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Pentacyclo[19.3.1.1^{2,6}.1^{9,13}.1^{14,18}]octacosa-1(25),2,4,6(28),9,11,13(27),14,16,18(26),21,23-dodecaene ([2.0.2.0]-*m*-Cyclophane)

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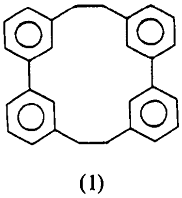
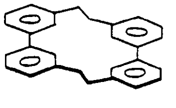
Abstract. $C_{28}H_{24}$, $M_r = 360{\cdot}5$, orthorhombic, $Pbca$, $a = 8{\cdot}968\,(4)$, $b = 12{\cdot}337\,(3)$, $c = 36{\cdot}75\,(1)$ Å, $V = 4066\,(3)$ Å^3, $Z = 8$, $D_x = 1{\cdot}18$ g cm^{-3}, D_m not measured, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}62$ cm^{-1}, $F(000) = 1536$, $T = 295$ K, final $R = 0{\cdot}044$ for 2175 observed reflections. The conformation of the title compound in the crystalline state is established by an X-ray study as being one which approaches D_2 symmetry, proposed to predominate for the compound in solution on the basis of NMR studies. The angles of twist between aromatic rings in the biphenyl systems are 46·8 (2) and 52·1 (2)° rather than ~30° as proposed for the molecule in solution or 89·9° as observed in an X-ray study of a related compound.

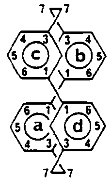
Introduction. The title compound (1), first prepared by Vögtle (1969), was noted by Leach & Reiss (1978) to have aromatic protons absorbing unusually far upfield in the NMR, and an '*anti*' conformation (1*a*) was proposed to predominate in solution to fit this finding. In 1981 (Olsson, Tanner, Thulin, Wennerström & Liljefors, 1981), the NMR spectrum was reinterpreted as showing a twisted D_2 conformation (1*b*) to predominate, and variable-temperature NMR behavior was noted and rationalized in terms of equilibrating enantiomeric D_2 forms. The angle of twist between adjacent aromatic rings was estimated to be about 30°. An X-ray study on the corresponding molecule with methoxyl groups in the 2 positions and methyl groups in the 5 positions found D_2 symmetry with twist angles of 89·9° between adjacent aromatic rings (Kaneda *et al.*, 1985). We recently found a better synthetic route to (1) (and many other cyclophanes) (Bates, White, Kane & Mishra, 1986), and when this compound was found to crystallize well, we performed an X-ray study on it to determine its conformation in the solid state.



(1)



(1*a*)



(1*b*)

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Experimental. Colorless crystals grown by slow evaporation from pentane at 263 K. Crystal dimensions 0·5 × 0·5 × 0·5 mm. Syntex $P2_1$ diffractometer. Cell constants from 25 reflections with $13 \leq 2\theta \leq 27°$. Systematic absences: $0kl$, $k = 2n$; $h0l$, $h = 2n$; $hk0$, $h = 2n$. $2\theta_{\max} = 50°$. Range of hkl: 0→10, 0→14, 0→43. Two check reflections every 98 data points showed 3·6% average decay, so linear decay correction applied. No absorption correction. 2175 of 3583 reflections with $I > 3\sigma(I)$ used in F^2 full-matrix refinement, $R_{\text{int}} = 0{\cdot}036$. Structure solved by *MULTAN*80 (Main *et al.*, 1980) using 288 highest E values; all non-H atoms found in first E map. Refinement of non-H atoms with isotropic temperature factors gave $R = 0{\cdot}13$; final refinement (253 parameters) of non-H atoms with anisotropic temperature factors after adding H atoms in calculated positions with isotropic temperature factors of 5·0 Å^2, $R = 0{\cdot}044$, $wR = 0{\cdot}049$, $S = 1{\cdot}8$, weighting scheme of Corfield, Doedens & Ibers (1967), with $p = 0{\cdot}03$. $(\Delta/\sigma)_{\max} = 0{\cdot}1$. $\Delta\rho = -1{\cdot}0 \rightarrow 1{\cdot}0$ e Å^{-3}. No anomalous-dispersion corrections. Atomic scattering factors from Cromer & Waber (1974). Programs *SDP* (Frenz, 1978), including plotter program *ORTEP*II (Johnson, 1976), run on PDP 11/34a.

Discussion. Fig. 1 shows two views of a molecule of (1), Table 1 lists the final positional and isotropic thermal parameters, and Table 2 gives bond distances and bond angles.* The molecules in the crystal are in twisted conformations (1*b*) with approximate D_2 symmetry as found in solution by Olsson *et al.* (1981). Each unit cell contains four molecules of each enantiomer.

How closely the molecules approach the D_2 symmetry observed for the analog with 2-methoxyls and 5-methyls (Kaneda *et al.*, 1985) can be seen by examining the parameters which would be the same with this symmetry. In Table 2, averaged distances and angles are given for each group of bonds which would be equivalent if the molecule had D_2 symmetry, since all the values which would be the same were within three standard deviations of the averaged values. Torsion angles C(3*a*)—C(7*a*)—C(7*d*)—C(3*d*) = −63·7 (2)° and C(3*b*)—C(7*b*)—C(7*c*)—C(3*c*) = −63·5 (2)° are also within experimental error of one another. However, other torsion angles show the conformation to be considerably more than experimental error away from having D_2 symmetry: C(2*a*)—C(3*a*)—C(7*a*)—C(7*d*) = 79·7 (2), C(2*b*)—C(3*b*)—C(7*b*)—C(7*c*) = 95·0 (2), C(2*c*)—C(3*c*)—C(7*c*)—C(7*b*) = 84·1 (2), and C(2*d*)—C(3*d*)—C(7*d*)—C(7*a*) = 94·1 (2)°. In addition, the angles of twist between the benzene rings within

Table 1. *Positional parameters and their e.s.d.'s*

$B_{\text{eq}} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$

	x	y	z	B_{eq}(Å^2)
C(1*a*)	1·2440 (3)	−0·0828 (2)	0·17100 (5)	3·30 (4)
C(1*b*)	1·3315 (2)	−0·0409 (2)	0·13950 (5)	3·42 (4)
C(1*c*)	0·9309 (2)	−0·0114 (2)	0·07899 (5)	3·45 (4)
C(1*d*)	0·8912 (2)	0·0598 (2)	0·11005 (6)	3·34 (4)
C(2*a*)	1·1436 (2)	−0·0152 (2)	0·18884 (5)	3·37 (4)
C(2*b*)	1·3304 (3)	−0·0956 (2)	0·10623 (6)	3·70 (5)
C(2*c*)	1·0634 (3)	0·0050 (2)	0·05988 (5)	3·76 (5)
C(2*d*)	0·8477 (2)	0·0146 (2)	0·14299 (6)	3·47 (4)
C(3*a*)	1·0524 (3)	−0·0530 (2)	0·21679 (5)	3·58 (4)
C(3*b*)	1·4020 (2)	−0·0545 (2)	0·07585 (6)	4·16 (5)
C(3*c*)	1·1114 (3)	−0·0670 (2)	0·03321 (5)	4·25 (5)
C(3*d*)	0·8183 (2)	0·0771 (2)	0·17342 (6)	3·72 (5)
C(4*a*)	1·0685 (3)	−0·1594 (2)	0·22772 (6)	4·53 (5)
C(4*b*)	1·4783 (3)	0·0425 (2)	0·07924 (6)	5·15 (6)
C(4*c*)	1·0220 (3)	−0·1544 (2)	0·02503 (6)	5·19 (6)
C(4*d*)	0·8295 (3)	0·1889 (2)	0·17029 (6)	4·27 (5)
C(5*a*)	1·1716 (3)	−0·2263 (2)	0·21115 (6)	5·17 (6)
C(5*b*)	1·4835 (3)	0·0966 (2)	0·11177 (7)	5·56 (6)
C(5*c*)	0·8893 (3)	0·1708 (2)	0·04277 (7)	5·53 (6)
C(5*d*)	0·8726 (3)	0·2354 (2)	0·13781 (7)	4·41 (5)
C(6*a*)	1·2570 (3)	−0·1892 (2)	0·18256 (6)	4·45 (5)
C(6*b*)	1·4082 (3)	0·0559 (2)	0·14170 (6)	4·49 (5)
C(6*c*)	0·8440 (3)	−0·1007 (2)	0·06995 (6)	4·41 (5)
C(6*d*)	0·9039 (3)	0·1718 (2)	0·10777 (6)	4·04 (5)
C(7*a*)	0·9343 (3)	0·0187 (2)	0·23315 (6)	4·36 (5)
C(7*b*)	1·3862 (3)	−0·1071 (2)	0·03916 (6)	5·15 (6)
C(7*c*)	1·2630 (3)	−0·0540 (2)	0·01621 (6)	5·22 (6)
C(7*d*)	0·7913 (3)	0·0258 (2)	0·21001 (6)	4·62 (5)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Numbers are average values for the bonds indicated and bonds which would be equivalent to these if the molecule possessed D_2 symmetry. Numbers in parentheses are e.s.d.'s in the least significant digits.

C(1*a*)–C(1*b*)	1·487 (2)	C(1*b*)–C(1*a*)–C(2*a*)	120·2 (2)
C(1*a*)–C(2*a*)	1·393 (2)	C(1*b*)–C(1*a*)–C(6*a*)	121·3 (2)
C(1*a*)–C(6*a*)	1·386 (2)	C(2*a*)–C(1*a*)–C(6*a*)	118·3 (2)
C(2*a*)–C(3*a*)	1·388 (2)	C(1*a*)–C(2*a*)–C(3*a*)	121·9 (2)
C(3*a*)–C(4*a*)	1·382 (3)	C(2*a*)–C(3*a*)–C(4*a*)	118·2 (2)
C(3*a*)–C(7*a*)	1·505 (3)	C(2*a*)–C(3*a*)–C(7*a*)	120·9 (2)
C(4*a*)–C(5*a*)	1·376 (3)	C(4*a*)–C(3*a*)–C(7*a*)	120·6 (2)
C(5*a*)–C(6*a*)	1·382 (3)	C(3*a*)–C(4*a*)–C(5*a*)	120·8 (2)
C(7*a*)–C(7*d*)	1·539 (3)	C(4*a*)–C(5*a*)–C(6*a*)	120·4 (2)
		C(1*a*)–C(6*a*)–C(5*a*)	120·3 (2)
		C(3*a*)–C(7*a*)–C(7*d*)	112·6 (2)

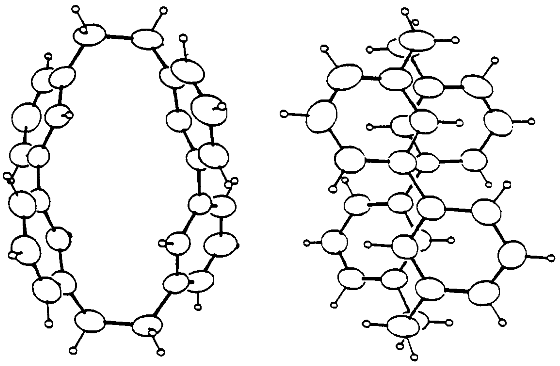

Fig. 1. *ORTEP* views of a molecule of the title compound, with 50% probability thermal ellipsoids.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates, and a packing diagram have been deposited with the British Libary Lending Division as Supplementary Publication No. SUP 42916 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

biphenyl groupings differ: 52·1 (2)° between rings *a* and *b*, and 46·8 (2)° between rings *c* and *d* [*cf.* ~30° proposed for the molecule in solution by Olsson *et al.* (1981) and 89·9° observed for the tetramethoxyl–tetramethyl analog by Kaneda *et al.* (1985)]. No doubt this angle is much larger in the latter compound to accommodate the bulky methoxyl groups.

The right-hand view of the molecule in Fig. 1 shows how the protons on C(2*a*)–C(2*d*) are magnetically shielded by an aromatic ring across the large ring. Using the equations of Johnson & Bovey (1958), we have calculated the upfield shift expected for the conformation observed in the crystal to be just what is observed in solution by NMR, so the conformation is essentially the same in both media, and probably represents the lowest energy minimum for the molecule.

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Structure of 3′-Acetamido-2,2-dichloro-4′,5′-dimethylacetophenone

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Abstract. $C_{12}H_{13}Cl_2NO_2$, $M_r = 274·15$, monoclinic, $P2_1/n$, $a = 17·645$ (2), $b = 14·645$ (1), $c = 10·5955$ (7) Å, $\beta = 107·191$ (7)°, $V = 2615·7$ (4) Å^3, $Z = 8$, $D_m = 1·41$, $D_x = 1·39$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 44·75$ cm^{-1}, $F(000) = 1136$, $T = 295$ K, final $R = 0·067$ for 3306 observed reflections. The acetyl groups in both the crystallographically independent molecules are in the *endo* conformation, whereas there is a conformational difference about the C(phenyl)—C(keto) bonds of the dichloroacetyl groups of the two molecules. The π-electron cloud in the keto bonds of the dichloroacetyl groups are more localized than those in related compounds. Intermolecular N—H···O hydrogen bonds link the molecules into infinite chains.

Introduction. The study of the structure–activity relationship of the widely used antibiotic chloramphenicol established the importance of the dichloroacetyl group (Dennis & Berberian, 1954). Acetanilide and its various derivatives possess a variety of antifungal, antibacterial, analgesic and anaesthetic activities (Burger, 1960; Banerjee, 1983).

The structure of the title compound was analysed as part of our studies on dichloroacetophenones and acetanilides (Chattopadhyay, Banerjee, Mazumdar & Podder, 1985; Haisa, Kashino, Ueno, Shinozaki & Matsuzaki, 1980).

Experimental. Pale-yellow plate-shaped crystals (from ethanol); density by flotation (benzene – bromoform); crystal size: 0·35 × 0·27 × 0·25 mm;symmetry from oscillation and Weissenberg photographs, $P2_1/n$ (systematic absences: $0k0$, k odd; $h0l$, $h+l$ odd); Rigaku AFC-5 four-circle diffractometer equipped with rotating anode; Ni-filtered Cu $K\alpha$ radiation; cell

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