Molecular Complexes. Part XXII.[1] Crystal and Molecular Structure of the Molecular Complex of Pyrene and Chloranil

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The crystal and molecular structure of the 1 : 1 complex of pyrene and chloranil has been determined by three-dimensional *X*-ray diffraction methods. Crystals are monoclinic, $a = 7{\cdot}52 \pm 0{\cdot}02$, $b = 13{\cdot}68 \pm 0{\cdot}03$, $c = 8{\cdot}93 \pm 0{\cdot}02$ Å, $\gamma = 96{\cdot}5 \pm 0{\cdot}2°$, space group $P2_1/b$. The structure was solved from visually estimated photographic data by the symbolic addition method and refined by least squares to R 0·076 (1001 independent reflections). In the crystal alternate pyrene and chloranil molecules form stacks along the a axis. The mean separation of the molecular planes, which are inclined at 2·8°, is 3·46 Å. The relative orientations of donor and acceptor are close to those predicted for the maximisation of charge-transfer interactions.

THE crystal and molecular structure of pyrene–chloranil was determined as part of a continuing programme of research into the structures π–π^* electron-donor–acceptor complexes of pyrene. After the work had been completed it was learnt that Krstanovic and Pepinski[2]

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[1] Part XXI, C. K. Prout and I. J. Tickle, *J.C.S. Perkin II*, 1973, 734.

[2] R. Pepinski, U.S. Armed Services Technical Information Agency, Document No. 285512; I. Krstanovic, personal communication.

had determined the structure 10 years previously although a full report with atomic parameters, *etc.*, has not been published.

EXPERIMENTAL

Preparation.—Laboratory grade pyrene and chloranil (2,3,5,6-tetrachlorobenzoquinone) were recrystallised from ethanol and 1,4-dioxan respectively. The complex was prepared by mixing a hot solution of pyrene with a hot saturated one of chloranil in ethyl acetate in the molar ratio 1·5 : 1. Intensely coloured dark green needle crystals of the complex crystallised on slow cooling.

Crystal Data.—$C_{22}H_{10}Cl_4O_2$, $M = 448{\cdot}2$. Monoclinic, $a = 7{\cdot}52 \pm 0{\cdot}02$, $b = 13{\cdot}68 \pm 0{\cdot}03$, $c = 8{\cdot}93 \pm 0{\cdot}02$ Å, $\gamma = 96{\cdot}5 \pm 0{\cdot}2°$, $U = 912{\cdot}7$ Å^3, $D_m = 1{\cdot}63$ (by flotation), $Z = 2$, $D_c = 1{\cdot}630$. Space group $P2_1/b$ (C_{2h}^5, No. 14). Cu-K_α radiation $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 60·4 cm^{-1}. Crystal size 0·6 × 0·3 × 0·3 mm.

TABLE 1

Atomic parameters * with standard deviations in parentheses. The numbering of the hydrogen atoms indicates the carbon atoms to which they are attached

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
Cl(1)	0·6661(2)	0·0950(1)	0·2055(2)	0·057(1)	0·063(1)	0·049(1)	0·029(1)	0·018(1)	−0·005(1)
Cl(2)	0·4806(2)	0·1320(1)	0·7856(2)	0·058(1)	0·056(1)	0·051(1)	−0·031(1)	0·000(1)	0·011(1)
O(1)	0·6229(6)	0·1893(3)	0·4924(5)	0·074(3)	0·040(2)	0·068(3)	0·007(4)	−0·007(5)	−0·019(4)
C(1)	0·5748(6)	0·0392(4)	0·3618(6)	0·025(3)	0·049(3)	0·042(3)	0·016(5)	0·004(4)	0·007(4)
C(2)	0·5678(7)	0·1033(4)	0·4953(6)	0·031(3)	0·041(3)	0·052(3)	0·011(5)	−0·008(5)	0·004(4)
C(3)	0·4884(7)	0·0564(4)	0·6346(5)	0·044(3)	0·040(3)	0·033(3)	−0·005(4)	−0·011(4)	0·017(5)
C(4)	−0·0586(8)	−0·1592(4)	0·3524(7)	0·047(4)	0·046(3)	0·063(4)	−0·037(6)	−0·016(6)	0·017(5)
C(5)	0·0264(7)	−0·0632(4)	0·3158(6)	0·030(3)	0·055(3)	0·049(3)	−0·008(5)	−0·011(5)	0·026(5)
C(6)	0·0950(8)	−0·0398(5)	0·1742(7)	0·045(4)	0·079(5)	0·053(4)	−0·009(6)	−0·006(5)	0·035(6)
C(7)	0·1784(9)	0·0537(6)	0·1433(7)	0·056(5)	0·101(6)	0·047(3)	0·012(8)	0·007(6)	0·033(7)
C(8)	0·1890(8)	0·1273(5)	0·2505(8)	0·040(4)	0·073(4)	0·068(4)	0·042(7)	−0·012(6)	0·003(6)
C(9)	0·1181(7)	0·1075(4)	0·3940(6)	0·034(3)	0·045(3)	0·054(3)	0·023(5)	−0·011(5)	0·006(4)
C(10)	0·1271(9)	0·1798(4)	0·5111(8)	0·060(4)	0·035(3)	0·084(5)	0·006(6)	−0·036(7)	0·006(5)
C(11)	0·0352(6)	0·0107(4)	0·4284(6)	0·021(3)	0·041(3)	0·044(3)	0·008(4)	−0·012(4)	0·012(4)
				U_{iso},					
H(4)	−0·067	−0·217	0·268	0·047					
H(6)	0·083	−0·095	0·086	0·055					
H(7)	0·238	0·070	0·034	0·063					
H(8)	0·251	0·200	0·223	0·057					
H(10)	0·192	0·253	0·488	0·051					

* The temperature factor T is given by: $\exp -2\pi^2[U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*]$.

Cell dimensions reported by Pepinsky:[2] $a = 13{\cdot}83$, $b = 9{\cdot}04$, $c = 7{\cdot}65$ Å, $\beta = 96°$, space group $P2_1/a$.

Cell dimensions were initially determined from zero-layer Weissenberg ($0kl$) and precession ($hk0$) photographs and were subsequently refined on a linear diffractometer. (The difference between the two sets was *ca.* 2σ.) 1001 Reflections from the layers 0—$6kl$ were estimated visually from Weissenberg photographs and scaled according to exposure time. Lorentz and polarisation, but no absorption corrections were applied. Normalised structure amplitudes $|E|$ were computed and the phases determined by the symbolic-addition method.[3] 6921 Triple-product sign relationships with probability argument $>1{\cdot}2$ among the 472 independent reflections with E value $>0{\cdot}9$ were stored. The starting phases and the symbols chosen by the program[4] (at a probability level of 0·9975) were: origin $2,\bar{2},1$, $2,7,5$, and $1,\bar{1},7$; Σ_1 $0,0,10$; symbols $4,\bar{2},2$, $2,\bar{1},6$, and $3,3,4$ which were positive, positive, and negative respectively in the correct solution.

The complete structure (except for the hydrogen atoms) was readily identified from the E map computed from 376 phased E values. The origin was shifted to $(0,\frac{1}{2},\frac{1}{2})$ and atomic co-ordinates from the E map, with individual isotropic temperature factors, were refined by the full-matrix least-squares method. In the first two cycles unit weights were assumed; two further cycles were computed with weighting scheme $w = [1 + (|F_o|/13)^2]^{-1}$ giving R 0·124. The eleven most intense reflections, of which several of low order appeared to be suffering from extinction, were given zero weight and three cycles were computed (full-matrix) on the assumption of anisotropic temperature factors. Hydrogen atoms were located with the aid of a difference-Fourier synthesis and were placed geometrically. After two further cycles without change of weighting scheme the final R was 0·060 for the 990 reflections used in the refinement and 0·076 for all observed reflections. The final difference-Fourier synthesis was featureless (limits of ρ_{diff}: $\pm 0{\cdot}3$; $\sigma(\rho) = 0{\cdot}16$ eÅ^{-3}).

The observed structure amplitudes and structure factors calculated from the final atomic parameters in Table 1 are given in Supplementary Publication SUP No. 20676 (8 pp., 1 microfiche).* The standard deviations in Table 1 were obtained from the diagonal elements of the inverse of the normal matrix. Atomic scattering factors for neutral atoms were taken from ref. 5, those for chlorine being corrected for the real part of the anomalous dispersion. Rollett and Ford's[6] ALGOL system was used for Fourier and least-squares calculations.

RESULTS AND DISCUSSION

The interatomic distances and interbonds angles shown in Figure 1 do not differ significantly from those

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* See note about Supplementary Publications in Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue.

[3] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[4] O. J. R. Hodder, C. K. Prout, and J. S. Rollett, unpublished work.

[5] 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[6] J. S. Rollett and G. Ford, unpublished work.

found for pyrene[7] or chloranil.[8] The inertial axes and deviations from the mean planes of the donor and acceptor components are shown in Figure 2. The in-plane translational vibrations of the component molecules are higher than the out-of-plane vibrations, as would be expected, but there is no significantly high in-plane libration in either molecule. Table 2 shows the bond lengths corrected for libration.[9]

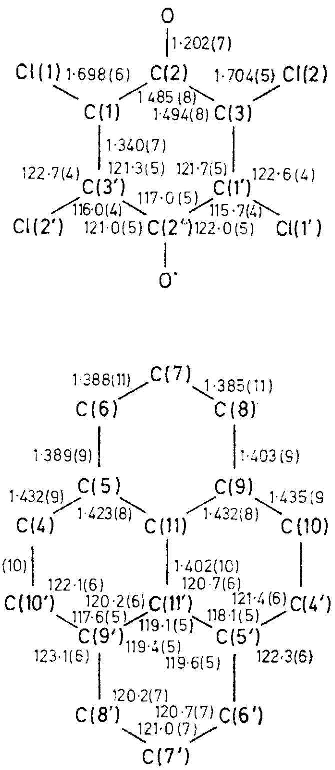

FIGURE 1 Interatomic distances (before libration correction) and interbond angles with standard deviations in parentheses. The co-ordinates of the primed and unprimed atoms are related by molecular inversion centres

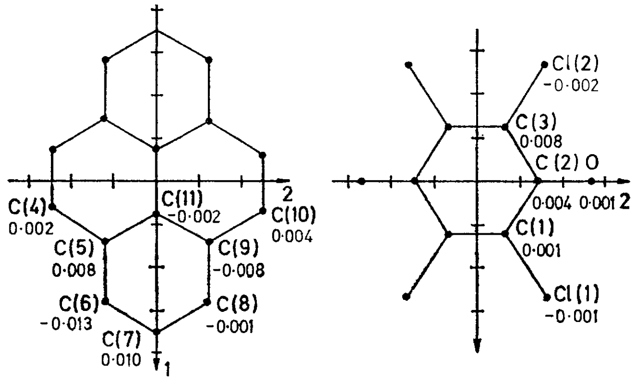

FIGURE 2 Molecular inertial axes of pyrene and chloranil together with the deviations from the mean planes; crystal symmetry 1

By comparison of the intermolecular contacts reported previously it appears that both determinations have led to the same structure; the projection of the acceptor onto the least-squares best plane of the donor (Figure 3) appears to be not significantly different from Herbstein's interpretation[10] of that previously found.[2]

TABLE 2

Bond lengths corrected for rigid-body thermal motion

(*a*) In pyrene			
C(4)–C(5)	1·438	C(7)–C(8)	1·389
C(4)–C(10')	1·346	C(8)–C(9)	1·406
C(5)–C(6)	1·392	C(9)–C(10)	1·440
C(5)–C(11)	1·428	C(9)–C(11)	1·438
C(6)–C(7)	1·392	C(11)–C(11')	1·407
(*b*) In chloranil			
Cl(1)–C(1)	1·703	C(1)–C(2)	1·491
Cl(2)–C(3)	1·709	C(1)–C(3')	1·345
O–C(2)	1·206	C(2)–C(3)	1·500

Primed atoms are related to the unprimed by the molecular inversion centre.

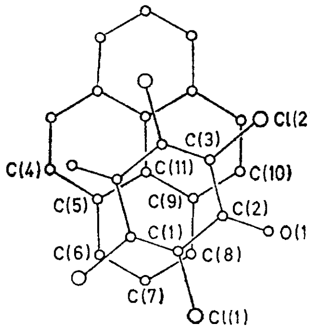

FIGURE 3 Projection of a chloranil molecule onto the least-squares best plane of the neighbouring pyrene

The structure consists of alternating donor and acceptor components stacked plane-to-plane; the stacking axis is parallel to the crystallographic *a* axis. Figure 4 shows a stereoscopic projection viewed normal to the molecular planes in one of the stacks. The mean perpendicular separation is 3·46 Å, and the angle between the plane normals is 2·8°. There is a short intermolecular contact (3·23 Å) between Cl(2) and the oxygen atom at the equivalent position $1 - x, \frac{1}{2} - y, \frac{1}{2} + z$.

Computation of the charge-transfer stabilisation as a function of the relative orientation of donor and acceptor for the complexes of pyrene with the quinoid donors chloranil and tetracyanoquinodimethane (TCNQ)[11] has shown that the relative degrees of mixing-in of excited states is sufficiently different to lead one to expect that the two complexes would have quite different donor–acceptor orientations of maximum stabilisation. In the TCNQ complex, the centre-on-centre orientation (with the long axes of the molecules parallel) is definitely

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[7] A. Camerman and J. Trotter, *Acta Cryst.*, 1956, **18**, 636.

[8] K. J. van Weperen and G. J. Visser, *Acta Cryst.*, 1972, *B*28, 338.

[9] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 757.

[10] F. H. Herbstein, *Perspectives in Structural Chem.*, 1971, **4**, 166.

[11] B. Mayoh and C. K. Prout, *J.C.S.*, *Faraday II*, 1972, 1072.

favoured, whereas in the choranil complex, orientations in which the quinone ring is located over a two-ring outer region of the pyrene are favoured. The centre-on-centre orientation is not observed in the TCNQ complex[12] and the observed orientation has a stabilisation of only 53% of the maximum. Furthermore small displacements from the observed position should increase the stabilisation. For the chloranil complex the situation is more encouraging; the observed position (Figure 4) is in a region of maximum stabilisation (90% of the maximum).

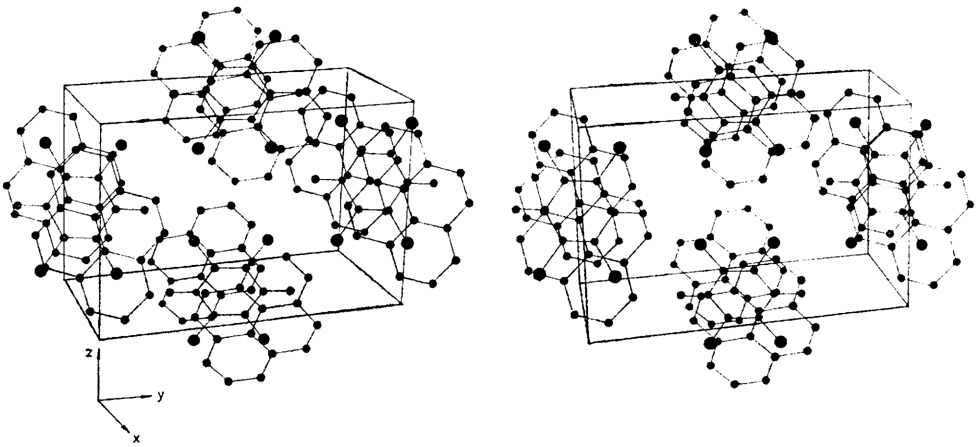

FIGURE 4 Stereoscopic view of the crystal packing. Rotation matrix:

0·264	−0·060	−0·963
0·222	0·975	0·000
0·938	−0·214	0·271

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[12] C. K. Prout, I. J. Tickle, and J. D. Wright, *J.C.S. Perkin II*, 1973, 528.