Crystal Structure of the 1:1 Molecular Complex of Chrysene and Tetrafluoro-p-benzoquinone (Fluoranil)

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The crystal and molecular structure of the title complex has been determined by three-dimensional X-ray diffraction methods. Crystals are monoclinic, $a = 6\cdot645$, $b = 7\cdot047$, $c = 19\cdot363$ Å, $\beta = 106\cdot6°$, space group $P2_1/c$, $Z = 2$. The structure was determined from 1 078 diffractometer data by Patterson and Fourier methods, and refined by least-squares methods to R $0\cdot070$. In the crystal, alternate planar chrysene and fluoranil molecules form stacks along the b axis. The mean separation of the molecular planes is $3\cdot23$ Å and the interplanar angle is $0\cdot7°$. The interplanar spacing is the same as in perylene–fluoranil, and is not solely determined by charge-transfer interactions, although the relative orientation of the two molecules favours such interactions as well as dipole–induced-dipole forces. There are no abnormally short contacts between the stacks, and the lattice structure is related to the poor photoconductivity of the complex. The dimensions of both molecules are in good agreement with known values.

ALTHOUGH the crystal structures of molecular complexes have been extensively studied,[1] the only complexes of the electron-donor chrysene or the electron-acceptor fluoranil whose structures are known are chrysene–7,7,8,8-tetracyanoquinodimethane [2] and perylene–fluoranil.[3] We have determined the crystal structure of the molecular complex of chrysene and fluoranil as part of a continuing investigation of the structural and electrical properties of molecular complexes.[4] In the chrysene–tetracyanoquinodimethane complex, chrysene molecules in neighbouring stacks overlap more than the equivalent tetracyanoquinodimethane molecules, and this is believed to be an important factor determining the high photoconduction efficiency of the complex. The observed

photoconduction of chrysene–fluoranil crystals is a factor of 10^5 less efficient than that of chrysene–tetracyanoquinodimethane. Thus, it is expected that, despite fluoranil being smaller than tetracyanoquinodimethane, the overlap of both chrysene and fluoranil molecules with those of the same type in adjacent stacks in the lattice should be poor. The crystal structure determination was carried out primarily to test this prediction.

EXPERIMENTAL

Slow evaporation of a solution of chrysene (chromatographed and zone-refined) and fluoranil (purified by repeated sublimation in a Pyrex tube, under argon) in chloroform

[1] C. K. Prout and J. D. Wright, *Angew. Chem. Internat. Edn.*, 1968, **7**, 659; F. H. Herbstein, *Perspectives in Structural Chem.*, 1971, **4**, 166.

[2] P. J. Munnoch and J. D. Wright, *J.C.S. Perkin II*, 1974, 1397

[3] A. W. Hanson, *Acta Cryst.*, 1963, **16**, 1147.

[4] V. M. Vincent and J. D. Wright, *J.C.S. Faraday I*, 1974, **70**, 58.

yielded dark purple crystals, elongated along b. The crystals tended to decompose by slow loss of fluoranil, but this was effectively prevented by sealing the crystal used for diffraction work in a Lindeman tube containing a trace of fluoranil. Unit-cell dimensions were obtained from a least-squares refinement based on 2θ angles for 38 high-angle general peaks, measured with a General Electric XRD 6 four-circle diffractometer. The intensities of 1 078 diffraction maxima, within a sphere defined by $2\theta < 109.7°$, were measured with the diffractometer by a stationary-crystal-stationary-counter technique,[5] converted to equivalent integrated values, and corrected for background and polarisation.

Crystal Data.—$C_{24}H_{12}O_2F_4$, $M = 408.4$, $a = 6.645 \pm 0.013$, $b = 7.047 \pm 0.012$, $c = 19.363 \pm 0.015$ Å, $\beta = 106.6 \pm 0.1°$, $U = 868.7$ Å^3, $D_m = 1.54$ (by flotation), $Z = 2$, $D_c = 1.561$. $F(000) = 416$. Space group $P2_1/c$ (C_{2h}^5,

were repeated, giving R 0.178. A difference Fourier synthesis revealed peaks in the regions where hydrogen atoms were expected but these were not sufficiently sharply defined to justify their use for locating the hydrogen atoms precisely. The difference synthesis also showed evidence for anisotropic thermal motion of the carbon, oxygen, and fluorine, and confirmed that the assignments of oxygen and fluorine atoms were correct, since no residual peaks were observed at the positions of these atoms. Three cycles of full-matrix least-squares refinement with anisotropic temperature factors reduced R to 0.141. Hydrogen atoms were then placed geometrically, assuming C–H 1.05 Å, to lie in the plane of the chrysene molecule, along the bisectors of the relevant C–C–C angles. They were assigned the isotropic temperature factors of the carbon atoms to which they were bonded. Six low-angle reflections with very high values of F_c, evidently suffering from extinction, were given zero weight at

Final atomic co-ordinates ($\times 10^4$) and thermal parameters ($\times 10^3$) * with standard deviations in parentheses

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	991(6)	332(6)	199(2)	37(2)	28(2)	44(3)	8(2)	14(2)	1(2)
C(2)	1 595(6)	268(6)	985(2)	38(2)	26(2)	43(3)	7(2)	8(2)	−3(2)
C(3)	125(7)	−453(6)	1 330(2)	46(3)	31(2)	41(2)	4(2)	14(2)	0(2)
C(4)	−1 861(7)	−1 085(6)	905(2)	44(3)	42(3)	57(3)	2(2)	22(2)	−2(2)
C(5)	−2 430(6)	−1 030(6)	167(2)	38(3)	37(3)	54(3)	−3(2)	16(2)	−1(2)
C(6)	3 575(7)	901(6)	1 424(2)	42(3)	42(3)	54(3)	−2(2)	11(2)	1(2)
C(7)	4 051(8)	787(7)	2 162(2)	57(3)	53(3)	49(3)	0(3)	−5(2)	−2(3)
C(8)	2 592(9)	65(8)	2 493(3)	79(4)	58(3)	39(3)	7(3)	8(3)	−3(2)
C(9)	671(8)	−555(7)	2 089(2)	60(3)	49(3)	45(3)	3(2)	23(2)	0(2)
C(10)	571(7)	4 956(6)	760(2)	49(3)	36(3)	41(3)	7(2)	11(2)	0(2)
C(11)	1 961(7)	5 610(6)	451(2)	40(3)	32(2)	48(3)	4(2)	8(2)	−4(2)
C(12)	1 524(7)	5 730(6)	−342(2)	43(3)	30(2)	55(3)	6(2)	21(2)	0(2)
O(1)	2 794(5)	6 337(5)	−627(2)	59(2)	49(2)	78(2)	−6(2)	44(2)	0(2)
F(1)	3 841(4)	6 239(4)	825(1)	34(1)	63(2)	75(2)	−8(1)	0(1)	−16(2)
F(2)	964(4)	4 874(4)	1 470(1)	76(2)	62(2)	33(2)	10(1)	15(1)	2(1)

	x/a	y/b	z/c	U_{iso}		x/a	y/b	z/c	U_{iso}
H(4)	−2 986	−1 665	1 147	32	H(7)	5 490	1 372	2 477	45
H(5)	−3 923	−1 534	−130	34	H(8)	3 017	−33	3 059	54
H(6)	4 735	1 426	1 204	38	H(9)	−403	−1 141	2 335	38

* The temperature factor T is given by $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)]$.

No. 14, second setting). Cu-K_α radiation, $\lambda = 1.5418$ Å; $\mu(\text{Cu-}K_\alpha) = 11.3$ cm^{-1}.

A three-dimensional sharpened Patterson synthesis computed from the diffractometer data enabled location of all non-hydrogen atoms. Observed structure amplitudes, with phases calculated from these atom co-ordinates, were used in a Fourier synthesis, yielding a more precise initial set of co-ordinates. Structure factors calculated from this model, with overall temperature and scale factors calculated by the DATFIX link of the 'X-Ray '70' system, produced an initial R of 0.311. At this stage it was not possible to distinguish oxygen from fluorine clearly on the Fourier map, so these atoms were assigned tentatively, following examination of a model of the trial structure. The co-ordinates and overall temperature and scale factors were refined by the full-matrix least-squares method, using unit weights for all reflections, for 3 cycles, giving a converged set of parameters with R 0.218. Two further cycles of similar refinement, with individual isotropic temperature factors, reduced R to 0.187. Examination of the peak heights and bond lengths in the fluoranil molecule on a second Fourier synthesis showed that O(1) and F(1) had been incorrectly assigned. These atoms were interchanged and the previous two cycles of refinement

this stage. Three further cycles of least-squares refinement, including but not refining the hydrogen atom parameters, produced a converged set of parameters with R 0.070 for all observed reflections with non-zero weight (0.091 for all 1 078 reflections).

The observed structure amplitudes, together with the structure factors calculated from the final atomic parameters of the Table are presented in Supplementary Publication No. SUP 21262 (6 pp., 1 microfiche).†

All calculations used the 'X-Ray' program system [6] either on the University of London CDC 7600 computer or on the University of Kent ICL 4130 computer. Atomic scattering factors for neutral atoms were taken from ref. 7.

RESULTS AND DISCUSSION

The crystal structure is shown in Figure 1, and the bond lengths and interbond angles, with their standard deviations (estimated by the BONDLA link of the 'X-Ray'

† See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

5 T. C. Furnas, ' Single-Crystal Orienter Instruction Manual,' General Electric Company, Milwaukee, Wisconsin, 1957.

6 ' X-Ray '67,' Program System, 1970 version, J. M. Stewart, F. A. Kundell, and J. C. Baldwin, Computer Science Centre, University of Maryland Technical Report TR 67 58.

7 ' International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 220.

program system, from the diagonal elements from the least-squares refinement), are in Figure 2. There are no significant differences between these dimensions and
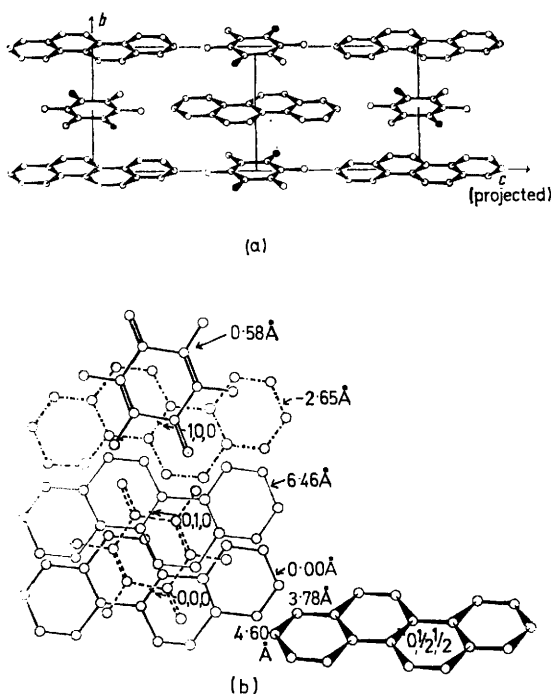

(a)

(b)

FIGURE 1   The molecular arrangement in the crystal of chrysene–fluoranil, projected (a) down the a axis and (b) on the plane of the chrysene molecule at 0,0,0. In (b), the projected positions of the origin; 0,1,0; 1,0,0; and 0,1/2,1/2 are shown. The distances given are relative heights of the molecular centres and of atoms C(8') and C(9') of the chrysene molecule at 0,1/2, 1/2 above the least-squares best plane through the chrysene at the origin. The transformation matrix from the fractional atomic co-ordinates of the monoclinic unit cell to the orthogonal (Å) best plane co-ordinates X, Y, and Z (with Z perpendicular to the molecule plane), is:

$$\begin{bmatrix} 0.5663 & 0.1179 & 18.0082 \\ 6.0884 & 2.7591 & -6.6593 \\ -2.6013 & 6.4833 & 2.5066 \end{bmatrix}$$

those reported previously either for the free molecules [8,9] or in complexes.[2,3] Both molecules are planar, the mean deviation from the least-squares best plane through the molecule (excluding hydrogen atoms) being 0.007 Å for chrysene and 0.004 Å for fluoranil. The angle between the two molecular planes is 0.7°. Figure 1(b) shows the fluoranil molecule projected on the least-squares best plane of the chrysene molecule. Each fluoranil molecule is substantially covered on both sides by chrysene molecules, and in this arrangement any significant deviation from the parallel would lead to a rapid increase in intermolecular repulsions. The observed relative orientation of the molecules provides reasonably good overlap of the first, third, and fifth highest-filled molecular orbitals of chrysene with the lowest-vacant orbital of

fluoranil, and is probably close to the position of best overlap, although no MO calculations have been performed to test this.[10] Interactions of the polar C=O groups of fluoranil with the polarisable π-electrons of neighbouring chrysene molecules are also favoured in the observed orientation. The mean interplanar spacing (3.23 Å) is the same as that in the perylene–fluoranil complex [3] (which also crystallises in a monoclinic space group) despite the appreciably higher ionisation potential of chrysene (7.75 eV) compared to that of perylene (7.15 eV). This is in marked contrast to the observation [2] that, for a series of complexes of tetracyanoquinodimethane, the interplanar spacings for complexes belonging to a given crystal system depend linearly on the donor ionisation potential, as predicted by perturbation theory. The absence of such a relationship in the fluoranil complexes suggests that forces other than charge-transfer resonance control the interplanar spacings. Charge-transfer is expected to be less important in fluoranil complexes, since fluoranil has a significantly lower electron affinity (2.48 eV) than that of tetracyanoquinodimethane (2.88 eV). The observed interplanar spacing in this complex is among the shortest known in molecular complexes, but this does not necessarily imply strong charge-transfer forces. There are only three contacts between
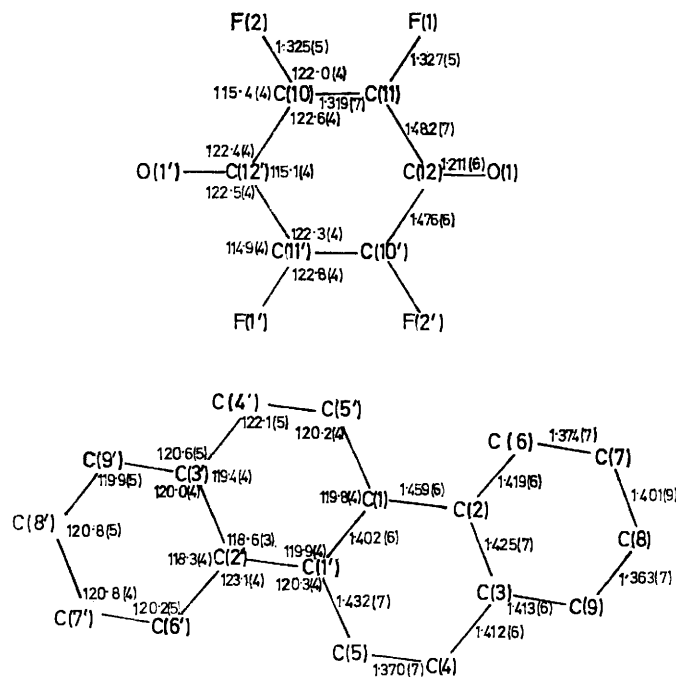

FIGURE 2   Bond lengths (Å) and interbond angles (deg.), with standard deviations in parentheses

chrysene and fluoranil which are shorter than the sum of the van der Waals radii [11] of the atoms involved [C(10') ··· C(4') 3·28, C(1) ··· C(12') 3·29, and C(2) ··· C(10) 3.38 Å].

[8] D. M. Burns and J. Iball, *Proc. Roy. Soc.*, 1960, *A*, **257**, 491.
[9] A. Meresse, C. Courseille, and Nguyen Ba Chanh, *Acta Cryst.*, 1974, **B30**, 524.

[10] B. Mayoh and C. K. Prout, *J.C.S. Faraday II*, 1972, **68**, 1072.
[11] S. C. Nyburg, ' *X*-Ray Analysis of Organic Structures,' p. 303, Academic Press, London, 1961.

The crystal structure is built up of the stacks of alternating donor and acceptor molecules characteristic of π–π^* electron-donor–acceptor complexes. The stacking axis is the b axis. The closest contact (3.29 Å) between molecules in adjacent stacks is between C(9) of chrysene at 0,0,0 and F(2′) of fluoranil at 1/2,1/2,0, but this is not shorter than expected from the C–H bond length and the van der Waals radii of H and F, and there is no evidence to suggest hydrogen bonding. There is no π-overlap between molecules of the same type in adjacent stacks (Figure 1), and this confirms the predic-tion made on the basis of photoconductivity data. Other poorly photoconducting molecular complexes (*e.g.* anthracene–tetracyanoquinodimethane [12]) also show a similar lack of overlap.

The lattice packing allows both components rather more vibrational freedom than is possible in many mole-cular complexes, as reflected in the values of the aniso-tropic temperature factors. However, the latter are not large enough to warrant consideration of disorder in the structure. This is supported by the good agreement between the dimensions of both molecules and those of previous determinations.

[12] R. M. Williams and S. C. Wallwork, *Acta Cryst.*, 1968, *B*, **24**, 168.