Molecular Complexes. Part XVII.[1] Crystal and Molecular Structure of Perylene–7,7,8,8-Tetracyanoquinodimethane Molecular Complex

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Crystals of the title 1 : 1 molecular complex are monoclinic. $a = 7{\cdot}32$. $b = 14{\cdot}55$. $c = 10{\cdot}88$ Å, $\gamma = 90{\cdot}4°$. space group $P2_1/b$, $Z = 2$. The structure has been determined from diffractometer data by direct methods and refined by least squares to R 0·064 for 1644 independent reflections. The dimensions of the component molecules have been corrected for rigid-body libration. The mode of overlap of the electron-donor and -acceptor molecules. which are stacked alternately plane-to-plane along the *a* axis of the crystal. is very close to that expected on the basis of maximisation of the donor–acceptor charge-transfer interaction.

In Part XIII of this series,[2] the variation of charge-transfer stabilisation with donor–acceptor orientation was calculated on a semi-empirical basis for a group of hypothetical molecular-pair complexes of perylene with aromatic π-electron donors. The complexes were chosen so that the quantum mechanical treatment was simplified by both donor and acceptor having the same (*mmm*) high point-group symmetry. For a given complex the orientation that maximised the charge-transfer interaction was compared with that found in the crystalline state. The crystal structures of the 1 : 1 complexes of perylene (I) with tetracyanoethylene,[3] fluoranil,[4] and pyromellitic dianhydride[5] had been reported, but not that of the 7,7,8,8-tetracyanoquinodimethane † (II) complex which it was believed was most likely to be determined by charge-transfer effects.

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† 7,7,8,8-Tetracyanoquinodimethane is cyclohexa-2,5-diene-1,4-diylidenedimalononitrile.

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

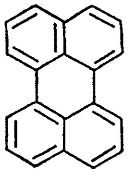
[2] B. Mayoh and C. K. Prout, *J.C.S. Faraday II*, 1972, 1072.

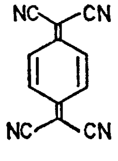
[3] I. Ikemoto, K. Yakushi, and H. Kuroda, *Acta Cryst.*, 1970, *B*, **26**, 800.

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

[5] J. C. A. Boeyens and F. H. Herbstein, *J. Phys. Chem.*, 1965, **69**, 2160.

Here we report the crystal and molecular structure of the perylene complex with (II) molecular complex.


(I)


(II)

EXPERIMENTAL

A large crystal was cut to dimensions *ca.* 0·7 × 0·6 × 0·35 mm.

Crystal Data.—$C_{32}H_{16}N_4$, $M = 456·5$. Monoclinic prismatic, $a = 7·32 \pm 0·02$, $b = 14·55 \pm 0·03$, $c = 10·88 \pm 0·02$ Å, $\gamma = 90·4 \pm 0·2°$, $U = 1154$ Å^3, $D_m = 1·32$, $Z = 2$, $D_c = 1·312$. Space group $P2_1/b$ (C^5_{2h}, No. 14). Mo-K_α radiation, $\lambda = 0·7107$ Å, μ(Mo-K_α) = 0·86 cm^{-1}.

Unit-cell dimensions were measured and three-dimensional *X*-ray intensity data collected on a Hilger and Watts linear diffractometer. 1644 independent reflections of the layers *hk*0—11 were taken as significantly (3σ) above background. Lorentz and polarisation, but not absorption, corrections were applied.

TABLE 1

Atomic parameters * with standard deviations in parentheses. Hydrogen atoms are numbered according to the carbon to which they are attached

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
C(1)	0·4365(4)	−0·0654(2)	0·0857(3)	0·0385(13)	0·0293(11)	0·0412(15)	0·0027(19)	−0·0003(21)	−0·0098(20)
C(2)	0·4835(3)	0·0269(2)	0·1253(2)	0·0301(12)	0·0296(11)	0·044(14)	−0·0060(18)	−0·0018(19)	−0·0045(18)
C(3)	0·5487(4)	0·0901(2)	0·0333(3)	0·0406(14)	0·0266(11)	0·0429(15)	−0·0045(19)	−0·0027(21)	−0·0100(20)
C(4)	0·4687(4)	0·0512(2)	0·2461(3)	0·0367(13)	0·0374(12)	0·0398(15)	−0·0063(20)	−0·0019(20)	−0·0088(20)
C(5)	0·4049(4)	−0·0125(2)	0·3363(3)	0·0442(15)	0·0535(16)	0·0389(15)	−0·0152(25)	0·0048(24)	−0·0095(24)
C(6)	0·5160(4)	0·1414(2)	0·2891(3)	0·0472(16)	0·0474(15)	0·0473(17)	−0·0252(24)	−0·0069(15)	−0·0051(24)
N(1)	0·3527(4)	−0·0645(2)	0·4079(3)	0·0716(19)	0·0817(20)	0·0491(18)	0·0090(29)	0·0179(28)	−0·0322(31)
N(2)	0·5537(5)	0·2132(2)	0·3225(3)	0·0819(21)	0·0541(16)	0·0814(22)	−0·0516(30)	−0·0280(34)	−0·0133(29)
C(7)	−0·0723(3)	−0·0524(2)	0·1022(2)	0·0252(11)	0·0374(12)	0·0437(15)	0·0069(20)	0·0020(20)	0·0044(19)
C(8)	−0·1403(4)	−0·0998(2)	0·2031(3)	0·0378(14)	0·0497(15)	0·0509(17)	0·0300(25)	0·0069(24)	0·0035(24)
C(9)	−0·1464(4)	−0·0610(3)	0·3202(3)	0·0445(16)	0·0759(21)	0·0434(18)	0·0307(30)	0·0073(26)	0·0080(29)
C(10)	−0·0850(4)	0·0266(3)	0·3390(3)	0·0440(16)	0·0777(21)	0·0397(16)	−0·0009(30)	−0·0007(26)	0·0190(30)
C(11)	−0·0133(4)	0·0782(2)	0·2405(3)	0·0331(14)	0·0542(16)	0·0448(16)	−0·0129(24)	−0·0008(22)	0·0139(23)
C(12)	0·0537(5)	0·1694(2)	0·2583(4)	0·0499(18)	0·0583(18)	0·0617(21)	−0·0499(31)	−0·0071(30)	0·0095(29)
C(13)	0·1238(5)	0·2186(2)	0·1636(4)	0·0503(18)	0·0454(16)	0·0783(24)	−0·0351(32)	−0·0029(33)	−0·0010(27)
C(14)	0·1303(4)	0·1807(2)	0·0452(3)	0·0431(16)	0·0361(13)	0·0609(19)	−0·0010(24)	−0·0027(26)	−0·0041(23)
C(15)	0·0656(3)	0·0924(2)	0·0212(3)	0·0298(13)	0·0340(12)	0·0445(14)	0·0070(20)	0·0009(21)	0·0058(19)
C(16)	−0·0057(3)	0·0395(2)	0·1200(2)	0·0267(12)	0·0367(12)	0·0388(14)	0·0007(19)	0·0008(19)	0·0053(19)

	x/a	y/b	z/c	U_{iso}		z/c	y/b	z/c	U_{iso}
H(1)	0·402(5)	−0·111(2)	0·151(3)	0·040	H(10)	−0·084(6)	0·056(3)	0·427(3)	0·060
H(3)	0·581(5)	0·154(2)	0·066(3)	0·040	H(12)	0·056(6)	0·194(3)	0·349(3)	0·060
H(8)	−0·188(5)	−0·166(2)	0·190(4)	0·050	H(13)	0·179(5)	0·283(2)	0·177(4)	0·060
H(9)	−0·197(6)	−0·099(3)	0·393(3)	0·060	H(14)	0·178(5)	0·218(2)	−0·028(3)	0·050

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

The structure was solved by the symbolic addition method [6] by use of the CSSA program developed by Hodder, Prout, and Rollett.[7] From the 723 independent normalised structure amplitudes (E values) > 1·0, the program chose 4 signed reflections as a starting set: $2,\bar{2},1$, E +4·43; $4,\bar{3},1$, E +4·26; and 7,4,7, E +2·91 as origin-determining phases, and $4,\bar{4},2$, E +3·37 from a Σ_1 relationship, and one symbolic phase, $4,\bar{2},1$, E 4·28, which was eventually determined as positive.

In the Fourier synthesis computed from the 504 signed E values obtained from the symbolic addition, the complete structure (excluding hydrogen) was readily identifiable. Atomic parameters were refined initially by full-matrix least-squares with isotropic temperature factors and unit weights for all observations, and then with anisotropic temperature factors, the weighting scheme: $w = [1 + (|F_o| - 4·5)^2/41]^{-1}$, and a block-diagonal approximation to the normal matrix, with the space and thermal parameters in two separate blocks. Hydrogen atoms were located in a difference-Fourier synthesis. The isotropic temperature factors of the hydrogen atoms were fixed, but the space parameters were refined with constraints (1·05 ± 0·02 Å) on the C–H bond lengths, by a development [8] of Waser's method.[9] On completion of the refinement R was 0·064 for 1644 reflections, and in a final difference-Fourier synthesis had no significant ($>3\sigma$) variations (estimated standard deviation of the electron density 0·1 e Å^{-3}).

The estimated standard deviations of the atomic parameters were calculated from the diagonal elements of the inverse of the normal matrix. The final atomic parameters are given in Table 1. Comparison of the phases calculated from these parameters with those obtained from the CSSA program showed that one phase (0,12,2, E 1·02) had been determined incorrectly. The observed structure amplitudes and structure factors calculated from the atomic parameters in Table 1 are listed in Supplementary Publication No. SUP 20628 (13 pp. 1 microfiche).†

Unless otherwise stated either Rollett's [10] NOVTAPE system, as modified by Hodder, or Rollett and Ford's [8]

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† See note about Supplementary Publications in Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

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

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

[8] J. S. Rollett and G. Ford, unpublished work; J. S. Rollett in, 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, p. 11.

[9] J. Waser, *Acta Cryst.*, 1963, **16**, 1091.

[10] O. J. R. Hodder and J. S. Rollett, unpublished work.

ALGOL system was used for calculations. Atomic scattering factors were those for the uncharged atoms taken from ref. 11.

RESULTS AND DISCUSSION

The perylene and molecules of (II) lie at the symmetry centres (0,0,0) and ($\frac{1}{2}$,0,0) respectively. The atomic thermal parameters were analysed in terms of molecular rigid-body motion. The translation and vibration tensors are specified in Table 2, and the inertial axes (with deviations of atoms from the mean molecular planes) are defined in Figure 1. As is frequently observed,[12] the libration of the molecule (II) is markedly anisotropic, the axis of greatest libration almost coinciding with the long axis of the molecule. The anisotropy of the librational tensor of the perylene molecule is less marked but the maximum librational amplitude is in the molecular plane. The standard deviations $\Sigma|[U_{ij}(\text{obs}) - U_{ij}(\text{calc})]^2(n - v)^{-1}|^{\frac{1}{2}}$ between n observed temperature parameters (referred to the orthogonal inertial axes) and those calculated from the v components of the rigid-body tensors were 0·0016 for perylene and 0·0042 for (II), compared with the average estimated standard deviation in the observed temperature factors (Table 1) of 0·0018 Å^2 (for both molecules) indicating, as expected from the molecular structure, the rigid-body approximation is considerably better for perylene than for (II). Cruickshank's libration correction[13] has been applied to the bond lengths (Table 3), but the differences are barely significant (*ca.* 1σ). The cyanide groups in the TCNQ molecule undoubtedly undergo non-rigid-body motion, so that the correction for these must be somewhat greater.

TABLE 2

Analysis of rigid-body thermal motion

Principal axes	Direction cosines relative to: Inertial axes			Direction cosines relative to: Orthogonal crystal axes		
(*a*) Perylene						
T Tensor/Å^2						
0·0400(6)	0·995	0·022	−0·100	−0·049	−0·344	−0·938
0·0322(7)	−0·017	0·999	0·043	0·442	0·835	−0·329
0·0226(10)	0·100	−0·041	0·994	0·896	−0·430	0·111
ω Tensor/deg.^{2}						
8·5(6)	0·953	0·187	−0·239	−0·111	−0·138	−0·984
3·9(3)	−0·249	0·933	−0·261	0·129	0·980	−0·152
11·5(3)	0·174	0·308	0·935	0·985	−0·144	−0·091
(*b*) (II)						
T Tensor/Å^2						
0·0423(17)	0·942	0·321	−0·101	0·089	0·074	−0·993
0·0205(23)	−0·279	0·912	0·300	0·559	0·822	0·112
0·0303(26)	0·188	−0·255	0·948	0·824	−0·565	0·032
ω Tensor/deg.^{2}						
26(4)	0·992	−0·009	−0·129	−0·041	−0·232	−0·972
2·6(1·0)	−0·009	0·993	−0·119	0·214	0·948	−0·235
7·6(0·6)	0·129	0·119	0·984	0·976	−0·218	0·011

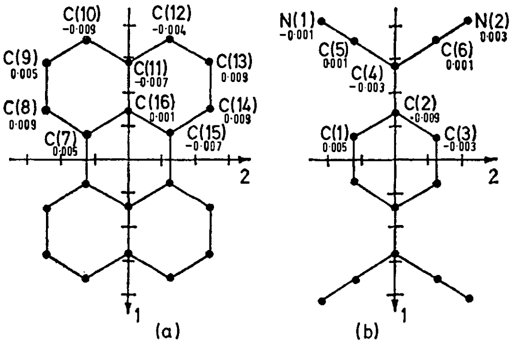

FIGURE 1 Molecular inertial axes of (a) perylene and (b) of (II) with deviations from the near planes (crystal symmetry both $\bar{1}$)

TABLE 3

Bond lengths (Å) corrected for rigid-body thermal motion. Uncorrected distances and interbond angles are given in Figure 2

(*a*) In (II)		(*b*) In perylene	
C(1)–C(2)	1·453	C(7)–C(8)	1·390
C(1)–C(3′)	1·353	C(7)–C(15′)	1·468
C(2)–C(3)	1·443	C(7)–C(16)	1·436
C(2)–C(4)	1·367	C(8)–C(9)	1·396
C(4)–C(5)	1·429	C(9)–C(10)	1·366
C(4)–C(6)	1·436	C(10)–C(11)	1·410
C(5)–N(1)	1·153	C(11)–C(12)	1·428
C(6)–N(2)	1·140	C(11)–C(16)	1·431
		C(12)–C(13)	1·356
		C(13)–C(14)	1·405
		C(14)–C(15)	1·395
		C(15)–C(16)	1·423

The co-ordinates of the primed and unprimed atoms are related by inversion about the molecular centres.

The interatomic distances and interbond angles, calculated from the atomic co-ordinates in Table 1 (*i.e.* before the libration correction), are shown in Figure 2.

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

[12] A. Hoekstra, T. Spoelder, and A. Vos, *Acta Cryst.*, 1972, *B*, **28**, 14.

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

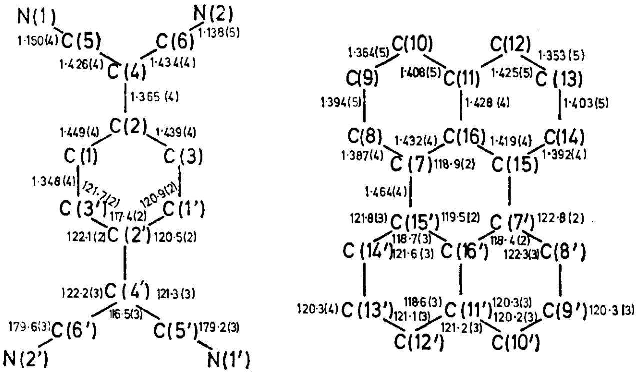

FIGURE 2 Interatomic distances (Å; before libration correction) and interbond angles (deg.) with standard deviations in parentheses

The bond lengths in (II) in the complex are in good agreement with those in (II) itself;[14] the differences between equivalent bond lengths are less than twice the standard deviation of either. The structures of a number of neutral hydrocarbon complexes of (II) are now known: anthracene,[15] hexamethylbenzene,[16] and pyrene.[1] Although there are possibly significant differences (up to 4σ) between the dimensions of perylene and (II) determined in this study and those found in other complexes, there appear to be no systematic differences which could be related to the charge-transfer interaction.

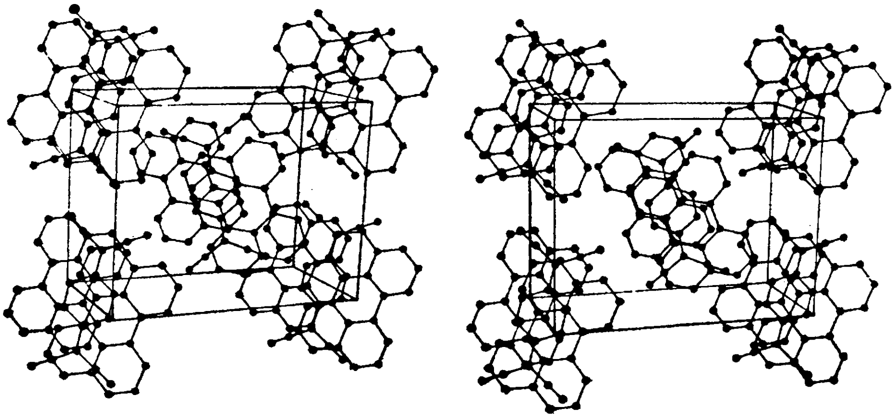

FIGURE 3 Stereoscopic view of the crystal packing. Rotation matrix:

$$\begin{matrix} 0{\cdot}177 & -0{\cdot}069 & -0{\cdot}982 \\ 0{\cdot}362 & 0{\cdot}932 & 0{\cdot}000 \\ 0{\cdot}915 & -0{\cdot}356 & 0{\cdot}190 \end{matrix}$$

Both molecules are planar within experimental error (Figure 1); the standard deviation of the atoms from the mean planes are 0·007 for perylene and 0·004 Å for (II), compared with a 0·003 Å mean σ in the atomic positions.

Figure 3 shows a stereo-projection viewed approximately normal to the molecules centred at (0,0,1) and ($\frac{1}{2}$,0,1). (The rotation matrix defines the transformation from orthogonal crystal axes *a*,*b**,*c* to plotter co-ordinates). The molecules are stacked alternately in characteristic plane-to-plane fashion along the crystal *a* axis. The mean perpendicular separation is 3·44 Å, *i.e.* that expected for an aromatic plane-to-plane van der Waals contact. The shortest interplanar contact is 3·39 Å from C(1) in (II) to C(8) of perylene. The inclination of the plane normals of the donor and acceptor is 4·1°.

In Figure 4 the molecule of (II) is shown projected on the least-squares best plane at the perylene. The overlap integral and hence the charge-transfer energy is maximised when the long axis of (II) lies along the C(7)–C(15′) bond with the centroid of the (II) over the mid-point of that bond. In the observed orientation the charge-transfer energy is not expected to be significantly less than the maximum value.

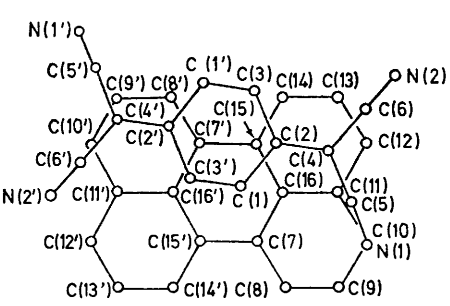

FIGURE 4 Projection of a molecule of (II) on the least-squares best plane of the neighbouring perylene

We thank the S.R.C. for a studentship (to I. J. T.), and Dr. J. D. Wright who supplied the crystal.

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[14] R. E. Long, R. A. Sparks, and K. N. Trueblood, *Acta Cryst.*, 1965, **18**, 932.

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

[16] R. H. Colton and D. E. Henn, *J. Chem. Soc.* (*B*), 1970, 1532.