

Triple-Layered [2.2]Metacyclophane, Methylated Derivative of the *ud* Isomer*

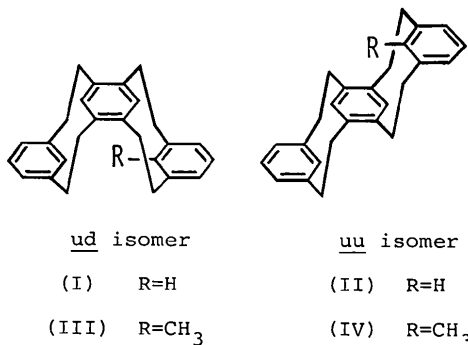
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Abstract. $C_{27}H_{28}$, FW 352.5, monoclinic, space group $P2_1/c$, $a = 10.090$ (2), $b = 14.501$ (2), $c = 13.677$ (3) Å, $\beta = 101.09$ (2)°, $U = 1063.8$ (7) Å³, $D_m = 1.200$ (by flotation), $D_x = 1.192$ g cm⁻³, $Z = 4$, $R = 0.055$ for 2636 non-zero reflexions. The molecular structure shows the existence of large steric repulsion between the terminal benzene rings, resulting from the substitution of a methyl group into one of the rings. There is disorder of the methyl group.

Introduction. As part of a series of structural studies on layered cyclophanes the X-ray structure determination of two geometrical isomers of triple-layered [2.2]metacyclophanes (I and II) and their methylated derivatives (III and IV) has been carried out. The molecular structures of (I) and (IV) have been reported (Kai, Yasuoka & Kasai, 1977; Hama, Kai, Yasuoka & Kasai, 1977).



In this paper the molecular structure of (III), which is expected to have most strained molecular structure of the four, will be described.

A Rigaku automated four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation was used for the measurement of lattice parameters and intensities. Diffraction intensities were measured by the θ - 2θ scan method at a rate of 4° min⁻¹ using a crystal with dimensions of 0.20 × 0.20 × 0.20 mm. Backgrounds were counted for 7.5 s before and after the scan of each peak. 2941 (2636 non-zero) unique data collected up to $2\theta = 120^\circ$ were corrected for the Lp effect but not for absorption [$\mu(\text{Cu } K\alpha) = 5.1$ cm⁻¹]. The structure was solved by

the direct method with *MULTAN* (Germain, Main & Woolfson, 1971). All the C atoms appeared clearly in the *E* map based on the set of signs with the highest figure of merit. The refinement was carried out by a block-diagonal least-squares procedure (*HBL5-V*; Ashida, 1973). After an anisotropic refinement of C atoms a difference Fourier map was computed in which all the peaks except a relatively high one could easily be attributed to the H atoms. The remaining peak is at a distance of 1.55 Å from C(8). By careful re-examination of the difference Fourier map the extra peak was assigned as the methyl C atom attached to C(8) as a result of a stacking disorder of the molecules, which was later confirmed by the refinement. Occupancies of these methyl C atoms, C(27) and C(27') bonded to C(24) and C(8) respectively, were determined from the peak heights in the difference Fourier map as 0.75 and 0.25, which were fixed in the later refinement. The H atoms with the lower occupancy could not be located uniquely; therefore the three methyl H atoms attached to C(27') and one to C(24) were not included in the structure factor calculation. The weighting schemes used were: $w = [\sigma(F_o)^2 + a|F_o| + b|F_o|^2]^{-1}$ and $w = c$ for observed and unobserved reflexions respectively. The final *R* value was 0.055 for the non-zero (0.065 for all) reflexions, and $R_w = 0.090$ with $a = 0.006$, $b = 0.004$ and $c = 0.959$. Atomic scattering factors for C were taken from Hanson, Herman, Lea & Skillman (1964), and for H from Stewart, Davidson & Simpson (1965). The final atomic parameters are listed in Table 1.†

Discussion.‡ A perspective view of the molecule with the atom numbering is given in Fig. 1 (*ORTEP*; Johnson, 1976). Interatomic distances and bond angles are given in Fig. 2, their e.s.d.'s being 0.004 Å and 0.2–0.3°, respectively. The molecular structure of (I) could be described as having *mm2* symmetry to a good

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33727 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

‡ The disordered methyl group with lower occupancy is excluded from the discussion.

* Structural Chemistry of Layered Cyclophanes. V.

Table 1. Fractional atomic coordinates with e.s.d.'s in parentheses

(a) C atoms ($\times 10^4$)

	x	y	z
C(1)	-1034 (2)	1482 (2)	741 (2)
C(2)	-1299 (3)	2052 (2)	-232 (2)
C(3)	-1614 (2)	3046 (2)	-30 (2)
C(4)	-2905 (3)	3328 (2)	49 (2)
C(5)	-3113 (3)	4153 (2)	485 (2)
C(6)	-2017 (3)	4665 (2)	943 (2)
C(7)	-713 (2)	4410 (2)	892 (2)
C(8)	-551 (2)	3639 (2)	318 (2)
C(9)	491 (2)	4784 (2)	1604 (2)
C(10)	766 (2)	4215 (2)	2598 (2)
C(11)	1054 (2)	3205 (1)	2453 (1)
C(12)	-21 (2)	2649 (1)	2003 (2)
C(13)	155 (2)	1826 (1)	1516 (2)
C(14)	1442 (2)	1427 (1)	1702 (2)
C(15)	2454 (2)	1888 (1)	2364 (1)
C(16)	2346 (2)	2808 (1)	2643 (1)
C(17)	3652 (2)	3320 (2)	3042 (2)
C(18)	4533 (2)	3533 (2)	2246 (2)
C(19)	4896 (2)	2651 (2)	1780 (2)
C(20)	5955 (2)	2106 (2)	2266 (2)
C(21)	6058 (3)	1190 (2)	2003 (2)
C(22)	5058 (3)	797 (2)	1321 (2)
C(23)	3982 (2)	1316 (2)	823 (2)
C(24)	3977 (2)	2269 (2)	980 (2)
C(25)	2689 (2)	826 (2)	354 (2)
C(26)	1854 (2)	590 (2)	1171 (2)
C(27)	2949 (3)	2906 (2)	344 (2)
C(27')*	861 (8)	3342 (6)	-10 (6)

(b) H atoms ($\times 10^3$)

	x	y	z
H(1A)	-91 (2)	87 (2)	58 (2)
H(1B)	-189 (2)	153 (2)	101 (2)
H(2A)	-50 (2)	200 (2)	-54 (2)
H(2B)	-209 (3)	178 (2)	-65 (2)
H(4)	-358 (3)	300 (2)	-11 (2)
H(5)	-399 (3)	436 (2)	55 (2)
H(6)	-219 (3)	512 (2)	125 (2)
H(8)	35 (3)	349 (2)	27 (2)
H(9A)	45 (2)	548 (2)	178 (2)
H(9B)	131 (2)	472 (2)	128 (2)
H(10A)	-2 (2)	427 (2)	284 (2)
H(10B)	160 (2)	449 (2)	302 (2)
H(12)	-93 (2)	292 (1)	196 (1)
H(15)	328 (2)	158 (1)	254 (1)
H(17A)	419 (2)	293 (2)	357 (2)
H(17B)	353 (2)	395 (2)	329 (2)
H(18A)	537 (3)	383 (2)	261 (2)
H(18B)	394 (2)	400 (2)	167 (2)
H(20)	657 (2)	240 (2)	289 (2)
H(21)	677 (3)	80 (2)	243 (2)
H(22)	502 (3)	11 (2)	123 (2)
H(25A)	282 (2)	27 (2)	2 (2)
H(25B)	210 (3)	126 (2)	-24 (2)
H(26A)	245 (2)	13 (2)	169 (2)
H(26B)	105 (2)	24 (2)	87 (2)
H(27A)†	347 (3)	346 (2)	24 (3)
H(27B)†	248 (4)	275 (3)	-24 (3)
H(27C)†	217 (4)	304 (2)	69 (3)

* C atom of the disordered methyl group of the lower occupancy [attached to C(8)].

† H atoms of the disordered methyl group of the lower occupancy could not be located.

approximation (Kai, Yasuoka & Kasai, 1977). Assuming the same symmetry for the structure of (III), except the methyl group, the mean structure was determined, which was compared with that of (I) in Table 2. Some noticeable features are revealed: (1) the values of $\sigma(\bar{x})$ of c and f and that of 4 are large, (2) the $\sigma(\bar{x})$ values of a and e are also large, (3) the non-bonded distance f is much longer (0.031 Å) than that in (I), (4) good agreement is observed between the bond distances and angles of (I) and (III) except those pointed out in (1), (2) and (3). The feature pointed out in (1) is due to the deformation of the molecular structure from the assumed $mm2$ symmetry by the introduction of a methyl group at C(24). The molecular structure is different from that of (IV). However, a similar effect of

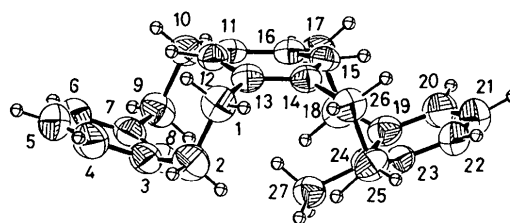


Fig. 1. Perspective view of the molecule illustrating the thermal ellipsoids (50%) and atom numbering. In Figs. 1–3 the disordered methyl carbon atom of the lower occupancy, C(27') attached to C(8), is omitted for clarity.

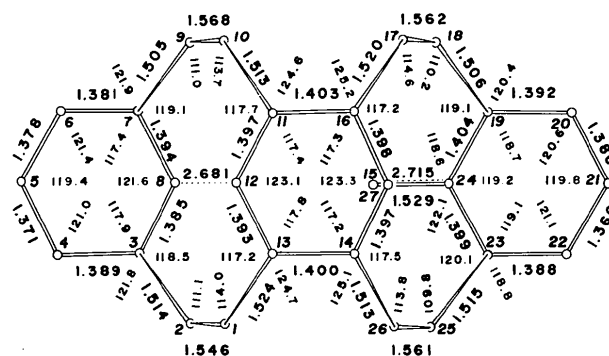


Fig. 2. Projection of the molecule onto the plane of C(11), C(13), C(14) and C(16) with selected bond distances and bond angles.

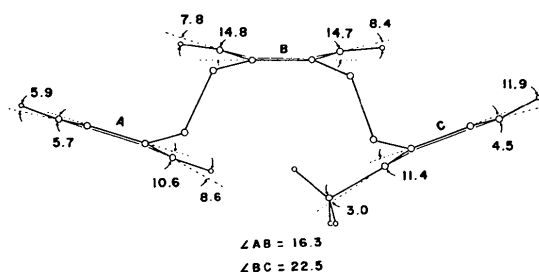
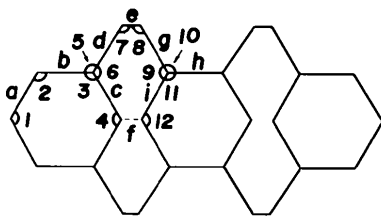


Fig. 3. Side view of the molecule indicating the out-of-plane deformations of the benzene rings. Each benzene-ring plane is defined by the central four C atoms in the ring.

Table 2. Mean molecular structures of (I) and (III)

The mean number is the mean bond distance, $\bar{x} = \Sigma x_i/n$, where x_i is the individual bond distance observed, and n is the number of chemically equivalent bond distances. The lower number is the estimated standard deviation of the mean, $\sigma(\bar{x}) = (s^2/n)^{1/2}$, where s is the variance, $s = \Sigma (x_i - \bar{x})^2/(n - 1)$.



Bond	<i>n</i>	(I)	(III)	Angle	<i>n</i>	(I)	(III)
<i>a</i>	4	1.3868 Å	1.3738 Å	<i>1</i>	2	120.15°	119.60°
		19	55			35	20
<i>b</i>	4	1.3920	1.3875	<i>2</i>	4	120.47	121.03
		21	23			6	17
<i>c</i>	4	1.3923	1.3955	<i>3</i>	4	118.03	118.28
		27	40			10	38
<i>d</i>	4	1.5060	1.5100	<i>4</i>	2	121.85	120.40
		0	26			15	120
<i>e</i>	4	1.5653	1.5593	<i>5</i>	4	121.50	120.73
		11	47			16	33
<i>f</i>	2	2.6665	2.6980	<i>6</i>	4	119.10	119.20
		49	170			12	33
<i>g</i>	4	1.5150	1.5175	<i>7</i>	4	110.78	110.53
		17	27			10	31
<i>h</i>	2	1.4005	1.4015	<i>8</i>	4	112.63	114.03
		5	15			28	20
<i>i</i>	4	1.3995	1.3963	<i>9</i>	4	117.35	117.40
		20	11			5	12
				<i>10</i>	4	124.30	124.90
						15	15
				<i>11</i>	4	117.70	117.43
						4	13
				<i>12</i>	2	123.30	123.20
						60	10

an electron-releasing methyl group on the deformation of the benzene rings to that in (IV) (Hama, Kai, Yasuoka & Kasai, 1977) is observed. (3) is due to the steric repulsion between the methyl group and the terminal benzene ring opposite it. The shortest non-bonded distance between H(8) and the methyl hydrogen atoms is 1.92 Å. Fig. 3 shows a side view of the molecule indicating the out-of-plane deformations of the benzene rings. The three benzene rings are in the boat conformation. They deviate from the mutually parallel position because of the large steric repulsion between them and the methyl group. The dihedral angles between the benzene planes, $\angle AB = 16.3^\circ$ and $\angle BC = 22.5^\circ$ (Fig. 3), are much larger than those in (I) (1.3 and 10.4° , respectively).

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Structure of Thiamine Free Base

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Abstract. $C_{12}H_{16}N_4OS$, 2,6a-dimethyl-6a,8,9,9a,10a,11-hexahydrofuro[2,3-*h*]thiachromine, monoclinic, $P2_1/c$, $a = 6.789$ (1), $b = 15.682$ (1), $c = 12.857$ (1) Å, $\beta = 116.84$ (1)°, $Z = 4$, $D_x = 1.44$, $D_m = 1.42$ g cm⁻³. Molecules related by a center of symmetry form a dimer through a pair of N-H...N

hydrogen bonds. One of the S-C bonds is unusually long (1.895 Å).

Introduction. Thiamine free base was obtained by passing carbon dioxide gas into a dioxane solution of a thiamine sodium salt. Its molecular structure has been