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

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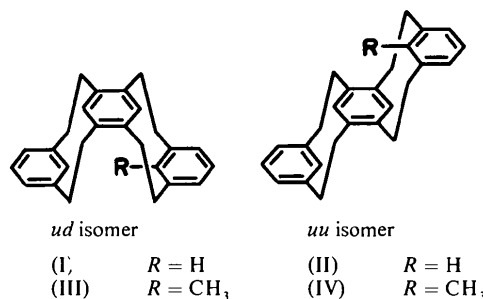*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, Japan*

**Abstract.** $C_{27}H_{28}$, FW 352·5, monoclinic, space group $P2_1/c$, $a = 7·651$ (1), $b = 19·856$ (1), $c = 14·556$ (1) Å, $\beta = 117·84$ (1)°, $D_m = 1·20$ (by flotation), $D_x = 1·197$ g cm$^{-3}$, $Z = 4$, $R = 0·059$ for 2531 non-zero reflexions. The central benzene ring has a chair conformation and the two terminal benzene rings have boat forms.

**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]metacyclophane (I and II) and their methylated derivatives (III and IV) has been carried out. The molecular and crystal structure of (I) has been reported

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* Structural Chemistry of Layered Cyclophanes. II.

(Kai, Yasuoka & Kasai, 1977). In this paper the molecular structure of (IV) will be described.



| *ud* isomer | | *uu* isomer | |
|---|---|---|---|
| (I) | $R = H$ | (II) | $R = H$ |
| (III) | $R = CH_3$ | (IV) | $R = CH_3$ |

A Rigaku automated four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation was used for the measure-

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

(*a*) C atoms (× 10⁴)

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| C(1) | 5960 (3) | −659 (1) | 3772 (2) |
| C(2) | 7049 (3) | −83 (1) | 3497 (2) |
| C(3) | 6215 (3) | 597 (1) | 3537 (2) |
| C(4) | 6928 (3) | 955 (1) | 4467 (2) |
| C(5) | 5844 (4) | 1489 (1) | 4562 (2) |
| C(6) | 3980 (3) | 1630 (1) | 3776 (2) |
| C(7) | 3218 (3) | 1277 (1) | 2844 (2) |
| C(8) | 4433 (3) | 807 (1) | 2712 (2) |
| C(9) | 1022 (3) | 1276 (1) | 2110 (2) |
| C(10) | −28 (3) | 709 (1) | 2423 (2) |
| C(11) | 752 (3) | 28 (1) | 2320 (2) |
| C(12) | 2615 (3) | −162 (1) | 3109 (2) |
| C(13) | 3775 (3) | −665 (1) | 2998 (2) |
| C(14) | 2957 (3) | −1046 (1) | 2079 (2) |
| C(15) | 1121 (3) | −852 (1) | 1290 (2) |
| C(16) | −49 (3) | −349 (1) | 1397 (2) |
| C(17) | −2216 (3) | −333 (1) | 595 (2) |
| C(18) | −3393 (3) | −923 (1) | 786 (2) |
| C(19) | −2541 (3) | −1597 (1) | 714 (2) |
| C(20) | −3135 (3) | −1874 (1) | −264 (2) |
| C(21) | −2036 (3) | −2373 (1) | −413 (2) |
| C(22) | −223 (3) | −2551 (1) | 403 (2) |
| C(23) | 422 (3) | −2284 (1) | 1392 (2) |
| C(24) | −865 (3) | −1858 (1) | 1572 (2) |
| C(25) | 2590 (3) | −2319 (1) | 2156 (2) |
| C(26) | 3730 (3) | −1724 (1) | 1954 (2) |
| C(27) | −380 (3) | −1662 (1) | 2666 (2) |

(*b*) H atoms (× 10³)

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| H(1*A*) | 613 (3) | −58 (1) | 452 (2) |
| H(1*B*) | 669 (3) | −112 (1) | 377 (2) |
| H(2*A*) | 684 (3) | −18 (1) | 273 (2) |
| H(2*B*) | 853 (3) | −11 (1) | 403 (2) |
| H(4) | 818 (3) | 81 (1) | 509 (2) |
| H(5) | 650 (3) | 174 (1) | 527 (2) |
| H(6) | 316 (3) | 200 (1) | 389 (2) |
| H(8) | 396 (3) | 57 (1) | 204 (2) |
| H(9*A*) | 67 (3) | 119 (1) | 134 (2) |
| H(9*B*) | 42 (3) | 172 (1) | 215 (2) |
| H(10*A*) | −155 (3) | 74 (1) | 194 (2) |
| H(10*B*) | 27 (3) | 79 (1) | 318 (2) |
| H(12) | 318 (3) | 11 (1) | 380 (1) |
| H(15) | 57 (3) | −111 (1) | 59 (2) |
| H(17*A*) | −231 (3) | −39 (1) | −16 (2) |
| H(17*B*) | −284 (4) | 13 (1) | 63 (2) |
| H(18*A*) | −479 (4) | −89 (1) | 27 (2) |
| H(18*B*) | −330 (3) | −84 (1) | 154 (2) |
| H(20) | −442 (3) | −168 (1) | −92 (2) |
| H(21) | −255 (4) | −258 (1) | −116 (2) |
| H(22) | 69 (4) | −288 (1) | 27 (2) |
| H(25*A*) | 321 (3) | −275 (1) | 209 (2) |
| H(25*B*) | 282 (3) | −228 (1) | 293 (2) |
| H(26*A*) | 519 (3) | −177 (1) | 244 (2) |
| H(26*B*) | 350 (3) | −177 (1) | 120 (2) |
| H(27*A*) | 24 (4) | −204 (1) | 321 (2) |
| H(27*B*) | −157 (3) | −152 (2) | 273 (2) |
| H(27*C*) | 45 (4) | −126 (2) | 292 (2) |

ment of lattice parameters and intensities. Systematic absences (*h0l* for *l* odd and 0*k*0 for *k* odd) indicated the space group $P2_1/c$. Intensities were measured by the $\theta$–$2\theta$ scan method at a rate of 4° min$^{-1}$ using a crystal with dimensions 0·1 × 0·2 × 0·3 mm. Backgrounds were counted for 7·5 s before and after the scan of each peak. 2918 unique data collected up to $2\theta$ = 120° were corrected for the Lp effect but not for absorption [$\mu$(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. All the H atoms were located by difference syntheses. The refinement was carried out by block-diagonal least-squares calculations (*HBLS*-V; Ashida, 1973) with anisotropic temperature factors for C atoms and isotropic for H atoms. 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* values were 0·059 for the non-zero reflexions and 0·073 for all the reflexions, and $R_w$ = 0·087 with $a = -0·127$, $b = 0·007$ and $c = 0·626$. 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.** An *ORTEP* (Johnson, 1976) drawing of the molecular structure is shown in Fig. 1 together with the atom numbering. Interatomic distances and bond angles are given in Fig. 2, their e.s.d.'s being 0·004 Å and 0·2° respectively. Assuming molecular symmetry

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* Tables of thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32881 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
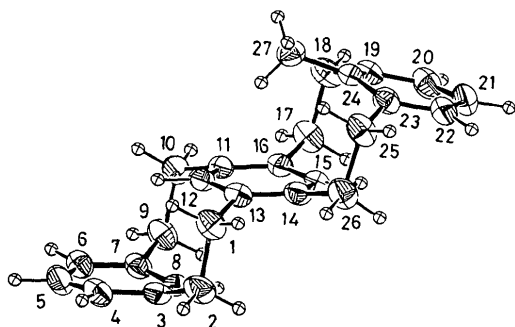


Fig. 1. Perspective view of the molecule illustrating the thermal ellipsoids (50%) and atom numbering.
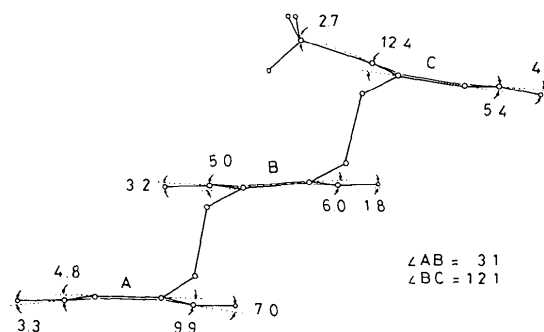


Fig. 3. Side view of the molecule indicating the out-of-plane deformations of the benzene rings. Each benzene-ring plane is defined by the central four C atoms in the ring.
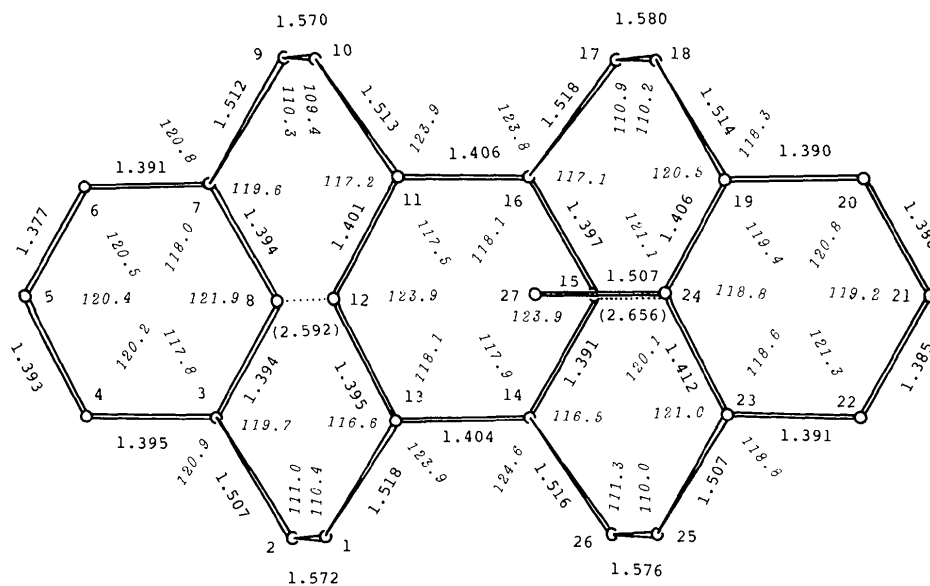


Fig. 2. Projection of the molecule onto the best plane of C(11), C(13), C(14) and C(16) with selected bond distances and bond angles.

Table 2. *Mean molecular structures of* (I) *and* (IV)

The upper 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, $s = \Sigma\,(x_i - \bar{x})^2/(n - 1)$.
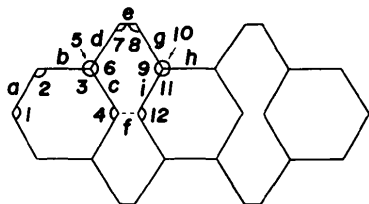


| Bond | $n$ | (I) | (IV) | Angle | $n$ | (I) | (IV) |
|---|---|---|---|---|---|---|---|
| a | 4 | 1·3868 Å | 1·3848 Å | 1 | 2 | 120·15° | 119·80° |
|  |  | 19 | 35 |  |  | 35 | 60 |
| b | 4 | 1·3920 | 1·3918 | 2 | 4 | 120·47 | 120·70 |
|  |  | 21 | 11 |  |  | 6 | 23 |
| c | 4 | 1·3923 | 1·4015 | 3 | 4 | 118·03 | 118·45 |
|  |  | 27 | 45 |  |  | 10 | 36 |
| d | 4 | 1·5060 | 1·5100 | 4 | 2 | 121·85 | 120·35 |
|  |  | 0 | 18 |  |  | 15 | 155 |
| e | 4 | 1·5653 | 1·5745 | 5 | 4 | 121·50 | 119·70 |
|  |  | 11 | 22 |  |  | 16 | 67 |
| f | 2 | 2·6665 | 2·6240 | 6 | 4 | 119·10 | 120·20 |
|  |  | 49 | 320 |  |  | 12 | 33 |
| g | 4 | 1·5150 | 1·5163 | 7 | 4 | 110·78 | 110·38 |
|  |  | 17 | 12 |  |  | 10 | 22 |
| h | 2 | 1·4005 | 1·4050 | 8 | 4 | 112·63 | 110·50 |
|  |  | 5 | 10 |  |  | 28 | 41 |
| i | 4 | 1·3995 | 1·3960 | 9 | 4 | 117·35 | 116·85 |
|  |  | 20 | 21 |  |  | 5 | 18 |
|  |  |  |  | 10 | 4 | 124·30 | 124·05 |
|  |  |  |  |  |  | 15 | 18 |
|  |  |  |  | 11 | 4 | 117·70 | 117·90 |
|  |  |  |  |  |  | 4 | 14 |
|  |  |  |  | 12 | 2 | 123·30 | 123·90 |
|  |  |  |  |  |  | 60 | 0 |

$2/m$, the mean bond distances and bond angles have been calculated and are listed in Table 2. The e.s.d., $\sigma(\bar{x})$, of each mean value was also calculated in order to estimate the correlation between chemically equivalent parts of the molecule. The average molecular structure of (I) with $mm2$ symmetry is also shown in Table 2. By comparing the two molecular structures some noticeable features are revealed: (1) the values of $\sigma(\bar{x})$ of $c$ and $f$ and that of $4$ are very large, (2) the non-bonded distance $f$ in (IV) is much shorter (0·043 Å) than that in (I), (3) the bridging methylene bond $e$ in (IV) is slightly (0·010 Å) longer than the corresponding bond in (I), and (4) good agreement is observed between the other bond distances and bond angles of (I) and (IV). (1) is

due to the deformation of the molecular structure from the assumed $2/m$ symmetry by the introduction of a methyl group at C(24). In the molecular structure of benzene derivatives it is well known that an electron-releasing substituent such as a methyl group causes a decrease in the endocyclic angle and an increase in the adjacent C—C bond distances because of the increase in $p$ character of the hybrid orbitals of these bonds. The endocyclic angle C(23)—C(24)—C(19) (118·8°) is significantly smaller than C(3)—C(8)—C(7) (121·9°). On the other hand, the average bond distance (1·409 Å) of C(23)—C(24) and C(19)—C(24) is slightly longer than that (1·394 Å) of C(3)—C(8) and C(7)—C(8). The features pointed out in (2) and (3) are probably related to the different conformations of the central benzene rings: a boat form in (I) and a chair form in (IV). Fig. 3 shows a side view of the molecular structure indicating the out-of-plane deformations of the benzene rings. The deformation angles in benzene ring $A$ are 9·9° at C(8) and 4·8° at C(5), which are equal to the corresponding angles in (I), 10·0 and 4·9° respectively. In ring $C$, however, the deformation angle at C(24) is relatively large (12·4°). The dihedral angles between the benzene planes (Fig. 3) are $\angle AB = 3\cdot1°$ and $\angle BC = 12\cdot1°$. These features are due to the steric repulsion between the methyl substituent and the central benzene ring. The different conformations of the central benzene rings in (I) (boat) and (IV) (chair) indicate an addition effect of the two terminal benzene rings on the out-of-plane deformation of the central benzene ring which has been described in part I of this series (Kai, Yasuoka & Kasai, 1977).

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