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Dibenzo-*p*-dioxin

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Abstract. $C_{12}H_8O_2$, monoclinic, *Cc*, $a = 11{\cdot}69(1)$, $b = 5{\cdot}09\ (1)$, $c = 15{\cdot}11\ (1)$ Å, $\beta = 100{\cdot}29\ (1)°$, $Z = 4$, $D_c = 1{\cdot}38$, $D_m = 1{\cdot}40\ (3)$ g cm^{-3} (by suspension). The C–C bond lengths average 1·38 (1) Å and the C–O–C angles average 115 (3)°; all of the carbon atoms are coplanar, and the oxygen atoms are displaced 0·16 (1) and 0·17 (1) Å from that plane.

Introduction. Slow evaporation of a dibenzo-*p*-dioxin ether solution yielded colorless crystals bounded by the {100}, {010}, and {001} faces. Distances from the center of mass to these face planes were 0·23, 0·09, and 0·45 mm (all ±0·01 mm), respectively, for the crystal used to collect reflection data. The crystal was mounted with **b** parallel to the φ axis of the diffractometer. Unit-cell parameters and intensity data were obtained using a G.E. XRD-5 manually operated quarter-circle diffractometer with Zr-filtered Mo K ($\lambda = 0{\cdot}71069$ Å) radiation and a scintillation detection system. Systematic absences hkl with $h+k$ odd and $h0l$ with l odd indicated space groups $C2/c$ or Cc; the latter proved to be the correct choice. No absorption or extinction corrections were made; the linear absorption coefficient is 1·01 cm^{-1}.

Data collection involved θ–2θ scans of 2° at 2° min^{-1}, with 20 s stationary background at each end of the scans. All 462 unique reflections with $0° < 2\theta < 40°$ were examined; only 233 had $I > 1{\cdot}5\sigma(I)$ and these were used for the refinement. Thus although it was possible to find crystals without the intense diffuse scattering and twinning problem reported earlier (Goldberg & Shmueli, 1973), a poor yield of usable data was obtained in spite of the relatively large crystal size and the long background counts used to maximize the number of 'observed' data. Four reflections measured periodically during the 23 h of data collection varied by less than 1σ and thereby indicated crystal and electronic stability.

The standard deviations for I were calculated by $\sigma(I) = (S + 9B + 0{\cdot}0016I^2)^{1/2}$ (where S = scan count, B = sum of the background counts, and $I = S - 2{\cdot}25B$), except for a number of reflections for which the two background readings differed by more than twice the calculated σ due to the tailing of the reflection peak. For the latter reflections the standard deviations were set equal to the deviation of the background readings from the mean background value. Neutral atom scattering factors were used (*International Tables for X-ray Crystallography*, 1974) for all atoms.

The trial structure was initiated by Patterson methods. Because of the paucity of 'observed' reflections, the two C_6H_4 moieties were refined as rigid groups with C–C = 1·395 Å, C–H = 0·95 Å and 120° bond angles at the carbon atoms. Least-squares refinement of the positions of these two groups and the two independent oxygen atoms, including refinement of individual isotropic temperature factors for all non-hydrogen atoms, gave $R = 0{\cdot}051$ and $R_w = 0{\cdot}053$. Removal of the molecular constraints (the H atoms were included at C–H = 0·95 Å but were not refined) led to $R = 0{\cdot}047$ and $R_w = 0{\cdot}045$. Although this drop in R_w is significant (Hamilton, 1965), the very low reflection:parameter ratio (4:1) and a severe correlation of the positional parameters of both C(3) with C(10) and C(4) with C(9) in the least-squares matrix led to the rejection of the unconstrained refinement. Consequently the parameters reported in this communication are those of the constrained refinement. It is important to point out that the bond distances and angles given for the central ring, as well as the best-planes calculations reported below, were all within one standard deviation of the corresponding values found for the unconstrained refinement. The standard deviation of an observation of unit weight was 1·06, and the final difference Fourier map had a

Table 1. *Fractional atomic coordinates and isotropic thermal parameters for dibenzo-p-dioxin*

	x	y	z	B (Å^2)
O(1)	−0·122*	0·232 (2)	0·25*	3·8 (3)
O(2)	0·1204 (8)	0·230 (3)	0·2555 (6)	5·7 (4)
C(1)	−0·054	0·417	0·299	5·2 (7)
C(2)	−0·100	0·586	0·355	4·4 (6)
C(3)	−0·028	0·760	0·409	7·3 (8)
C(4)	0·090	0·764	0·408	4·8 (6)
C(5)	0·136	0·595	0·351	4·1 (5)
C(6)	0·064	0·422	0·297	3·3 (5)
C(7)	0·044	0·087	0·194	3·0 (5)
C(8)	0·095	−0·090	0·143	4·7 (6)
C(9)	0·027	−0·263	0·086	3·7 (5)
C(10)	−0·094	−0·259	0·079	5·3 (6)
C(11)	−0·145	−0·082	0·129	5·3 (6)
C(12)	−0·076	0·091	0·187	4·6 (5)
H(C2)	−0·181	0·584	0·356	5·0
H(C3)	−0·060	0·876	0·448	5·0
H(C4)	0·140	0·883	0·445	5·0
H(C5)	0·217	0·598	0·350	5·0
H(C8)	0·177	−0·093	0·148	5·0
H(C9)	0·062	−0·384	0·051	5·0
H(C10)	−0·140	−0·377	0·039	5·0
H(C11)	−0·227	−0·079	0·124	5·0

* Origin-determining parameter.

maximum peak of only 0·09e Å^{-3}. The 'unobserved' reflections all had $\Delta F/\sigma(F)$ of less than 2·1. Atomic positional and thermal parameters are given in Table 1, Fig. 1 gives the atom numbering scheme as well as the central ring parameters, and Fig. 2 is a schematic drawing of the packing pattern.*

Discussion. The relatively large e.s.d.'s associated with the final structural parameters, a consequence of the small percentage of intense reflections, preclude detailed bond-angle and bond-distance comparisons but do not negate the most important observation: the near planarity of dibenzo-*p*-dioxin. Table 2 summarizes the planarity aspects of the molecule. The dihedral angle between planes 1 and 2 (the two phenylene rings) is 175·9(9)°; that between the two C_6H_4SN moieties is 173·9(4)°. More significant, however, is the low χ^2 value for plane 6, the best plane through the 12 carbon atoms. This suggests that our results are best summarized as finding the carbon atoms all coplanar, with the oxygen atoms each displaced 0·17(1) Å from the carbon plane, on the same side of the plane. Although three previous dibenzo-*p*-dioxin structure reports involving di-, tetra-, and hexachloro substituted molecules (Boer & North, 1972; Boer, van Remoortere, North & Neuman, 1972; Cantrell, Webb & Mabis, 1969) and the structure of the dibenzo-*p*-dioxin TCNQ complex (Goldberg & Shmueli, 1973) indicated planar or nearly planar dioxin molecules, it is still somewhat unexpected to find the unsubstituted molecule nearly planar in view of the 126–144° angles-of-fold found for a number of similar heterocyclic molecules which have S and/or CH_2 in place of the two oxygen atoms of dibenzo-*p*-dioxin (see Gillean, Phelps & Cordes, 1973, and references therein). Phenoxthionine, C_6H_4–O–S–C_6H_4, is also folded 138·5° (Hosoya, 1966).

The C–O bond distances in dibenzo-*p*-dioxin agree with the 1·36–1·39 Å range of average values found in the dioxin structures mentioned above and the C–O–C angles are in general agreement with the 115–118° values reported in the same structures. There are no intermolecular distances in the stacking of the molecules that are shorter than normal packing separations.

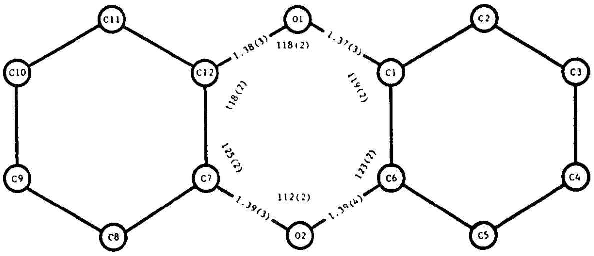

Fig. 1. The atom numbering sequence employed, and the central ring bond distances and bond angles in dibenzo-*p*-dioxin.

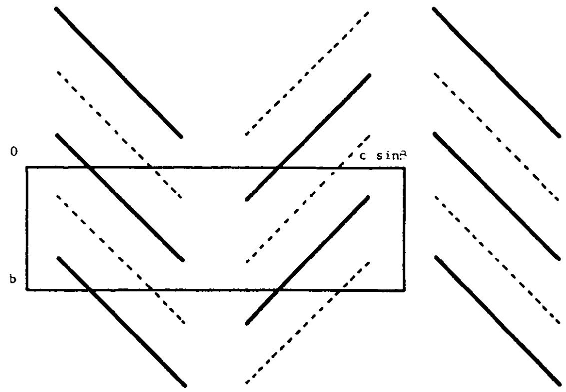

Fig. 2. Schematic drawing of the crystal packing of dibenzo-*p*-dioxin as viewed along the *a* axis. The view is parallel to the longest dimension of the molecule; the dotted lines indicate molecules displaced ½ along **a** (perpendicular to the drawing).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30379 (1 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Displacements from best planes in dibenzo-p-dioxin*

The asterisks indicate the atoms used to calculate the best planes; weighting was proportional to $1/\sigma_\perp^2$, where $\sigma_\perp$ is the positional e.s.d. normal to the plane.

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6
C(1)	−0·11 (1)	−0·26 (1)	0·00 (1)*	0·03 (1)*	0·09 (1)*	0·16 (1) Å
O(2)	−0·24 (1)	−0·14 (1)	0·03 (1)*	0·00 (1)*	0·10 (1)*	0·17 (1)
C(1)	0*	−0·12 (3)	−0·06 (3)*	−0·16 (3)	−0·04 (3)*	0·03 (3)*
C(2)	0*	−0·21 (3)	0·03 (3)*	−0·17 (3)	−0·00 (3)*	0·07 (3)*
C(3)	0*	−0·17 (3)	0·08 (3)*	−0·27 (3)	−0·03 (3)*	0·05 (3)*
C(4)	0*	−0·04 (3)	0·03 (3)*	−0·35 (3)	−0·09 (3)*	−0·02 (3)*
C(5)	0*	0·05 (3)	−0·07 (3)*	−0·33 (3)	−0·13 (3)*	−0·06 (3)*
C(6)	0*	0·01 (2)	−0·11 (2)*	−0·24 (2)	−0·10 (2)*	−0·03 (2)*
C(7)	−0·06 (2)	0*	−0·19 (2)	−0·09 (2)*	−0·06 (2)*	0·01 (2)*
C(8)	−0·15 (3)	0*	−0·20 (3)	0·01 (3)*	−0·01 (3)*	0·06 (3)*
C(9)	−0·11 (2)	0*	−0·28 (2)	0·07 (2)*	−0·02 (2)*	0·04 (2)*
C(10)	0·01 (3)	0*	−0·36 (3)	0·02 (3)*	−0·09 (3)*	−0·02 (3)*
C(11)	0·10 (3)	0*	−0·35 (3)	−0·07 (3)*	−0·14 (3)*	−0·07 (3)*
C(12)	0·07 (3)	0*	−0·27 (3)	−0·13 (3)*	−0·12 (3)*	−0·05 (3)*
χ^2	0	0	16	18	115	18

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trans-Bis(diethylphenylphosphine)(difluorophosphonato)chloroplatinum(II)

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Abstract. $(Et_2PPh)_2PtCl(PF_2O)$, $PtClP_3F_2OC_{20}H_{30}$, orthorhombic, $P2_12_12_1$, $a=22\cdot062$ (3), $b=14\cdot801$ (2), $c=7\cdot541$ (1) Å, $M=647\cdot92$, $Z=4$, $D_x=1\cdot75$ g cm^{-3}. The coordination of platinum is square-planar with the diethylphenylphosphine ligands in positions *trans* to one another. The molecular structure confirms that the difluorophosphonato group is bonded to the metal through the phosphorus rather than the oxygen atom.

Introduction. Unit-cell dimensions were determined from measurements of 17 high 2θ angle reflexions with Mo $K\alpha_1$ ($\lambda=0\cdot70926$ Å) radiation. The intensities, from a prismatic crystal sealed in a Lindemann glass capillary and with approximate dimensions $0\cdot01\times0\cdot008\times0\cdot01$ cm, were collected on a Stoe 4-circle diffractometer with graphite monochromated Mo $K\alpha$ radiation. Measurements were carried out with standard background counts and θ–2θ scan of fixed range for $2\theta\le45°$. Three standard reflexions, which were monitored at regular intervals, did not display any significant variations due to crystal deterioration. Of the 1882 reflexions which were recorded, 81 were rejected because the peak count was less than the background count. Lorentz and polarization but no absorption ($\mu_{\text{Mo}\,K\alpha}=63\cdot1$ cm^{-1}) corrections were applied.

The space group $P2_12_12_1$ was unambiguously indicated by the observed systematic absences $h00$ (h odd), $0k0$ (k odd) and $00l$ (l odd). A Patterson synthesis was interpreted to yield a self-consistent set of coordinates for the platinum, and the remaining atoms, except for hydrogen, were located from subsequent difference syntheses. In the final cycles of the full-matrix least-squares refinement, adoption of anisotropic temperature factors for the fluorine and oxygen atoms, in addition to those for platinum, chlorine and phosphorus, led to an improvement in the generalized index

Table 1. *Atom coordinates* ($\times10^4$) *and isotropic temperature factors* (Å $\times10^3$)

	x	y	z	U
Pt	1285 (1)	499 (1)	62 (2)	*
Cl	1183 (3)	−925 (4)	1456 (10)	*
P(1)	2329 (2)	467 (4)	445 (8)	*
P(2)	231 (2)	431 (4)	−236 (9)	*
P(3)	1336 (3)	1826 (4)	−1242 (9)	*
F(1)	941 (6)	2514 (8)	−263 (26)	*
F(2)	1961 (6)	2262 (9)	−1190 (22)	*
O	1102 (8)	1869 (11)	−3066 (22)	*
C(11)	2623 (10)	1368 (14)	1866 (30)	50 (6)
C(12)	3171 (13)	1800 (20)	1503 (41)	83 (9)
C(13)	3433 (13)	2485 (20)	2748 (41)	84 (9)
C(14)	3057 (12)	2666 (18)	4161 (35)	72 (8)
C(15)	2499 (12)	2274 (16)	4471 (35)	75 (8)
C(16)	2265 (10)	1614 (16)	3317 (33)	58 (7)
C(21)	2600 (10)	−568 (17)	1556 (32)	58 (6)
C(22)	3284 (12)	−554 (20)	1921 (38)	85 (9)
C(31)	2764 (11)	534 (18)	−1629 (35)	70 (7)
C(32)	2515 (14)	−216 (20)	−2976 (43)	91 (10)
C(41)	18 (9)	−515 (15)	−1670 (27)	44 (5)
C(42)	342 (10)	−655 (15)	−3113 (31)	54 (6)
C(43)	212 (11)	−1385 (17)	−4296 (32)	65 (7)
C(44)	−319 (12)	−1922 (18)	−3913 (39)	74 (8)
C(45)	−659 (11)	−1769 (17)	−2421 (36)	70 (8)
C(46)	−488 (11)	−1068 (16)	−1247 (34)	60 (7)
C(51)	−185 (11)	1402 (16)	−1192 (33)	58 (7)
C(52)	−862 (12)	1235 (18)	−1420 (38)	77 (8)
C(61)	−133 (11)	262 (16)	1966 (33)	61 (7)
C(62)	74 (14)	1022 (19)	3219 (42)	89 (10)

* Anisotropic temperature factor components are listed in Table 2.