Molecular Complexes. Part XVI.[1] Crystal Structure of the 1 : 1 Molecular Complex of Pyrene and 7,7,8,8-Tetracyanoquinodimethane

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The crystal and molecular structure of the title π complex has been determined by three-dimensional *X*-ray diffraction methods. Crystals are monoclinic, $a = 7{\cdot}14$, $b = 14{\cdot}73$, $c = 10{\cdot}01$ Å, $\gamma = 102{\cdot}5°$, space group $P2_1/b$, $Z = 2$. Two determinations of the structure were made: from 1084 visually estimated photographic data by the symbolic addition method, and from 1068 diffractometer data by Patterson and Fourier methods: each was refined by least-squares methods to *R* 0·136 and 0·137, respectively. In the crystal alternate pyrene and tetracyanoquinodimethane molecules form stacks along the *a* axis. The mean separation of the molecular planes, which are inclined at an angle of 6·3°, is 3·50 Å. The relative orientation of the two molecules is not that predicted by MO calculations of charge-transfer interactions, and reflects the influence of lattice packing requirements and dipole–dipole interactions. In both determinations the molecular dimensions found for tetracyanoquinodimethane are in good agreement with known values, whereas those found for pyrene are not. Thermal vibration parameters suggest that the pyrene molecule is disordered.

THE crystal structure of the molecular complex of pyrene and 7,7,8,8-tetracyanoquinodimethane has been determined as part of our continuing systematic investigation of the crystal structure of molecular complexes.

EXPERIMENTAL

Unintentionally, two sets of intensity data were collected simultaneously at Canterbury and Oxford. In Canterbury the complex was prepared by slow evaporation of an equimolar solution of pyrene and tetracyanoquinodimethane in chloroform. In Oxford the complex was prepared by the slow evaporation of an ethyl acetate solution of the two in the molar ratio 1·25 : 1. The crystals obtained from ethyl acetate were largely very dark green twinned needles. However, the sample contained a few tabular single crystals. The solution in chloroform appeared to give only single crystals, also very dark green with a needle habit. Subsequent *X*-ray photography showed both single crystals to be identical. In Oxford the intensities of 1040 reflections from the layers 0—6*kl* and 316 reflections from the layers *hk*0—2 were estimated visually from Weissenberg photographs. Lorentz and polarisation corrections were applied. The measured intensities were placed on a common scale by the method of Rollett, Hamilton, and Sparks [2] to give a total of 1084 independent reflections. The merging *R* value was 0·059. In Canterbury the unit-cell dimensions were obtained from a least-squares refinement based on 2θ angles for about 30 high-angle general peaks measured with a General Electric XRD 6 four-circle diffractometer. The intensities of 1068 diffraction maxima within a sphere defined by angles less than 100·8° were measured with the diffractometer by a stationary-crystal–stationary-counter technique,[3] and corrected for background and polarisation.

Crystal Data (Determined at Canterbury).—$C_{28}H_{14}N_4$, $M = 406{\cdot}5$, $a = 7{\cdot}14 \pm 0{\cdot}01$, $b = 14{\cdot}73 \pm 0{\cdot}01$, $c = 10{\cdot}01 \pm 0{\cdot}01$ Å, $\gamma = 102{\cdot}5 \pm 0{\cdot}1°$, $U = 1028$ Å^3, $D_m = 1{\cdot}30$ (by flotation), $Z = 2$, $D_c = 1{\cdot}302$. Space group $P2_1/b$ (C^5_{2h}, No. 14). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 6{\cdot}3$ cm^{-1}.

Normalised structure amplitudes were computed from the Oxford visual data and the phases were determined by the symbolic addition method.[4] 7422 Triple products with probability argument $>0{\cdot}7$ among the 443 independent reflections with *E* values $>1{\cdot}0$ were stored. The starting phases and the symbol chosen by the program (at a probability level of 0·9975) were:

Origin	$(6,\bar{3},2)$	3·916	+
	$(4,\bar{1},1)$	3·207	+
	$(1,\bar{13},2)$	3·459	+
Symbol	$(2,\bar{1},1)$	2·150	+ *A*

(No Σ_1 relationships)

295 phases were obtained in the first stage and the solution *A* positive was indicated. Substitution for this symbol and extension of the sign-determining process gave a total of 372 phases at a probability level of 0·88.

All the carbon and nitrogen atoms were clearly identifiable in the *E* map. On the assumption of individual isotropic temperature factors, the atomic co-ordinates from this map were refined (full-matrix). In the first three cycles, unit weights were assumed. Two further cycles were computed with weighting scheme $w = [1 + (F_o/p)^2]^{-1}$ where $p = 10$, giving *R* 0·166. The weighting scheme was then revised; 6 strong reflections with very high values for F_c were given zero weight and the weighting scheme parameter *p* altered to 8. Three cycles of full-matrix least-squares refinement with anisotropic temperature factors, and a difference-Fourier synthesis were computed. The hydrogen atoms in the tetracyanoquinodimethane were readily located but those in the pyrene were very poorly resolved. The latter were placed geometrically and two further cycles of refinement were computed with the hydrogen temperature factors and the C–H bond geometries fixed, assuming C–H 1·08 Å. The final *R* was 0·101 for the 1078 reflections with non-zero weight and 0·136 for all 1084 observed reflections. Comparison of the phases calculated from these parameters with those obtained by the CSSA program [4] showed that one phase $(3,\bar{2},1$, with *E* 1·409) had been determined incorrectly at the upper probability limit.

An independent trial structure, obtained from a sharpened Patterson synthesis computed from the Canterbury diffractometer data, was refined by the least-squares method.

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[1] Part XV, C. K. Prout, T. Morley, I. J. Tickle, and J. D. Wright, preceding paper.

[2] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, 1965, **18**, 129.

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

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

After three cycles of isotropic full-matrix refinement of the model containing all atoms except hydrogen, with unit weights for all reflections, R was reduced to 0·234. A further three cycles of anisotropic full-matrix least-squares refinement with identical conditions produced a final R of 0·137 for the 1068 reflections (0·132 excluding unobserved reflections).

Both sets of observed structure amplitudes and structure factors calculated from the final atomic parameters, together with the Canterbury final atomic parameters and molecular dimensions, are presented in Supplementary Publication No. SUP 20597 (18 pp., 1 microfiche).* The Oxford final atomic parameters are given in the Table.

Atomic positional ($\times 10^4$) and thermal * ($\times 10^3$) parameters, with standard deviations in parentheses

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	10165(7)	5930(3)	4620(6)	39(3)	26(2)	81(4)	−6(4)	31(5)	9(4)
C(2)	9570(7)	5185(3)	3661(5)	34(3)	27(2)	72(4)	−6(4)	28(4)	8(4)
C(3)	9430(7)	4243(3)	4122(6)	45(3)	26(2)	75(4)	−13(4)	21(5)	9(4)
C(4)	9142(7)	5357(3)	2384(6)	46(3)	29(2)	73(4)	2(4)	32(5)	7(4)
C(5)	9196(9)	6275(4)	1895(6)	66(4)	41(3)	73(4)	6(5)	33(6)	11(5)
C(6)	8563(8)	4621(4)	1442(6)	58(4)	47(3)	69(4)	4(5)	25(5)	8(5)
C(7)	5406(10)	6591(5)	3916(10)	60(4)	51(4)	135(7)	79(8)	62(8)	36(6)
C(8)	4747(10)	5626(7)	3399(8)	48(4)	153(8)	79(6)	13(9)	36(6)	80(9)
C(9)	4263(13)	5468(9)	2133(11)	80(6)	150(9)	126(9)	69(13)	47(11)	83(12)
C(10)	3636(12)	4550(8)	1745(11)	68(6)	112(7)	138(7)	−4(12)	8(10)	58(11)
C(11)	3518(10)	3766(7)	2521(10)	58(5)	120(7)	122(7)	−78(11)	23(9)	42(9)
C(12)	4139(9)	3947(5)	3947(10)	43(3)	67(4)	162(8)	−25(10)	57(8)	10(6)
C(13)	4067(11)	3260(6)	4805(12)	62(5)	76(5)	179(9)	37(12)	82(11)	34(7)
C(14)	4719(7)	4870(4)	4363(6)	33(3)	55(3)	87(4)	13(6)	33(5)	18(5)
N(1)	9192(10)	7000(4)	1507(7)	118(5)	46(3)	114(5)	44(6)	59(7)	33(6)
N(2)	8130(9)	4045(4)	673(6)	92(4)	53(3)	91(4)	−25(6)	5(6)	1(5)
				U_{iso}					
H(1)	1019	658	425	40					
H(3)	901	371	343	40					
H(7)	544	718	326	60					
H(9)	435	603	143	110					
H(10)	319	444	72	90					
H(11)	301	307	214	90					
H(13)	356	255	448	90					

* The temperature factor T is given by $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{12}a^*c^*hl + 2U_{12}a^*b^*hk)]$. † Hydrogen atoms are numbered according to the carbon atom to which they are attached.

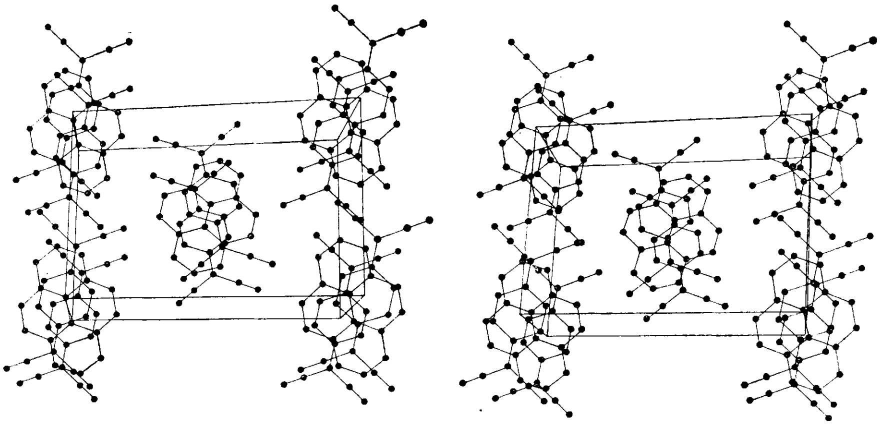

FIGURE 1 Generalised stereoscopic projection. The transformation matrix from the orthogonal crystal axes a, b^*, c to a set of orthogonal axes X, Y, Z with Z perpendicular to the plane of the paper, is

$$\begin{array}{ccc} 0{\cdot}238 & -0{\cdot}006 & -0{\cdot}971 \\ 0{\cdot}027 & 1{\cdot}000 & 0{\cdot}000 \\ 0{\cdot}971 & -0{\cdot}026 & 0{\cdot}238 \end{array}$$

All calculations in Oxford used Rollett and Ford's ALGOL system [5] on the Oxford KDF 9 computer. All calculations in Canterbury used the 'X-Ray '63' program system [6] on the SRC Chilton Atlas computer. Atomic scattering factors for neutral atoms were taken from ref. 7.

RESULTS AND DISCUSSION

The crystal structure is shown in stereoscopic projection in Figure 1, and the bond distances and interbond angles, with their standard deviations (from the Oxford analysis) are in Figure 2. The differences between equivalent bond lengths and bond angles from

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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

[6] 'X-Ray '63' program system, 1967 version, J. M. Stewart, University of Maryland Computer Science Centre Technical Report, 67—58.

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

the two analyses do not exceed 2σ. However, there are significant differences in the temperature factors obtained from the two sets of data which may be due to the different treatments of background owing to our neglect, in both cases, to correct for thermal diffuse scatter. The neglect of thermal diffuse scatter which systematically reduces the intensities of certain groups of reflections may contribute to the relatively poor bond lengths found in the pyrene molecule.

The crystal structure is built up from isolated pyrene and tetracyanoquinodimethane molecules alternating in plane-to-plane stacks characteristic of π–π^* electron-donor–acceptor complexes. The dimensions of the tetracyanoquinodimethane molecule differ from those found in the free compound[8] by $<2\sigma$. The dimensions of the pyrene molecule are in relatively poor agreement with those from other determinations.[9-12] The fact that almost identical dimensions were derived for the pyrene in the two independent determinations suggests that discrepancies between the dimensions observed in this structure and those expected for pyrene are not due to systematic errors in data collection and processing. The electron density in the plane of the pyrene molecule (Figure 3) is not well resolved, but the thermal vibration ellipsoids cannot be interpreted in terms of a symmetric rigid-body translation–oscillation motion. These features, which are taken from the Oxford results, are almost indistinguishable from those obtained from the Canterbury results. It is thought that the atomic parameters which have been obtained for a single pyrene molecule lying at a centre of symmetry are a result of averaging the parameters of one or more pairs of disordered orientation related by the symmetry centre. However, we know of no practical method of testing this hypothesis.

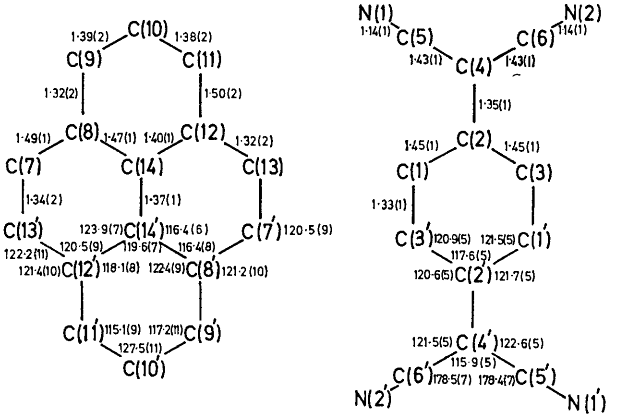

FIGURE 2 Bond lengths and interbond angles, with standard deviations (Oxford results)

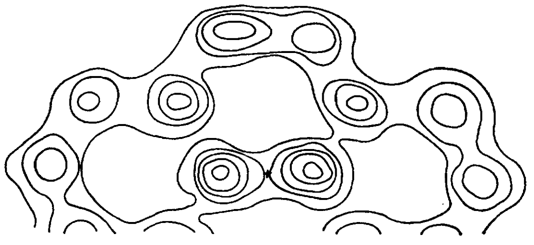

FIGURE 3 Electron density contour map in the plane of the pyrene molecule (Oxford results). Contour spacing 1 eÅ^{-3} starting at 1 eÅ^{-3}

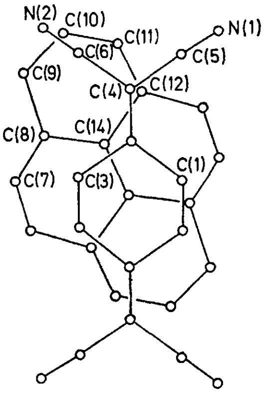

FIGURE 4 Projection of the tetracyanoquinodimethane molecule on the least-squares best plane of the pyrene molecule

Figure 4 shows the tetracyanoquinodimethane acceptor projected on the least-squares best plane of the pyrene donor. Calculations[13] show that in this orientation the electron-donor–acceptor interaction is only 53% of the likely maximum which is found when the longest axes and centres of symmetry of the two molecules are superimposed. We have discussed the problem of centre-on-centre overlap previously.[1,13] The mean perpendicular separation between the planes of adjacent donor and acceptor components is 3·50 Å, the same as that found in the pyrene complexes of the less effective acceptor 1,2,4,5-tetracyanobenzene[1] and larger than that (3·32 Å) observed for pyrene–pyromellitic dianhydride.[12] The plane of the tetracyanoquinodimethane molecule is inclined at an angle of 6·3° to that of the pyrene.

There is only one contact $<3{\cdot}5$ Å [C(1) $\cdots$ C(12) at $1-x$, $1-y$, $1-z$] between pyrene and tetracyanoquinodimethane within the stack, although there are a number of short (3·5—3·6 Å) contacts between molecules of the latter, and two very short contacts [C(3) $\cdots$ N(1) at x, $y-\frac{1}{2}$, $\frac{1}{2}-z$, 3·31, and C(5) $\cdots$ N(2) at $2-x$, $1-y$, $-z$, 3·32 Å]. These suggest that the network of tetracyanoquinodimethane molecules which extends in two dimensions in directions normal to the stacking axis, is made fairly rigid by strong intermolecular dipole–dipole interactions between the cyanide groups, and the pyrene molecules are held loosely within this network. This is consistent with the postulated pyrene disorder.

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