calculations (Dewar & Thiel, 1977; Bischof & Friedrich, 1982) yielded 3.1 and 2.9 Å respectively. The X-ray structure analysis presented in this paper has been undertaken to clarify the situation.

Experimental. Single crystals obtained by recrystallizing (II) from pentane solutions. Colorless crystal (0.3 × 0.2 × 0.2 mm) mounted on top of a glass capillary used for investigation. Lattice parameters derived from setting angles ($15 \leq 2\theta \leq 30^\circ$) of 39 machine-centered reflections (Siemens-Stoe AED2, monochromatic Mo $K\alpha$ radiation). Data collection (θ - 2θ scans, $2\theta \leq 50^\circ$, index range 0 to 11, 0 to 11 and 0 to 13) yielded 287 observed independent reflections with $I > 2.5\sigma(I)$ (643 unique reflections; 727 unobserved); equivalent reflections merged ($R_{\text{int}} = 0.017$). Systematic absences $0kl$ $k + l = 2n + 1$; $h00$ $h = 2n + 1$; $h0l$ $h + l = 2n + 1$; $0k0$ $k = 2n + 1$; $00l$ $l = 2n + 1$. Two standard reflections (004: $I_{\text{max}} 20530$, $I_{\text{min}} 20143$; 120: 9666, 9500) measured every 2 h, no significant fluctuations observed. Lorentz and polarization corrections as well as an empirical [ψ scans of two reflections with $10 < 2\theta < 22^\circ$, min. transmission 0.9 (max. = unity)] absorption correction applied.

The crystal system is tetragonal with space group $P\bar{4}n2$ (D_{2d}^8). Structure solved readily by direct methods and positions of H atoms taken from Fourier maps. Final refinement by a cascaded block-matrix procedure based on F with anisotropic temperature factors for all non-H atoms and isotropic for H covered with $wR = 0.024$ ($R = 0.025$).[‡] $S = 3.0$. Max. Δ/σ

* 4,7,12,15-Tetrahydro[2.2]parabenzenophane.

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[‡] Lists of structure factors, anisotropic thermal parameters, dihedral angles and non-bonded distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42666 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$, H $\times 10^3$) and isotropic temperature factors ($\times 10^3$)

	x	y	z	$U_{eq}^*/U(\text{\AA}^2)$
C(1)	3574 (2)	1031 (2)	3966 (2)	43 (1)
C(2)	4076 (2)	360 (3)	5392 (2)	52 (1)
C(3)	2562 (2)	174 (2)	3121 (2)	45 (1)
C(4)	4411 (3)	2607 (2)	3414 (2)	49 (1)
H(1)	324 (3)	-57 (2)	568 (2)	66 (5)
H(2)	405 (2)	125 (2)	617 (2)	54 (5)
H(3)	203 (2)	-85 (2)	348 (2)	50 (5)
H(4)	364 (3)	357 (3)	359 (2)	65 (5)
H(5)	548 (2)	288 (2)	396 (2)	60 (5)

* $U_{eq} = \frac{1}{3} \text{trace } U$, U signifying the diagonalized U matrix.

≤ 0.0005 [y C(4)]; largest features in final difference Fourier map: $+0.08$ and $-0.09 e \text{\AA}^{-3}$. Weighting scheme $w = 1/\sigma^2(F)$, calculations performed on a Data General Eclipse computer. Program packages: COSY85 (Stoe & Cie, 1985), STRUCSY (refinement) (Stoe & Cie, 1984) and SHELXTL (Sheldrick, 1983). Scattering factors including anomalous dispersion from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates are listed in Table 1, bond distances (in \AA) in Fig. 1 and angles in Table 2; Fig. 1 shows a view of the paracyclophane together with the numbering of the atoms. (II) forms discrete chiral $C_{16}H_{20}$ molecules with ideal D_2 symmetry due to crystallographic reasons ($Z = 2$, $P4n2$). The conformation of the two cyclohexadiene rings is best described as distorted from a boat to a twist-like conformation. The deviation of C(4) and C(4A) from the least-squares plane defined by C(1), C(3), C(1A), C(3A) is $0.371(6) \text{\AA}$. The double bonds are slightly non-planar, the angle between the lines C(1), C(3) and C(1A), C(3A) being $7.5(2)^\circ$. The length of the double bonds in the ring is $1.322(2) \text{\AA}$; this is as expected as are the $C_{sp^2}-C_{sp^3}$ distances in the ring [$1.501(3)$ and $1.508(2) \text{\AA}$]. The distance between C(1) and C(2) is $1.508(2) \text{\AA}$, a value identical to the corresponding distances in (I) (Hope, Bernstein & Trueblood, 1972) and [2.2]-metacyclophane (III) (Kai, Yasuoka & Kasai, 1977) with $1.509(1)$ and $1.506(1) \text{\AA}$ respectively. The $C_{sp^2}-C_{sp^3}$ distances in the ethano bridges of (I) (1.562\AA), (II) [$1.572(4) \text{\AA}$] and (III) [$1.568(1) \text{\AA}$] do not differ significantly. In the tetrahydro compound (II) the two ethano bridges are non-planar with an angle of $47.4(2)^\circ$ [\angle C(2), C(2B)/C(2A), C(2AB)].

The non-bonding distances between C(1) and C(1A) and between C(1A) and C(1AB) are $2.789(3) \text{\AA}$. This value deviates from those derived from MINDO/3 (Bingham *et al.*, 1975; Bischof, 1976, 1979) and MINDO/1 (Dewar & Thiel, 1977; Bischof & Friedrich, 1982) calculations. Nevertheless the agreement can be considered fairly good in view of the methods involved.

Table 2. Bond angles ($^\circ$)

C(2)-C(1)-C(3)	121.6 (2)	C(2)-C(1)-C(4)	119.2 (1)
C(3)-C(1)-C(4)	118.7 (2)	C(1)-C(2)-C(2B)	111.9 (1)
C(1)-C(3)-C(4A)	122.1 (2)	C(1)-C(4)-C(3A)	111.1 (1)
C(1)-C(2)-H(1)	109 (1)	C(1)-C(3)-H(3)	119 (1)
C(1)-C(2)-H(2)	114 (1)	C(4A)-C(3)-H(3)	119 (1)
H(1)-C(2)-H(2)	107 (2)	C(1)-C(4)-H(4)	108 (1)
H(1)-C(2)-C(2B)	110 (1)	C(1)-C(4)-H(5)	111 (1)
H(2)-C(2)-C(2B)	106 (1)	H(4)-C(4)-H(5)	105 (2)
		H(4)-C(4)-C(3A)	112 (1)
		H(5)-C(4)-C(3A)	110 (1)

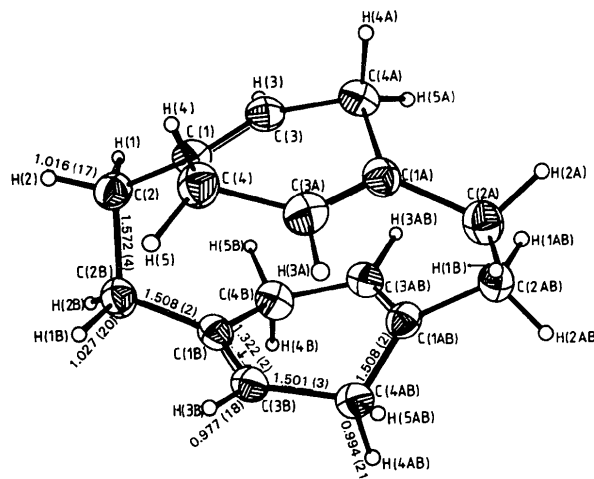


Fig. 1. The molecular structure and atomic-numbering scheme of (II). The thermal ellipsoids include 50% probability and H atoms are drawn as spheres of radius 0.1\AA .

References

- BINGHAM, R. C., DEWAR, M. J. S. & LO, D. H. (1975). *J. Am. Chem. Soc.* **97**, 1255-1256.
- BISCHOF, P. (1976). *J. Am. Chem. Soc.* **98**, 6844-6849.
- BISCHOF, P. (1979). *Quantum Chem. Program Exch.* **12**, 383.
- BISCHOF, P. & FRIEDRICH, G. (1982). *J. Comput. Chem.* **3**, 486-494.
- DEWAR, M. J. S. & THIEL, W. (1977). *J. Am. Chem. Soc.* **99**, 4899-4907.
- GLEITER, R., SPANGET-LARSEN, J., HOPF, H. & MLYNEK, C. (1984). *Chem. Ber.* **117**, 1987-1990.
- HOPE, H., BERNSTEIN, J. & TRUEBLOOD, K. N. (1972). *Acta Cryst.* **B28**, 1733-1743.
- HOPF, H. (1982). *Angew. Chem.* **94**, 485-496.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JENNY, W. & REINER, J. (1970). *Chimia*, **24**, 69-71.
- KAI, Y., YASUOKA, N. & KASAI, N. (1977). *Acta Cryst.* **B33**, 754-762.
- MARSHALL, J. L. & FOLSOM, T. K. (1971). *Tetrahedron Lett.* pp. 757-760.
- MARSHALL, J. L. & HALL, L. (1981). *Tetrahedron*, **37**, 1271-1275.
- SHELDRICK, G. M. (1983). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen, Federal Republic of Germany.
- Stoe & Cie (1984). *STRUCSY. Structure System Program Package*. Stoe & Cie, Darmstadt, Federal Republic of Germany.
- Stoe & Cie (1985). *COSY85. Diffractometer Control Program of the Siemens/Stoe AED2*. Stoe & Cie, Darmstadt, Federal Republic of Germany.