

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

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(Received 7 January 1963)

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

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

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 \AA.

### 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.

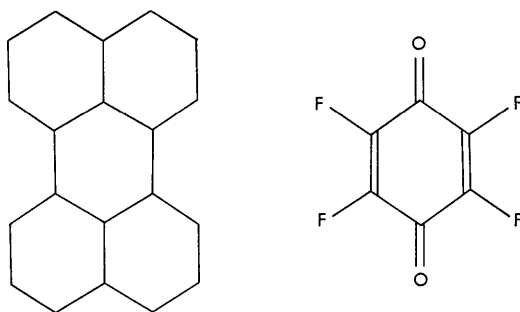


Fig. 1. The perylene-fluoranil complex.

### Experimental

#### Crystal data

Monoclinic.

$$a = 17.13 \pm 0.01, b = 7.49 \pm 0.01, c = 6.97 \pm 0.01 \text{ \AA}; \\ \beta = 90.40 \pm 0.05^\circ; V = 894.2 \text{ \AA}^3.$$

Formula  $C_{20}H_{12}, C_6F_4O_2$ ; 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  $P2_1/n$  ( $C_{2h}^5$ ) (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  $a$ , 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 re-measured, on a freshly-prepared specimen.

Of the 1994 reflections accessible to the spectrogoniometer (that is, those for which  $2\theta \leq 165.4^\circ$ ) 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 012 indicated roughly the plane in which the molecules must lie, and a study of the  $hk0$  weighted reciprocal-lattice 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.



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

Atom	$Q$ (e.Å <sup>-3</sup> )	$Q_{xx}$ (e.Å <sup>-5</sup> )	$Q_{yy}$ (e.Å <sup>-5</sup> )	$Q_{zz}$ (e.Å <sup>-5</sup> )	$Q_{xy}$ (e.Å <sup>-5</sup> )	$Q_{xz}$ (e.Å <sup>-5</sup> )	$Q_{yz}$ (e.Å <sup>-5</sup> )
C 1	10.3	-90.2	-96.5	-108.7	2.5	0.3	5.2
	<i>10.4</i>	<i>-91.0</i>	<i>-99.5</i>	<i>-104.5</i>	<i>0.9</i>	<i>0.0</i>	<i>3.7</i>
C 2	10.2	-95.2	-90.3	-108.0	-1.0	0.9	7.8
	<i>10.3</i>	<i>-95.0</i>	<i>-91.4</i>	<i>-106.0</i>	<i>-0.9</i>	<i>0.5</i>	<i>5.9</i>
C 3	10.0	-87.6	-91.8	-104.7	-2.4	1.1	3.7
	<i>10.2</i>	<i>-89.9</i>	<i>-94.7</i>	<i>-102.0</i>	<i>-0.1</i>	<i>1.5</i>	<i>2.3</i>
C 4	8.5	-67.1	-78.1	-83.0	4.4	1.8	1.0
	<i>8.5</i>	<i>-67.2</i>	<i>-76.0</i>	<i>-82.1</i>	<i>1.3</i>	<i>1.0</i>	<i>0.9</i>
C 5	8.8	-80.4	-69.6	-87.5	-1.6	-0.0	7.1
	<i>9.0</i>	<i>-78.8</i>	<i>-74.2</i>	<i>-86.9</i>	<i>-0.9</i>	<i>-0.5</i>	<i>4.7</i>
C 6	8.5	-68.0	-80.1	-81.9	-5.8	-1.3	2.1
	<i>8.4</i>	<i>-68.1</i>	<i>-75.9</i>	<i>-79.1</i>	<i>-2.5</i>	<i>-0.4</i>	<i>2.0</i>
C 7	7.8	-69.7	-64.3	-70.3	13.3	4.8	2.2
	<i>7.8</i>	<i>-66.0</i>	<i>-64.1</i>	<i>-67.6</i>	<i>7.4</i>	<i>2.9</i>	<i>1.7</i>
C 8	7.9	-77.5	-52.9	-70.8	5.5	2.6	6.2
	<i>8.0</i>	<i>-72.5</i>	<i>-59.0</i>	<i>-70.1</i>	<i>2.3</i>	<i>1.5</i>	<i>4.5</i>
C 9	7.9	-77.2	-54.9	-72.5	-8.3	-3.1	5.1
	<i>8.1</i>	<i>-74.0</i>	<i>-59.8</i>	<i>-71.9</i>	<i>-4.2</i>	<i>-1.3</i>	<i>2.9</i>
C10	7.5	-59.3	-63.6	-64.2	-12.5	0.1	-5.2
	<i>7.6</i>	<i>-59.3</i>	<i>-62.4</i>	<i>-62.5</i>	<i>-6.7</i>	<i>-1.8</i>	<i>-2.5</i>
C11	9.2	-80.0	-83.4	-91.8	6.6	2.2	-0.3
	<i>9.4</i>	<i>-81.4</i>	<i>-85.8</i>	<i>-90.2</i>	<i>4.8</i>	<i>1.5</i>	<i>0.7</i>
C12	9.6	-97.6	-77.5	-98.1	-2.3	0.3	4.6
	<i>9.8</i>	<i>-95.4</i>	<i>-80.5</i>	<i>-97.6</i>	<i>-1.8</i>	<i>0.7</i>	<i>1.2</i>
C13	9.2	-80.0	-84.8	-90.3	-6.9	-2.3	0.0
	<i>9.4</i>	<i>-81.5</i>	<i>-86.2</i>	<i>-88.8</i>	<i>-3.8</i>	<i>-1.7</i>	<i>0.6</i>
O14	11.8	-116.8	-88.3	-97.0	-2.6	-0.4	2.1
	<i>11.7</i>	<i>-106.4</i>	<i>-90.3</i>	<i>-95.4</i>	<i>-1.3</i>	<i>0.1</i>	<i>0.7</i>
F15	13.4	-107.8	-113.3	-111.3	9.8	2.2	-6.9
	<i>13.7</i>	<i>-110.0</i>	<i>-113.7</i>	<i>-113.2</i>	<i>4.6</i>	<i>1.0</i>	<i>-4.2</i>
F16	13.2	-103.8	-113.3	-110.8	-11.6	-0.6	-4.0
	<i>13.5</i>	<i>-106.4</i>	<i>-112.2</i>	<i>-111.2</i>	<i>-5.2</i>	<i>-0.3</i>	<i>-2.3</i>

Table 3. *Final atomic positions*

Atom	$\pm(x, y, z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$		
	$x$	$y$	$z$
C 1	0.0474	-0.1478	-0.0664
C 2	0.0834	0.0125	0.0023
C 3	0.0384	0.1605	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
O14	0.1556	0.0150	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. ( $F_T <  \Delta F  \leq 2F_T$ or $0.2F_o <  \Delta F  \leq 0.4F_o$ )	224
3. ( $2F_T <  \Delta F  \leq 3F_T$ )	11
4. ( $3F_T <  \Delta F  \leq 4F_T$ )	1

$\Delta F = |F_o| - |F_c|$ .  
 $F_T$  = 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.

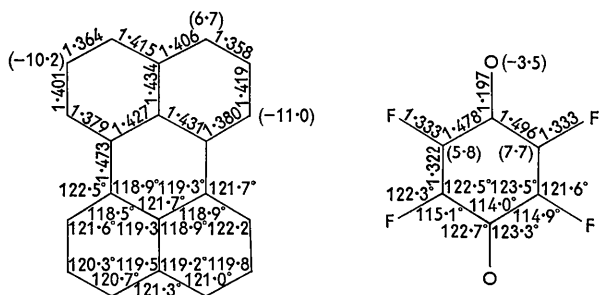


Fig. 2. Molecular geometry; distances are given in Å, and angles in degrees. Estimated standard deviation of bond lengths is 0.005 Å; of angles, 0.5°. Quantities in parenthesis are distances of atoms from molecular plane, multiplied by 1000. They are given only when such distance exceeds the estimated 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°, which is close to the corresponding value of 64.9° 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:

$$0.2523x - 2.7956y + 6.4647z = 0 \quad \text{and} \\ 0.2554x - 2.5775y + 6.5435z = 3.2718 \quad \text{respectively.}$$

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'*-tetramethyl-*p*-phenylenediamine.

Both planes are nearly parallel (within 1°) to *a*. They make angles of 21.9° and 20.1° with *c*, and are

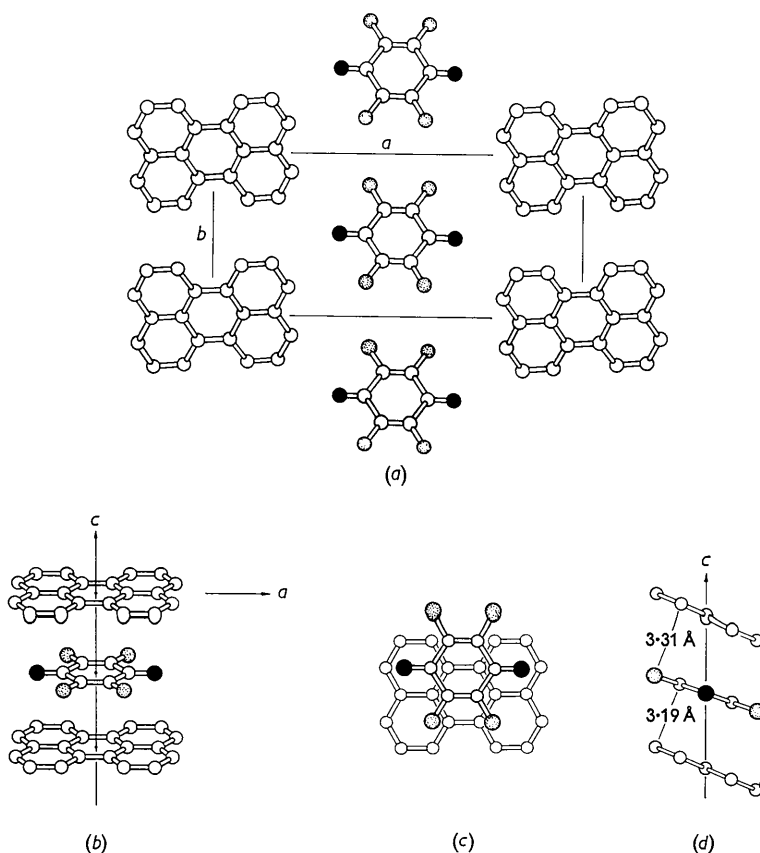


Fig. 3. Structural details. (a) One layer of the structure, near plane  $z = 0$ , (b) A portion of the  $z$  axis, showing overlap. (c) Two overlapping molecules, viewed along normal to average molecular plane. (d) Overlapping molecules, viewed approximately along *a*. The non-parallelism of adjacent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

inclined to each other at 1.8°. The effect of non-parallelism is to increase the minimum distance of the fluorine atoms from the plane of the overlapping perylene molecule (in the region of overlap, Fig. 3*c, 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 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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(Received 7 November 1962)

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

\* 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.