

SHORT STRUCTURAL PAPERS

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1,1-Dichloro-2,5-diphenylcyclopropabenzene

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Abstract. $C_{19}H_{12}Cl_2$, orthorhombic, $P2_12_12_1$, $a=12.2605$ (5), $b=17.0255$ (9), $c=7.3649$ (6) Å at 22°C; $D_x=1.34$ g cm $^{-3}$ for $Z=4$; $F(000)=640$. Direct methods were used to determine the structure from four-circle diffractometer intensity measurements. Full-matrix least-squares refinement converged with R at 0.060. The cyclopropabenzene system is not quite planar and the phenyl substituents are twisted and bent from the plane of the benzene ring in the cyclopropabenzene system.

Introduction. Weissenberg and precession photographs showed systematic absences uniquely consistent with the orthorhombic space group $P2_12_12_1$ ($h00$ with h odd, $0k0$ with k odd, $00l$ with l odd).

A colourless crystal, $0.625 \times 0.275 \times 0.163$ mm, was used for intensity measurements. 900 independent reflexions (maximum $\theta=55^\circ$; Cu $K\alpha$, $\lambda=1.5418$ Å) were measured on a Hilger and Watts diffractometer with the $\omega-2\theta$ scan technique. Of these, 745 with $F_o^2 > 3\sigma(F_o^2)$ were regarded as observed. The intensities were corrected for absorption ($\mu=36.87$ cm $^{-1}$ for Cu $K\alpha$) with *ABSOR* (Templeton & Templeton, 1973), and for Lorentz and polarization effects with the local program *HILGOUT*.

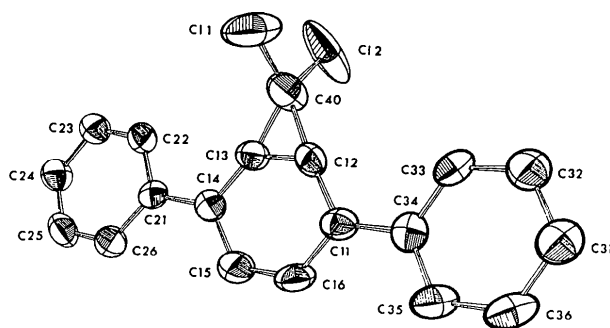


Fig. 1. A perspective view of 1,1-dichloro-2,5-diphenylcyclopropabenzene.

The structure was solved with *MULTAN* (Main, Woolfson & Germain, 1971). An *E* map computed from 154 phased and weighted normalized structure factors ($R_{Karlé}=0.32$) revealed the positions of 18 out of 21 non-hydrogen atoms. The approximate positions of the two missing C atoms were calculated and included in a model for a least-squares refinement cycle. A difference synthesis revealed the missing Cl atom.

The positional and thermal parameters were refined by full-matrix least squares to an R ($=\sum|F_o|-|F_c|/\sum|F_o|$) of 0.088. Although a difference synthesis showed the approximate positions of the H atoms it was decided to use calculated positions (C-H=0.95 Å) with isotropic thermal parameters fixed at 5.0 Å 2 . Because an examination of the intense, low angle, structure factors showed evidence of extinction, an extinction parameter was also refined in the final stages. This model, with refinement of positional and anisotropic parameters for all non-hydrogen atoms, converged with $R=0.060$. R for all 900 reflexions is 0.073. In the final cycle, the largest positional shift was 0.14 σ and the average shift 0.05 σ . The standard error in an observation of unit weight is 2.9. For C and Cl the scattering factors of Cromer & Mann (1968) were used and for H those of Stewart, Davidson & Simpson (1965). Anomalous dispersion corrections (Cromer, 1965) were applied for Cl. A final difference synthesis with all data showed no peaks greater than 0.38 e Å $^{-3}$.

Final positional and thermal parameters are given in Tables 1 and 2 with the labelling shown in Fig. 1. Bond distances and angles are given in Fig. 2. The maximum estimated standard deviations are 0.02 Å and 1°. Only the C-Cl distances have been corrected for thermal motion with the riding model (Busing & Levy, 1964).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31636 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Positional and thermal parameters ($\times 10^4$) for the non-hydrogen atoms with estimated standard deviations in parentheses

Thermal parameters are in the form: $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	72 (5)	146 (2)	3303 (6)	406 (9)	55 (1)	481 (1)	-8 (3)	296 (9)	-9 (4)
Cl(2)	-1639 (2)	36 (2)	556 (11)	98 (3)	55 (1)	1922 (40)	-6 (2)	207 (9)	-77 (4)
C(11)	1138 (9)	1028 (6)	-1343 (16)	82 (10)	58 (5)	173 (30)	0 (6)	1 (13)	3 (10)
C(12)	457 (8)	526 (6)	-313 (17)	65 (9)	50 (5)	313 (31)	9 (5)	4 (15)	10 (11)
C(13)	524 (8)	-266 (6)	-347 (16)	87 (10)	47 (5)	270 (27)	-2 (5)	33 (5)	-2 (10)
C(14)	1262 (9)	-725 (6)	-1297 (15)	89 (10)	50 (5)	195 (31)	7 (6)	-14 (15)	-10 (10)
C(15)	1891 (11)	-231 (7)	-2406 (16)	137 (12)	56 (6)	314 (32)	15 (7)	73 (17)	0 (11)
C(16)	1845 (10)	583 (7)	-2388 (15)	126 (12)	59 (6)	213 (28)	-5 (7)	74 (15)	6 (10)
C(21)	1336 (10)	-1579 (6)	-1151 (14)	99 (10)	46 (4)	120 (27)	6 (7)	-11 (13)	-10 (8)
C(22)	556 (9)	-1996 (6)	-217 (17)	106 (11)	77 (5)	262 (31)	13 (6)	10 (17)	-6 (10)
C(23)	582 (9)	-2802 (7)	-65 (18)	111 (10)	53 (5)	302 (33)	8 (6)	19 (17)	-8 (11)
C(24)	1432 (12)	-3202 (6)	-877 (18)	127 (12)	44 (5)	353 (41)	10 (7)	21 (19)	-18 (11)
C(25)	2215 (10)	-2803 (8)	-1797 (21)	102 (12)	71 (7)	351 (36)	31 (7)	7 (18)	-13 (14)
C(26)	2171 (10)	-1998 (7)	-1927 (17)	117 (13)	53 (5)	270 (31)	14 (6)	26 (18)	-4 (12)
C(31)	1048 (12)	3505 (6)	-826 (17)	136 (13)	50 (5)	208 (29)	-13 (7)	1 (17)	-13 (10)
C(32)	247 (10)	3058 (6)	-27 (16)	144 (13)	49 (5)	231 (28)	-3 (7)	28 (18)	-17 (10)
C(33)	291 (8)	2247 (6)	-204 (14)	106 (10)	47 (5)	182 (24)	-15 (6)	7 (15)	20 (9)
C(34)	1121 (10)	1896 (6)	-1221 (14)	95 (10)	44 (5)	189 (31)	-1 (6)	-28 (15)	-6 (9)
C(35)	1916 (9)	2358 (7)	-1991 (15)	112 (10)	54 (5)	221 (29)	-22 (7)	45 (16)	-11 (10)
C(36)	1868 (10)	3160 (7)	-1832 (17)	112 (12)	60 (6)	219 (30)	-34 (6)	27 (17)	5 (11)
C(40)	-250 (9)	97 (6)	919 (20)	120 (10)	43 (4)	599 (41)	-8 (6)	108 (21)	-10 (14)

Table 2. Positional parameters for the hydrogen atoms ($\times 10^3$)

	x	y	z
H(C15)	239	-48	-323
H(C16)	234	86	-316
H(C22)	-2	-172	35
H(C23)	2	-308	57
H(C24)	147	-376	-79
H(C25)	280	-308	-235
H(C26)	272	-173	-257
H(C31)	103	406	-68
H(C32)	-33	330	63
H(C33)	-24	193	37
H(C35)	251	212	-263
H(C36)	239	348	-241

Calculations were carried out at the University of Canterbury with IBM 360/44 and Burroughs B6718 computers. The structure factor calculations and least-squares refinements were carried out with *CUCLS* and Fourier summations with *FOURIER*. These are highly modified versions of *ORFLS* (Busing, Martin & Levy, 1962) and *FORDAP* (Zalkin, 1965).

Discussion. The main structural features of 1,1-dichloro-2,5-diphenylcyclopropabenzene (I) (Halton & Milsom, 1971) agree well with those of cyclopropa[*b*]naphthalene (II) (Billups *et al.*, 1973) and dimethyl 2,5-diphenylcyclopropabenzene-1,1-dicarboxylate (III) (Carstensen-Oeser, Müller & Dürr, 1972), the only hitherto reported cyclopropabenzene. As with the dicarboxylate (III) the results may be compared with those of *p*-terphenyl (Rietveld, Maslen & Clews, 1970). There are no unusual features in the bond distances or angles of the phenyl substituents. However, the annelation of the cyclopropene ring to the practically planar *p*-terphenyl group apparently results in a distor-

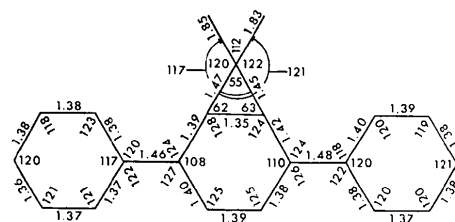


Fig. 2. Bond distances and angles in 1,1-dichloro-2,5-diphenylcyclopropabenzene.



Fig. 3. A perspective view of the molecule down the C(12)-C(16) vector.

tion of the planes of the terminal rings from the approximate plane of the cyclopropabenzene ring system (Fig. 3). The angles between the planes of the terminal phenyl groups and the plane of the central benzene ring are 9.8 and 9.9° (Table 3). Furthermore there is severe compression of the central six-membered ring with the internal angles about the C atoms α to the three-membered ring differing significantly from 120° [$108(1)$ and $110(1)^\circ$ about C(14) and C(11), respectively].

Perhaps the most interesting facet of cyclopropabenzene chemistry is the expectation of partial localization of the π -electron framework and a tendency towards cyclohexatriene character. While the theoretical models on which these predictions are based have failed to agree on the direction of bond localization, either (IVa) (Longuet-Higgins & Coulson, 1946) or (IVb) (Cheung, Cooper & Manatt, 1971), cyclopropa-

Table 3. *Least-squares planes*

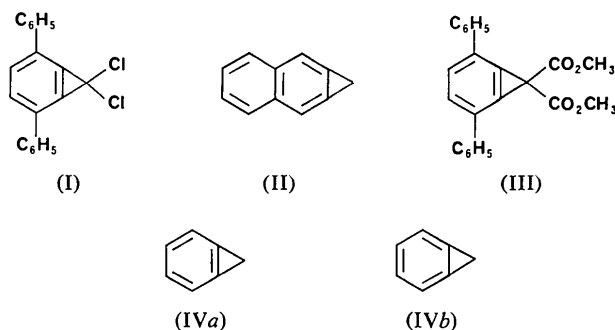
Distances of atoms from planes in Å

Plane 1		Plane 2		Plane 3	
Cl(1)	0.0	C(12)	0.0	C(11)	-0.018
Cl(2)	0.0	C(13)	0.0	C(12)	0.007
C(40)	0.0	C(40)	0.0	C(13)	0.021
				C(14)	-0.035
				C(15)	0.025
				C(16)	0.001
Plane 4		Plane 5			
C(21)	-0.005	C(31)	-0.007		
C(22)	-0.003	C(32)	0.004		
C(23)	0.000	C(33)	-0.006		
C(24)	0.001	C(34)	0.010		
C(25)	0.001	C(35)	-0.012		
C(26)	-0.004	C(36)	0.011		

Interplanar angles

1-3	88.5°	2-1	88.0°	3-4	9.9°	4-5	8.5°
1-4	82.9	2-3	3.4	3-5	9.8		
1-5	81.4						

benzene does show chemical properties consistent with either bond localization or severe deformation of the six-membered ring (Halton, 1973). Structure determinations of suitable cyclopropabenzene derivatives are thus expected to provide significant insight to the nature of the bonding patterns in these compounds.



It is clear that the structural information for (I), reported here, while showing severe compression of the six-membered ring, provides no evidence for the presence of bond localization either in the direction (IVa)

or (IVb); although the bridge bond is short [1.35 (1) Å] there are no significant differences between the remaining bonds of the six-membered ring. The length of the bridge bond falls midway between that of (II) 1.368 (6) Å and (III) 1.333 (8) Å and the suggestion (Billups *et al.*, 1973) that the ester function of (III) could be responsible for the shortened nature of this bond could also have some bearing here.

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