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The Crystal and Molecular Structure of Dibenzofuran

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Dibenzofuran, $C_{12}H_8O$, forms colourless orthorhombic crystals with four molecules in the unit cell of dimensions $a = 7·65 \pm 0·02$, $b = 5·90 \pm 0·01$, $c = 19·32 \pm 0·02$ Å. The intensity-statistics test decided in favour of space group *Pnam* rather than *Pna*2_1. The gross structure was solved by the method of the weighted reciprocal lattice combined with trial-and-error procedures taking advantage of the analogy with similar structures. The parameters were refined by three-dimensional least-squares methods utilizing 539 observed reflexion intensities obtained photographically with Cu K radiation, to a final R index of 0·092. The bond lengths and bond angles of the molecule show no abnormalities; they have estimated standard deviations of about 0·007 Å and 0·45° respectively for non-hydrogen atoms. The individual five or six-membered rings are planar but the six-membered rings make a significant dihedral angle (1·2°) with the five-membered ring. A crystallographic mirror plane normal to the c axis passes through the oxygen atom of the molecule. Some physical properties of the compound are compared with those of fluorene and carbazole. A theoretical calculation has been made to account for the lengthening of the C(6)–C(6') contact bond, a characteristic feature of this type of molecule with a phenanthrenoid arrangement of rings.

Introduction

The investigation of the crystal and molecular structure of dibenzofuran, $C_{12}H_8O$, is part of a programme of research on heterocyclic compounds in our laboratory being carried out because of their important uses as drugs, dyes and because many of the cancer-arresting substances are heterocyclic. The objects of the present investigation were twofold: (*a*) to explain the physical properties such as cleavage, melting point, *etc.* in relation to crystal structure and (*b*) to obtain molecular dimensions of sufficient accuracy to form a basis for discussion and comparison with theories of molecular structure. Extensive theoretical calculations have been done from the standpoint of π-electron delocalization to account for the irregular deviations of bond lengths within a ring from the values of standard conjugated distances. Preliminary results on the crystal structure analysis of this compound were reported by Banerjee (1971, 1972). Thereafter a comprehensive three-dimensional least-squares refinement was carried out with anisotropic temperature factors and hydrogen-atom contributions and the results are presented here.

Experimental

Repeated crystallizations by sufficiently slowing down the rate of evaporation of the solvent at room temperature (27 °C) from a solution in alcohol yielded colourless transparent crystals lath-like in habit, platy on the (001) face, with lengths parallel to the shortest crystallographic axis, **b**. The crystals exhibited a perfect cleavage parallel to the (001) plane and displayed extinction parallel to their length. The cell dimensions were determined from single-crystal oscillation and Weissenberg photographs about the a and b axes using a good crystal. Diffraction effects show the following systematic absences: $h0l$ absent if $h = 2n + 1$ and $0kl$ absent if $k + l = 2n + 1$. This X-ray data and dimensional considerations indicate that the four molecules in the unit cell must either occupy general positions in space group $Pna2_1$ or lie across the mirror planes in the space group *Pnam*. This ambiguity in space group was resolved in favour of *Pnam* by the statistics test of Wilson (1949). The crystal density was measured by flotation in an aqueous solution of $ZnSO_4$. The crystal data are given in Table 1. The integrated intensities of 539 reflexions were visually estimated from zero and

upper-level equi-inclination Weissenberg multiple-film photographs of the crystal around the a and b axes with Cu K radiation and put on same scale by cross-layer comparison. The ratio of maximum to minimum intensity was very high for certain reflexions in the $h0l$ and $h1l$ series and a sheet of aluminum foil of known thickness was interleaved between the films for proper correlation of spots. Lorentz–polarization and spot-shape corrections were applied but no corrections for absorption were made as the crystal used was small ($0.35 \times 0.30 \times 0.25$ mm) and contained no heavy atoms ($\mu = 6.39$ cm^{-1}). The sample sublimes and was therefore sealed in a Lindemann-glass capillary of 0.3 mm internal bore.

Table 1. *Crystal data*

Compound	Dibenzofuran
	C$_{12}$H$_8$O
Unit cell	Orthorhombic

$a = 7.65 \pm 0.02, b = 5.90 \pm 0.01, c = 19.32 \pm 0.02$ Å

M.W. 168·2	$d_{calc} = 1.275$ g cm^{-3}
M.p. 87 °C	$d_{obs} = 1.270$ g cm^{-3}
B.p. 228 °C	$V = 869$ Å^3
$F(000) = 325$	$Z = 4$

Absent spectra:

$h0l$	$h = 2n + 1$
$0kl$	$k + l = 2n + 1$

Space group *Pnam*

Determination and refinement of the structure

The trial model was adopted by utilizing the existing knowledge of heterocyclic chemistry of other similar compounds, and the number of possibilities for a trial structure were limited by using refractive-index (1·55 along **a** and 1·75 along **b**) and cleavage-direction data. Approximate positional parameters of the molecule in the unit cell were obtained by a combination of a weighted reciprocal-lattice plot for $0kl$ reflexions and a trial-and-error method together with analogy, at a subsequent stage, with carbazole (Kurahashi, Fukuyo, Shimada, Furusaki & Nitta, 1968; Lahiri, 1968), whose formal configuration, crystal data and space group are very similar to those of dibenzofuran. The structure factors calculated for the zero layers on this basis produced a R value of 0·32.

Using the above data an initial three-dimensional isotropic refinement by block-diagonal least-squares methods on an IBM 1620 computer and a subsequent full-matrix least-squares refinement on a CDC 3600 using the computer program *ORFLS*, written by Busing, Martin & Levy (1962), led to the complete solution of the structure. The positional and individual isotropic thermal parameters were refined for all atoms except the hydrogen atoms, whose contributions were included in the structure-factor calculations keeping

Table 4. *Parameters of hydrogen atoms and their e.s.d.'s*

All values are multiplied by 10^4.

	x	y	z	B
H(1)	288 (6)	841 (8)	382 (2)	5·51
H(2)	188 (6)	584 (9)	471 (2)	5·35
H(3)	43 (6)	244 (10)	449 (2)	5·15
H(4)	12 (6)	139 (8)	330 (2)	5·06

Table 2. *Structure factors*

Table 3. *Positional and thermal vibrational parameters of non-hydrogen atoms and their e.s.d.'s*

The expression B is defined by $B = \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\right]$.
All the values in the table are multiplied by 10^4.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	2350 (6)	6967 (9)	3764 (3)	187 (9)	375 (48)	47 (2)	7 (12)	−18 (4)	−36 (5)
C(2)	1772 (6)	5442 (10)	4257 (3)	199 (9)	562 (43)	35 (2)	60 (14)	−9 (4)	−14 (6)
C(3)	969 (6)	3436 (10)	4081 (3)	190 (9)	523 (45)	33 (2)	33 (13)	4 (3)	17 (5)
C(4)	695 (6)	2843 (9)	3395 (3)	151 (8)	362 (44)	50 (2)	−9 (11)	−3 (3)	1 (6)
C(5)	2052 (6)	6327 (9)	3075 (3)	158 (8)	352 (44)	39 (2)	32 (11)	10 (3)	22 (5)
C(6)	1262 (6)	4317 (8)	2883 (2)	136 (7)	332 (40)	34 (2)	−8 (1)	−4 (3)	−9 (4)
O(7)	2580 (6)	7659 (9)	2500 (*)	225 (10)	361 (41)	46 (2)	−42 (12)	0*	0*

* Parameters constrained by symmetry.

Table 5. *Bond lengths and bond angles of non-hydrogen atoms*

	Bond lengths				Bond angles	
	Experimental (1)	Theoretical (1)*	(2)†	Difference (1)–(2)		
C(1)–C(2)	1·383 (8) Å	1·380	1·395	−0·003	C(2)–C(1)–C(5)	115·3 (0·5)°
C(2)–C(3)	1·377 (8)	1·402	1·398	+0·025	C(1)–C(2)–C(3)	122·1 (0·5)
C(3)–C(4)	1·386 (8)	1·391	1·393	+0·005	C(1)–C(5)–C(6)	123·9 (0·5)
C(4)–C(6)	1·387 (7)	1·407	1·402	+0·020	C(2)–C(3)–C(4)	121·4 (0·5)
C(1)–C(5)	1·401 (8)	1·404	1·397	+0·003	C(3)–C(4)–C(6)	118·5 (0·5)
O(7)–C(5)	1·418 (6)	1·382	1·385	−0·029	C(4)–C(6)–C(5)	118·9 (0·4)
C(6)–C(5)	1·382 (7)	1·402	1·398	+0·020	C(6)–C(5)–O(7)	112·9 (0·4)
C(6)–C(6′)	1·480 (6)	1·468	1·468	−0·012	C(5)–O(7)–C(5′)	104·4 (0·4)
					C(1)–C(5)–O(7)	123·2 (0·5)
					C(5)–C(6)–C(6′)	105·6 (0·4)

* Calculated by the author.
† Dewar *et al.*

Table 6. *Bond lengths and bond angles associated with hydrogen atoms*

	Bond lengths		Bond angle		Bond angle
C(1)–H(1)	0·95 (5) Å	C(2)–C(1)–H(1)	129·7°	C(2)–C(3)–H(3)	117·4°
C(2)–H(2)	0·91 (5)	C(1)–C(2)–H(2)	117·8	C(4)–C(3)–H(3)	120·9
C(3)–H(3)	1·07 (5)	C(5)–C(1)–H(1)	115·1	C(3)–C(4)–H(4)	118·9
C(4)–H(4)	0·98 (5)	C(3)–C(2)–H(2)	120·0	C(6)–C(4)–H(4)	123·5

them fixed in their calculated positions with isotropic temperature factors equal to those of the atoms to which they are covalently bonded. Starting with an initial value of 40%, the final residual value obtained was 14·5% after three cycles. The non-hydrogen atoms were further refined with anisotropic temperature factors of the form exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. An attempt was also made to refine the positional parameters of hydrogen atoms holding their isotropic temperature factors constant; the R value converged to 0·092 after 3 cycles. The observed and calculated structure factors are given in Table 2. The final values of the atomic parameters with relevant temperature factors are listed in Tables 3, 4, 5 and 6. The bond lengths and bond angles are found to be consistent with existing accepted values (Fig. 1). The different C–C bond distances for chemically equivalent bonds in six-membered rings vary from 1·377 to 1·401 Å, a range of some 3σ. The standard deviations in bond lengths involving non-hydrogen atoms lie in the range 0·006 to 0·008 Å with an average of 0·007 Å and a mean standard deviation of 0·048 Å for C–H bonds. The corresponding standard deviations in bond angles involving non-hydrogen atoms range from 0·4 to 0·5° with an average of 0·45° and the average e.s.d. for bond angles involving hydrogen atoms is 2·7°. The equation of the planes with deviations of atoms from various planes are given in Tables 7 and 8.

Table 7. *Equations of the least-squares planes*

1. Dibenzofuran plane (1)
   $-0.890X + 0.457Y + 0.000Z - 0.285 = 0$
2. Benzene ring plane (2) with atoms 1′, 2′, 3′, 4′ and 6′
   $-0.890X + 0.456Y - 0.018Z - 0.233 = 0$
3. Furan ring plane (3) with atoms 5, 6, 7, 5′ and 6′
   $-0.891X + 0.455Y + 0.000Z - 0.299 = 0$
4. Benzene ring plane (4) with atoms 1, 2, 3, 4, 5 and 6
   $-0.890X + 0.456Y + 0.018Z - 0.410 = 0$

Table 8. *Deviations of the atoms from various planes*

The least-squares plane is determined by the atoms marked by an asterisk.

	Plane numbers			
	1	2	3	4
C(1)	−0·009 Å	−0·090 Å	−0·030 Å	−0·001* Å
C(2)	−0·026	−0·124	−0·046	−0·001*
C(3)	−0·020	−0·111	−0·037	0·000*
C(4)	0·007	−0·060	−0·009	0·003*
C(4′)	0·007	0·003*	−0·009	−0·061
C(3′)	−0·020	−0·000*	−0·037	−0·112
C(2′)	−0·026	−0·001*	−0·046	−0·126
C(1′)	−0·009	−0·001*	−0·030	−0·091
O(7)	0·020	−0·015	−0·001*	0·016
C(5)	0·021	−0·036	−0·001*	0·004*
C(6)	0·017	−0·032	−0·000*	−0·005*
C(6′)	0·017	−0·005*	−0·000*	−0·032
C(5′)	0·021	0·004*	0·001*	−0·037

Discussion

A points of considerable interest appeared after the completion of the X-ray analysis of the structure, *viz.* the stretching of the C(6)–C(6′) contact bond linking the two benzenoid rings. To look for a theoretical justification of this experimental finding the point was
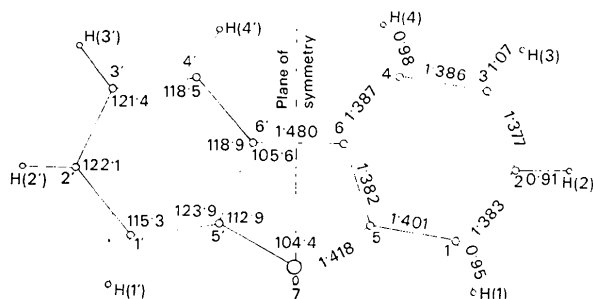

Fig. 1. The dibenzofuran molecule.

investigated by molecular orbital calculations of bond lengths *via* mobile bond orders from a self-consistent-field approach using π-electron orbitals on all atoms in the molecule ring.

The relations (Coulson & Golebiewski, 1961; Nishimoto & Forster, 1966), widely used by many workers with successful agreements, used to convert the respective π-bond orders, *p*, to their bond length, *r*, were as follows

$$r_{CC} = 1.517 - 0.18p$$

$$r_{CO} = 1.410 - 0.18p .$$

The lengthening is in fact a characteristic feature of aromatic molecules containing a phenanthrenoid arrangement of rings and the cause is generally attributed to the steric effects due to hydrogen overcrowding. Typical examples are perylene (Camerman & Trotter, 1964; 1·471 Å), chrysene (Burns & Iball, 1960; 1·468 Å) and phenanthrene (Kay, Okaya & Cox, 1971; 1·457 Å). In the regular model of these molecules, the hydrogen atoms in the *ortho* positions of the bond concerned are 0·68 Å closer together than the van der Waals radii 2·4 Å. If hydrogen overcrowding is the major cause of the C–C bond lengthening, the study of molecules free from steric hindrance may help to decide the point. Dibenzofuran is ideal in that sense since the molecule concerned

has a non-bonded H(4)···H(4') distance (Fig. 1) in the regular model 0·2 Å greater than the normal van der Waals separation of 2·4 Å. Therefore, hydrogen overcrowding does not arise in the present case. Yet the contact bond C(6)–C(6') is observed to be 1·480 (7) Å. The experimental observation along with the consistent theoretically calculated value (1·468 Å) suggests that π-electron delocalization rather than the steric effect is the main cause of this lengthening. The result of the present MO calculations is in good accord with the experimental findings of dibenzoselenophene by Hope, Knobler & McCullough (1970).

Dibenzofuran crystal belongs to the same space group as carbazole and fluorene where the oxygen atom in the dibenzofuran is been replaced by N–H or C respectively. It resembles carbazole and fluorene in both cell dimensions and parameters. The molecular plane of dibenzofuran makes an angle of 62·9° with the *a* axis while the corresponding angles are 61° in carbazole and 55·2° in fluorene. The tendency for sublimation of these types of compound are probably due to non-existence of any strong intermolecular attractive force apart from the van der Waals forces. The distance of closest approach between carbon atoms of adjacent molecules is 3·74 Å and that between carbon and oxygen atoms 3·43 Å (Table 9). The packing is uniform in the **a** and **b** directions, and a
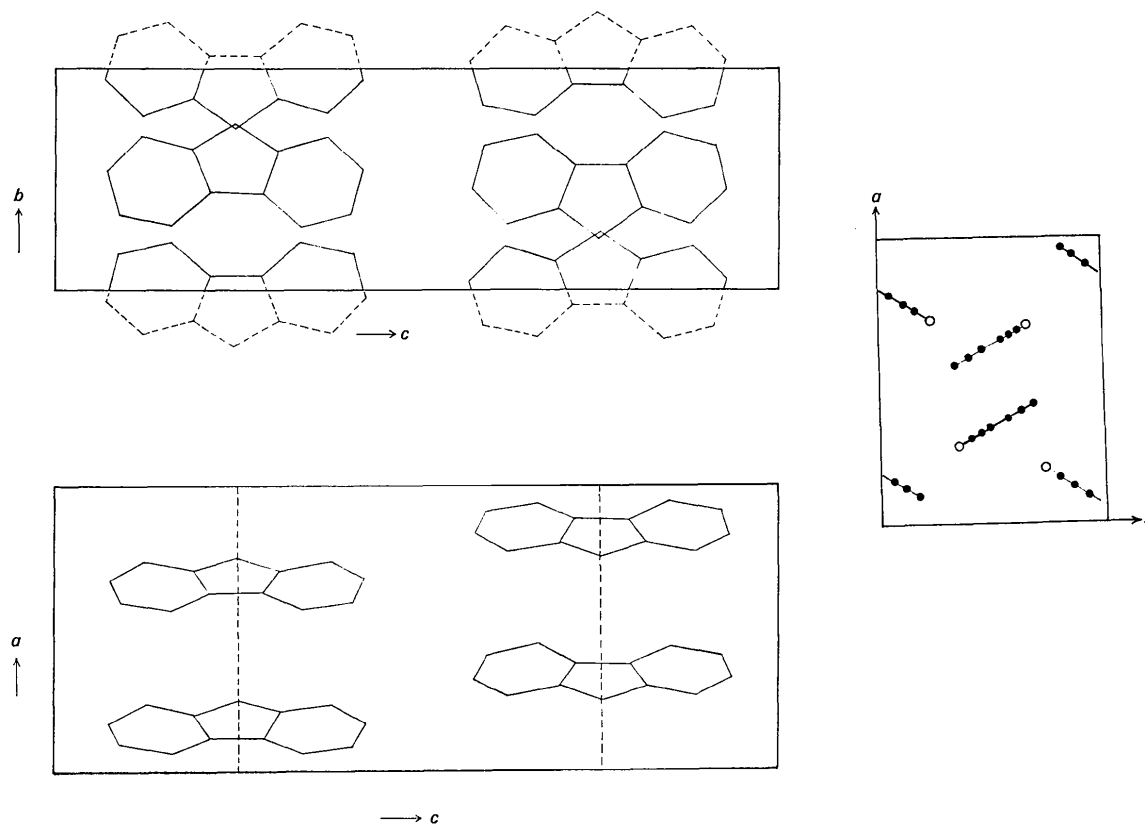

Fig. 2. The three projections of the unit cell.

large gap around $z=0$ and $z=c/2$ explains cleavage, the flakes being parallel to the (001) plane. The crossed packing of the molecules, apparent from the projection in Fig. 2, explains the positive optical sign of dibenzofuran. The bond angles in the five-membered rings vary from 104·4 to 112·9° with an average of 108·5° and those in the six-membered rings in the range 115·3 to 123·9° with an average of 119·6°. The individual six and five-membered rings are strictly planar but the whole molecule is not in a plane. In fact the molecule appears to have taken a slight 'boat' configuration, the benzene rings showing a dihedral angle of 1·2° with the furan ring. It is interesting that this result is similar to those observed in the cases of carbazole and dibenzoselenophene, molecules of nearly identical size and shape.

Table 9. *Some intermolecular distances*

C(1),	I–C(3), II	3·99 Å	O(7),	I–O(1), IV	3·83 Å
C(1),	I–C(4), II	3·76	C(1),	I–V(1), V	3·88
O(7),	I–C(4), II, VIII	3·80	C(3),	I–C(2), VI	3·96
C(2),	I–C(2), III	3·98	C(4),	I–C(2), VI	3·94
C(3),	I–C(2), III	3·89	C(3),	I–C(3), VII	3·98
O(7),	I–C(4), IV, V	3·96	C(4),	I–C(4), VII	3·85
O(7),	I–C(5), IV, V	3·65	C(5),	I–C(4), VII	3·77
O(7),	I–C(6), IV, V	3·42	C(6),	I–C(4), VII	3·74

Positions:

I	$x,$	$y,$	z	V	$\frac{1}{2}+x,$	$1\frac{1}{2}-y,$	z
II	$x,$	$1+y,$	z	VI	$\frac{1}{2}-x,$	$\frac{1}{2}-y,$	z
III	$-x,$	$1-y,$	$1-z$	VII	$\frac{1}{2}+x,$	$\frac{1}{2}-y,$	z
IV	$\frac{1}{2}+x,$	$1\frac{1}{2}-y,$	$\frac{1}{2}-z$	VIII	$x,$	$1+y,$	$\frac{1}{2}-z$

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Crystal Structure of La2(MoO4)3, a New Ordered Defect Scheelite Type

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La2(MoO4)3 crystallizes with monoclinic symmetry, space group $C2/c$, and lattice constants $a=$ 17·006 (4), $b=$ 11·952 (2), $c=$ 16·093 (3), $\beta=$ 108·44 (3)°. Its crystal structure has been determined from single-crystal counter data and refined to a conventional R value of 0·055 for the 2031 structure factors greater than three standard deviations. The structure is related to the scheelite (CaWO4) structure from which it can be derived through vacancy ordering of $\frac{1}{3}$ of the Ca sites. It comprises 9 scheelite subcells. There are 12 formula units per unit cell. Nearest-neighbor environments of the cations resemble those of scheelite: La is in eightfold and Mo in slightly distorted tetrahedral oxygen coordination. One third of the oxygen atoms are coordinated by one Mo and two La atoms, the other two thirds are coordinated by one Mo and one La atom. Interatomic distances reflect the differences in coordination. The structure is discussed and compared to the other known defect scheelite structures, Eu2(WO4)3 and Bi2(MoO4)3.

Introduction

The discovery of ferroelectricity (Borchardt & Bierstedt, 1966) and ferroelasticity (Aizu, 1969) in

Gd2(MoO4)3 has stimulated extensive work in many laboratories and has led to thorough investigations of the rare-earth molybdates and tungstates with compositions L2(MoO4)3 and L2(WO4)3, where L is a rare earth element. These compounds belong to at least five structural types: the Eu2(WO4)3 structure (Templeton

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