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# The Crystal Structure of the 1:1 Perylene-Fluoranil Complex

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The crystal is monoclinic,  $P2_1/n$ , with

a = 17.13, b = 7.49, c = 6.97 Å,  $\beta = 90.40^{\circ}, Z = 2$ .

The structure was determined by trial-and-error methods, and refined by three-dimensional differential syntheses. The fluoranil molecule was found to be planar, and the perylene molecule nearly so. The two molecules overlap each other, and the average distance between their mean planes is 3.23 Å.

### Introduction

The 1:1 complex of perylene and fluoranil (Fig. 1) is a charge-transfer complex exhibiting moderately high photoconductivity. The X-ray analysis was undertaken in order to facilitate the interpretation of the electronic and optical properties of the crystal, currently under investigation by Dr W. G. Schneider of the Division of Pure Chemistry.



Fig. 1. The perylene-fluoranil complex.

# Experimental

Crystal data Monoclinic.

$$\begin{array}{c} a = 17 \cdot 13 \pm 0 \cdot 01, \ b = 7 \cdot 49 \pm 0 \cdot 01, \ c = 6 \cdot 97 \pm 0 \cdot 01 \ \text{\AA}; \\ \beta = 90 \cdot 40 \pm 0 \cdot 05^{\circ}; \ V = 894 \cdot 2 \ \text{\AA}^3. \end{array}$$

Formula C<sub>20</sub>H<sub>12</sub>, C<sub>6</sub>F<sub>4</sub>O<sub>2</sub>; F.W. 432·36.

 $D_m$  (measured density) = 1.60 g.cm<sup>-3</sup>.

$$D_x$$
 (calculated density) = 1.605 g.cm<sup>-3</sup>.

Z=2.

 $\mu = 12.8 \text{ cm}^{-1}$  (Cu  $K\alpha$ ).

Space group  $P2_1/n$  ( $C_{2\hbar}^5$ ) (from precession photographs, and examination of reflections with XRD 5 spectrogoniometer).

Molecular symmetry: centre.

The crystals, grown from toluene solution, are

shiny, opaque, and bluish black, but decompose in air, leaving a yellow-green residue. The usual form is the prism  $\{110\}$ , elongated in the c direction. Many of these prisms are modified to a lath shape by the pinacoid  $\{100\}$ . One such lath was cut to give a specimen of dimensions  $0.2 \times 0.3 \times 0.4$  mm, with the shortest edge parallel to  $\mathbf{a}$ , and the longest parallel to **b**. It was mounted with **b** parallel to the fibre axis. Unit cell parameters and relative intensities were obtained from this specimen on the General Electric XRD 5 spectrogoniometer and goniostat. Cu  $K\alpha$ radiation and a scintillation counter were used, and reasonable monochromatization was achieved by means of a  $K\beta$  filter and a reverter (pulse-height analyser). The 'moving-crystal moving-counter' method of Furnas was used (1957). The goniostat settings were precomputed. Absorption corrections were deemed to be unnecessary, and were not made.

The accumulation of extraneous material due to gradual decomposition of the specimen caused some non-uniform, low-angle background scattering, which was believed to jeopardize the accurate measurement of some of the low intensities. For this reason, all of the weaker reflections with  $2\theta \leq 65^{\circ}$  were remeasured, on a freshly-prepared specimen.

Of the 1994 reflections accessible to the spectrogoniometer (that is, those for which  $2\theta \leq 165 \cdot 4^{\circ}$ ) 1632 were observed. The range of observed intensities is about 1 to 48,000.

#### Structure determination

The very high intensities of the reflections 002 and 012indicated roughly the plane in which the molecules must lie, and a study of the hk0 weighted reciprocallattice section suggested their orientations. Their positions were, of course, fixed by symmetry; each had to lie on a centre. A trial structure was thus easily deduced, and was refined somewhat with the aid of h0l and hk0 electron-density projections. Refinement was completed by means of a threedimensional Fourier synthesis, and several threedimensional differential syntheses. In the later stages, net coordinate shifts were obtained by comparison of  $F_o$  and  $F_c$  syntheses. The scattering-factor curves used for the associated structure-factor calculations were those of Freeman (1959); the contribution of the hydrogen atoms was included, using reasonable assumed positions.

Comparison of observed and calculated peak heights and curvatures indicated a considerable anisotropy of thermal motion, which, while not of fundamental interest, was considered likely to interfere with the estimation of finite summation corrections. The most seriously affected atoms were therefore represented in structure-factor calculations by galaxies of two or four fractional atoms, suitably disposed (Kartha & Ahmed, 1960). The coordinates and temperature factors used in the final structure-factor calculations (corresponding to the penultimate stage of refinement) are given in Table 1. The quantities  $\Delta B_1$  and  $\Delta B_2$ do not appear in the calculations; they merely indicate the magnitude of the anisotropy represented by the corresponding distributions of fractional atoms. Peak heights and curvatures are given in Table 2; there is fair agreement between observed and calculated quantities. Much of the anisotropic thermal motion is reasonably attributable to a libration of each molecule about its centre, of r.m.s. amplitude 1.5° for pervlene, and  $2.4^{\circ}$  for fluoranil. However, libration corrections to the atomic positions were considered too small to be significant, and have not been applied. Difference Fourier projections along **b** and **c** showed no details inconsistent with the proposed structure. The ultimate atomic positions are given in Table 3. The greatest coordinate shift in the last cycle of refinement was 0.002 Å, or about half the subsequently estimated standard deviation of coordinates.

# Assessment of results

Stereochemical plausibility, agreement between observed and calculated peak heights, and the appearance of the difference projections all suggest that the proposed structure is correct. The final proof, however, is to be found in the reasonable agreement between observed and calculated structure amplitudes. A summary of the agreement is given in Table 4; the observed structure amplitudes range from 0.6 to 141.5,  $F_c(000) = 440$ , and the agreement residual  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.11$ , for observed reflections only. A complete list of  $F_o$  and  $F_c$  is available from the author, on request.

The standard deviations of coordinates have been estimated by Cruickshank's method (Lipson & Cochran, 1953). The mean values are: for carbon, 0.0036; oxygen, 0.0029; fluorine, 0.0026 Å. Because of finite summation effects, and the anisotropy of thermal motion, individual values differ from the mean by as much as 35%.

Table 1. Parameters used	l in last	structure-factor	calculation
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$\mathbf{Atom}$	x	y	z	В	$\Delta B_1$	$\Delta B_2$	Atom	$\boldsymbol{x}$	$\boldsymbol{y}$	z	B	$\Delta B_1$	$\Delta B_2$
C 1	0.0475	-0.1478	-0.0662	2.37		<u> </u>	C11	0.0413	-0.1523	0.4391	2.93		
C 2	$0.0844 \\ 0.0827$	$0.0022 \\ 0.0229$	$-0.0015 \\ 0.0058$	$2 \cdot 20$	0.59	-	C12	$0.0870 \\ 0.0848$	$- \begin{array}{c} 0.0054 \\ 0.0206 \end{array}$	0·5045 0·4950	$2 \cdot 40$	0.94	
C 3	0.0385	0.1603	0.0675	2.40			C13	0.0358	0.1603	0.5631	2.90		_
C 4	0·1009 0·0888	$-0.2770 \\ -0.2928$	$-0.1273 \\ -0.1300$	3.16	1.24		014	$0.1568 \\ 0.1542$	$-0.0058 \\ 0.0359$	₀ 0·5065 0·4923	$3 \cdot 22$	1.49	0.86
C 5	$0.1678 \\ 0.1662$	$0.0104 \\ 0.0412$	$-0.0010 \\ 0.0112$	2.66	1.31			$0.1562 \\ 0.1549$	$0.0032 \\ 0.0269$	$0.4795 \\ 0.5193$			
C 6	$0.0814 \\ 0.0714$	$0.3042 \\ 0.3188$	$0.1283 \\ 0.1355$	3.43	0.94		F 15	0.0924 0.0776 0.0864	-0.2783 -0.3009 -0.2783	$0.3886 \\ 0.3768 \\ 0.3639$	3.40	1.28	0.86
C 7	0.1818	-0.2570	-0.1109	3.43	1.75	0.38		0.0836	-0.3009	0.4014			
	$0.1726 \\ 0.1818 \\ 0.1726$	-0.2842-0.2531-0.2882	-0.1368 -0.1295 -0.1182				F 16	0.0825 0.0664 0.0701	0.2996 0.3126 0.2026	0.6051 0.6304 0.6338	<b>3</b> ∙ <b>4</b> 0	1.52	0.98
C 8	0.2144	-0.1028	-0.0430	3.04	2.07	0.39		0.0697	0.2320 0.3196	0.6018			
	0.2096 0.2141	-0.1354	-0.0745 -0.0614				H17	0.0662	-0.4048	-0.1790	5.00		_
	0.2141 0.2100	-0.1411	-0.0561				H18	0.0416	0.4211	0.1792	5.00		
C 9	0.2054	0.1722	0.0580	3.24	1.49	0.34	H19	0.2128	-0.3780	-0.1724	5.00	_	_
	$0.1993 \\ 0.2050$	0.1968 0.1661	$0.0872 \\ 0.0748$				H20	0.1860	0.4444	0.1826	$5 \cdot 00$	-	
	0.1996	0.2029	0.0703				H21	0.2747	-0.1119	-0.0568	5.00	_	_
C 10	$0.1646 \\ 0.1519 \\ 0.1622 \\ 0.1544$	0.3108 0.3396 0.3112 0.3392	0.1257 0.1406 0.1481 0.1182	3.43	1.68	0.56	H22	0.2654	0.1927	0.0740	5.00		

Table 2.	Peak	heights	and	curvatures
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Values in italics are from  $F_c$  differential synthesis

Atom	$(e. \overset{Q}{A^{-3}})$	$(e. A^{-5})$	$(e. A^{-5})$	$(e. A^{-5})$	$\substack{ \substack{ \varrho xy \ (e. A^{-5}) } }$	$(e. A^{-5})$	$\substack{ \varrho_{yz} \\ ({\rm e. \AA^{-5}}) }$
C 1	10·3 10·4	$\begin{array}{c} -90 \cdot 2 \\ -91 \cdot 0 \end{array}$	-96.5 -99.5	-108.7 -104.5	$2 \cdot 5$ $0 \cdot 9$	$\begin{array}{c} 0 \cdot 3 \\ \theta \cdot \theta \end{array}$	$5 \cdot 2 \\ 3 \cdot 7$
C 2	10·2 10·3	-95.2 - 95.0	-90.3 -91.4	-108.0 -106.0	$\begin{array}{c} -1 \cdot 0 \\ -\theta \cdot 9 \end{array}$	0.9 0.5	$7\cdot 8$ $5\cdot 9$
C 3	10·0 10·2	-87.6 -89.9	-91.8 -94.7	-104.7 -102.0	$-2.4 \\ -0.1$	$1 \cdot 1$ $1 \cdot 5$	${3\cdot 7} olimits 2\cdot 3$
C 4	8·5 8·5	$-67 \cdot 1 - 67 \cdot 2$	-78.1 -76.0	$- \frac{83 \cdot 0}{- 82 \cdot 1}$	$4 \cdot 4$ $1 \cdot 3$	1·8 1·0	$1 \cdot 0$ $\theta \cdot 9$
C 5	8·8 <i>9</i> ·0	-80.4 -78.8	-69.6 -74.2	-87.5 -86.9	$\begin{array}{c} -1 \cdot 6 \\ -0 \cdot 9 \end{array}$	$\begin{array}{c} - 0 \cdot 0 \\ - \theta \cdot 5 \end{array}$	$7 \cdot 1$ $4 \cdot 7$
C 6	$8\cdot 5$ $8\cdot 4$	-68.0 -68.1	-80.1 -75.9	$-81 \cdot 9$ $-79 \cdot 1$	$-5.8 \\ -2.5$	$-1.3 \\ -0.4$	$2 \cdot 1 \\ 2 \cdot 0$
C 7	7·8 7·8	-69.7 - 66.0	- 64.3 - 64.1	-70.3 -67.6	$13\cdot 3$ $7\cdot 4$	$4 \cdot 8$ $2 \cdot 9$	$2 \cdot 2 \\ 1 \cdot 7$
C 8	7·9 <i>8</i> ·0	-77.5 -72.5	-52.9 -59.0	-70.8 -70.1	$5 \cdot 5$ $2 \cdot 3$	$2 \cdot 6 \\ 1 \cdot 5$	$6.2 \\ 4.5$
C 9	$7 \cdot 9 \\ 8 \cdot 1$	-77.2 -74.0	-54.9 -59.8	-72.5 -71.9	$- \frac{8 \cdot 3}{- 4 \cdot 2}$	-3.1 -1.3	$5 \cdot 1 \ 2 \cdot 9$
C10	7·5 7·6	-59.3 -59.3	-63.6 -62.4	$- 64 \cdot 2 \\ - 62 \cdot 5$	-12.5 - 6.7	$0.1 \\ -1.8$	$-5.2 \\ -2.5$
C11	$9 \cdot 2$ $9 \cdot 4$	-80.0 -81.4	-83.4 -85.8	$-91.8 \\ -90.2$	$6 \cdot 6$ $4 \cdot 8$	$2 \cdot 2$ $1 \cdot 5$	$egin{array}{c} - 0.3 \\ 0.7 \end{array}$
C12	$9{\cdot}6$ $9{\cdot}8$	-97.6 -95.4	-77.5 -80.5	-98.1 -97.6	-2.3 -1.8	0·3 0·7	$4.6 \\ 1.2$
C13	$\begin{array}{c} 9 \cdot 2 \\ 9 \cdot 4 \end{array}$	-80.0 -81.5	- 84.8 - 86.2	-90.3 -88.8	-6.9 -3.8	$-2.3 \\ -1.7$	$\begin{array}{c} 0 \cdot 0 \\ 0 \cdot 6 \end{array}$
014	$\frac{11\cdot8}{11\cdot7}$	-116.8 -106.4	-88.3 -90.3	-97.0 -95.4	-2.6 -1.3	$- \begin{array}{c} 0 \cdot 4 \\ 0 \cdot 1 \end{array}$	$2 \cdot 1 \\ 0 \cdot 7$
F15	13·4 13·7	-107.8 - 110.0	-113.3 -113.7	$-111\cdot 3$ $-113\cdot 2$	$9.8 \\ 4.6$	$2 \cdot 2 \\ 1 \cdot 0$	-6.9 -4.2
F16	$13\cdot 2$ $13\cdot 5$	-103.8 -106.4	-113.3 -112.2	-110.8 -111.2	-11.6 -5.2	$\begin{array}{c} - 0 \cdot 6 \\ - \theta \cdot 3 \end{array}$	-4.0 -2.3

# Table 3. Final atomic positions

Ŧ	(x,	y,	z;	$\frac{1}{2} + x$ ,	$\frac{1}{2} - y$ ,	$\frac{1}{2} + z$ )
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Atom	x	$\boldsymbol{y}$	z
C 1	0.0474	-0.1478	-0.0664
C 2	0.0834	0.0125	0.0023
C 3	0.0384	0.1602	0.0677
C 4	0.0947	-0.2849	-0.1287
C 5	0.1669	0.0257	0.0052
C 6	0.0766	0.3114	0.1318
C 7	0.1773	-0.2708	-0.1239
C 8	0.2120	-0.1192	-0.0588
C 9	0.2023	0.1847	0.0725
C10	0.1582	0.3252	0.1330
C11	0.0414	-0.1522	0.4393
C12	0.0858	0.0077	0.4996
C13	0.0357	0.1601	0.5629
014	0.1556	0.0120	0.4993
F15	0.0850	-0.2896	0.3828
F16	0.0744	0.3060	0.6177

### **Description of the structure**

Individual characteristics of the two molecules are indicated in Fig. 2. The fluoranil molecule may be

# Table 4. Agreement summary

	Category	Number of reflections
1.	$ \Delta F  \leq F_T$ or $ \Delta F  \leq 0.2F_o$	1758
2.	$(F_T <  \Delta F  \le 2F_T \text{ or } 0.2F_o <  \Delta F  \le 0.4F_o)$	224
3.	$(2F_T <  \Delta F  \le 3F_T)$	11
4.	$(3F_T <  \Delta F  \le 4F_T)$	1
	$\Delta F =  F_o  -  F_c .$ $F_T$ = estimated minimum observable struct	ure amplitu

 $F_T$  = estimated minimum observable structure amplitude for reflection concerned.

considered planar, as no atom lies more than about twice its estimated standard deviation from the mean plane. However, two atoms of the perylene molecule lie about three times their estimated standard deviations from its mean plane, and the implied departure from planarity may be significant. There is of course, no reason to believe that the molecule should be precisely planar, and certain physical measurements indicate that it is not (Clar, 1950; Bergmann, Fischer & Pullman, 1951). Perhaps the most surprising aspect of the apparent departure from planarity is its smallness.



Fig. 2. Molecular geometry; distances are given in Å, and angles in degrees. Estimated standard deviation of bond lengths is 0.005 Å; of angles,  $0.5^{\circ}$ . Quantities in parenthesis are distances of atoms from molecular plane, multiplied by 1000. They are given only when such distance exceeds the estimated standard deviation.

Differences in length of as much as 0.018 Å are found between chemically equivalent but crystallographically distinct bonds. For the pairs of bonds concerned,  $\sigma = [\sigma(l_1)^2 + \sigma(l_2)^2]^{\frac{1}{2}} = 0.0072$  Å. Thus  $\Delta l =$ 0.018 Å =  $2.5\sigma$ . The difference might be significant, but is scarcely great enough to warrant discussion. The bond lengths found for perylene are reasonably close to the less precise values given by Donaldson, Robertson & White (1953). The shape of the fluoranil molecule is generally similar to that found for chloranil by Chu, Jeffrey & Sakurai (1962). The angle between adjacent C-F bonds is  $63.9^{\circ}$ , which is close to the corresponding value of  $64.9^{\circ}$  for chloranil.

The molecular packing is illustrated in Fig. 3. The structure can be considered as consisting of layers like that shown in Fig. 3(a), stacked by the operation of the *n* glide so that perylene and fluoranil molecules overlap (Fig. 3b, c, d).

The mean planes of the perylene and fluoranil molecules (in crystallographic coordinates) are:

0.2523x - 2.7956y + 6.4647z = 0 and 0.2554x - 2.5775y + 6.5435z = 3.2718 respectively.

The average distance between these planes (in the region of overlap) is 3.23 Å. A similarly short distance has been reported by Wallwork (1961) for the complex of chloranil with NNN'N'-tetramethyl-p-phenyl-enediamine.

Both planes are nearly parallel (within  $1^{\circ}$ ) to **a**. They make angles of  $21 \cdot 9^{\circ}$  and  $20 \cdot 1^{\circ}$  with **c**, and are



Fig. 3. Structural details. (a) One layer of the structure, near plane z = 0, (b) A portion of the z axis, showing overlap. (c) Two overlapping molecules, viewed along normal to average molecular plane. (d) Overlapping molecules, viewed approximately along a. The non-parallelism of adjacent molecules is somewhat exaggerated.

inclined to each other at  $1.8^{\circ}$ . The effect of nonparallelism is to increase the minimum distance of the fluorine atoms from the plane of the overlapping perylene molecule (in the region of overlap, Fig. 3c, d) by 0.08 Å to 3.31 Å, and to decrease the corresponding distance for fluoranil carbon atoms by 0.04 Å to 3.19 Å. This result is consistent both with F–C repulsion and C–C attraction. As might be expected, the shortest intermolecular distances are found between overlapping molecules; these have minimum values of 3.29 Å for C–C, 3.34 Å for C–O, and 3.36 Å for C–F. Minimum distances between non-overlapping molecules are 3.39 Å for C–O, 3.45 Å for F–F, 3.46 Å for C–F, and 3.53 Å for C–C.

The specimen material was supplied by Dr W. G. Schneider. All computations for the project were carried out by Dr  $\overline{F}$ . R. Ahmed, using the IBM 650 computer of the Canadian Army Directorate of

Personnel Statistics, and the IBM 1620 computer of the National Research Council. Their assistance, and the continued encouragement of Dr W. H. Barnes, are gratefully acknowledged.

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# Probability Distribution Connected with Structure Amplitudes of Two Related Crystals. II. Probability Distribution of the Product

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The paper deals with the probability distributions connected with the product of the structure amplitudes of a pair of related crystals and they represent, essentially, a generalization of the usual statistics to a pair of crystals. Expressions are derived for the distribution of the normalized 'correlation intensity',  $Z = |F_N| |F_P| / \sigma_N \sigma_P$ , and the 'normalized correlation amplitude',  $Y = Z^{\frac{1}{2}}$ , where  $|F_N|$  and  $|F_P|$  are the structure amplitudes of the two crystals containing N and P atoms respectively (P < N) and  $\sigma_N$  and  $\sigma_P$  are the root-mean-square values of  $|F_N|$  and  $|F_P|$ . One limiting form of the general distribution characterizes the usual statistics of a single crystal while the other corresponds to the two crystals being independent or 'non-related'. On the basis of these results a statistical criterion is proposed for use as an index to measure the 'degree of relatedness' between two compounds in practice. A critical assessment of the relative merits of the tests developed in this paper and the function P(w) suggested in Part I is also made.

#### Introduction

In Part I Ramachandran, Srinivasan & Sarma (1963) considered the problem of the probability distribution of the difference in structure amplitudes of two crystals both when they are related to and when they are independent of each other. From the results thus obtained it was suggested that the distribution function could be used in practice for testing the degree of isomorphism of two compounds. In this paper we shall be mainly concerned with the corresponding problem of the distribution of the product of the two structure amplitudes.\* Such a product is in the nature of an intensity and, in fact, the intensity from a single crystal can be considered to be the product of two ideally isomorphous, identical

<sup>\*</sup> The nature of the general assumptions made and also the conditions of applicability *etc.* are the same as in Part I. So also the notation used here follows closely that of Part I.