Crystal Structure of the 1 :1 Molecular Complex of Chrysene and 7,7,8,8-Tetracyanoquinodimethane

By **Peter J. Munnoch** and **John D. Wright,*** University Chemical Laboratory, University of Kent at Canterbury, Canterbury, Kent CT2 7NH

The crystal and molecular structure of the title complex has been determined by three-dimensional *X*-ray diffraction methods. Crystals are triclinic, $a = 7{\cdot}255$, $b = 7{\cdot}995$, $c = 9{\cdot}210$ Å, $\alpha = 99{\cdot}8$, $\beta = 89{\cdot}7$, $\gamma = 92{\cdot}9°$, space group $P\bar{1}$, $Z = 1$. The structure was determined from 1288 diffractometer data by Patterson and Fourier methods and refined by least-squares methods to R 0·104. In the crystal, alternate chrysene and tetracyanoquinodimethane molecules form stacks along the *a* axis. The mean separation of the molecular planes is 3·37 Å and the interplanar angle is 3·4°. The interplanar separations in a series of related tetracyanoquinodimethane complexes are shown to be dependent on crystal system as well as orbital energies. The relative orientation of the two molecules is not ideal for maximum overlap of highest-filled-donor and lowest-vacant-acceptor orbitals, and suggests that dipole–dipole interactions and interactions involving other donor and acceptor orbitals are also important in determining orientation. The dimensions of both molecules are in good agreement with known values, and no disorder is apparent.

ALTHOUGH the crystal structure of chrysene [1] is known, no crystal structures of molecular complexes between chrysene and π-electron acceptor molecules have been reported. We have determined the crystal structure of the molecular complex of chrysene and 7,7,8,8-tetracyanoquinodimethane (tcnq) as part of an investigation of the relationship between structure and photoconductivity of molecular complexes. Pure crystals of this complex exhibit photoconduction which is several orders of magnitude more efficient than that for most other complexes of this type, and structural information is essential for the interpretation of this phenomenon.[2]

EXPERIMENTAL

Slow evaporation of a solution of chrysene (chromatographed and zone refined) and tetracyanoquinodimethane (purified by repeated sublimation in a Pyrex tube, under argon) in chloroform yielded very dark brown crystals, elongated along *a*. Unit-cell dimensions were obtained from a least-squares refinement based on 2θ angles for 20 high-angle general peaks measured with a General Electric XRD 6 four-circle diffractometer. The intensities of 1288 diffraction maxima, within a sphere defined by

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[1] D. M. Burns, *Acta Cryst.*, 1956, **9**, 314.

[2] V. M. Vincent and J. D. Wright, *J.C.S. Faraday I*, 1974, **70**, 58.

$2\theta < 110°$, were measured with the diffractometer by a stationary-crystal–stationary-counter technique,[3] converted to equivalent integrated values, and corrected for background and polarisation.

Crystal Data.—$C_{30}H_{16}N_4$, $M = 432{\cdot}4$. Triclinic, $a = 7{\cdot}255 \pm 0{\cdot}003$, $b = 7{\cdot}995 \pm 0{\cdot}004$, $c = 9{\cdot}210 \pm 0{\cdot}006$ Å, $\alpha = 99{\cdot}8 \pm 0{\cdot}1$, $\beta = 89{\cdot}7 \pm 0{\cdot}1$, $\gamma = 92{\cdot}9 \pm 0{\cdot}1°$, $U = 525{\cdot}7$ Å^3, $D_m = 1{\cdot}35$ (by flotation), $Z = 1$, $D_c = 1{\cdot}362$. Space group $P\bar{1}$ (C_i^1, No. 2). Cu-K_α radiation, $\lambda = 1{\cdot}5418$Å; μ(Cu-K_α) $= 6{\cdot}6$ cm^{-1}.

TABLE 1

Final atomic co-ordinates ($\times 10^4$) and thermal parameters ($\times 10^3$) * with standard deviations in parentheses

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	−268(7)	816(7)	−83(6)	18(3)	29(3)	23(4)	−4(2)	1(2)	8(3)
C(2)	−840(7)	1978(7)	1222(6)	17(3)	29(3)	24(4)	−3(2)	2(2)	2(3)
C(3)	−844(7)	1438(7)	2594(6)	15(3)	31(3)	30(4)	−4(2)	−2(2)	1(3)
C(4)	−298(8)	−216(8)	2692(6)	24(3)	41(4)	25(4)	2(3)	4(3)	14(3)
C(5)	255(7)	−1287(7)	1489(7)	21(3)	28(3)	35(4)	−2(3)	3(3)	10(3)
C(6)	−1392(8)	3630(7)	1154(7)	25(3)	30(3)	35(4)	−4(3)	2(3)	8(3)
C(7)	−1905(9)	4693(8)	2400(8)	32(4)	27(4)	55(5)	2(3)	2(3)	0(3)
C(8)	−1898(9)	4152(9)	3752(7)	38(4)	44(4)	37(4)	6(3)	2(3)	−8(3)
C(9)	−1405(8)	2558(8)	3868(7)	33(4)	48(4)	29(4)	4(3)	0(3)	1(3)
C(10)	4481(7)	1166(7)	1231(6)	18(3)	23(3)	22(4)	−2(2)	1(2)	5(3)
C(11)	4561(7)	1627(7)	−206(6)	25(3)	27(3)	26(4)	2(3)	1(3)	9(3)
C(12)	4925(7)	−521(7)	1385(6)	24(3)	30(3)	22(3)	1(3)	3(2)	12(3)
C(13)	3949(7)	2318(7)	2440(6)	19(3)	28(3)	22(4)	0(2)	1(2)	8(3)
C(14)	3510(8)	4012(8)	2314(6)	30(3)	34(4)	20(3)	0(3)	1(3)	−1(3)
C(15)	3808(7)	1904(7)	3883(7)	20(3)	29(3)	30(5)	4(2)	3(3)	0(3)
N(1)	3185(8)	5367(7)	2220(6)	65(4)	32(4)	46(4)	17(3)	4(3)	7(3)
N(2)	3678(8)	1625(7)	5053(7)	63(4)	48(4)	27(4)	12(3)	13(3)	9(3)

	x/a	y/b	z/c	U_{iso}
H(4)	−308	−579	3728	38
H(5)	631	−2499	1608	38
H(6)	−1391	4048	130	38
H(7)	−2319	5908	2323	51
H(8)	−2325	4979	4699	51
H(9)	−1408	2193	4906	51
H(11)	4287	2857	−352	38
H(12)	4822	−888	2426	25

* The temperature factor T is given by $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)]$.

A three-dimensional sharpened Patterson synthesis enabled location of all nonhydrogen atoms. Observed structure amplitudes, with phases calculated from these atom co-ordinates, were used in a Fourier synthesis, providing a more precise initial set of co-ordinates. Structure factors calculated from this model, with overall temperature and scale factors calculated by the DATFIX link of the '*X*-Ray '70 ' system, produced an initial R of 0·338. The co-ordinates and individual isotropic temperature factors were refined by the full-matrix least-squares method, using unit weights for all reflections, for 3 cycles, giving a converged set of parameters with R 0·144. A difference-Fourier synthesis was then computed, revealing the positions of the hydrogen atoms. Three further cycles of full-matrix least-squares refinement were then calculated, using anisotropic temperature factors for C and N, and isotropic temperature factors (fixed at the values appropriate to the relevant bonded carbon atoms) for hydrogen, and varying all positional co-ordinates. Refinement converged with R 0·114. At this stage it was apparent that several strong reflections with very high values of F_c were notably inaccurate. A much smaller crystal was therefore mounted, and the intensities of the 13 strongest maxima were remeasured, along with a set of representative medium intensity maxima for scaling purposes, and substituted into the original data set. It was also evident that refinement had shifted the hydrogen atoms somewhat out of the planes of the two molecules, and that the C–H bond lengths were rather short (typically *ca.* 0·9 Å). The hydrogen atoms were therefore placed geometrically, with C–H 1·05 Å, to lie in the relevant molecular plane along the bisector of the relevant C–C–C angle. Three cycles of refinement, varying only C and N positions and anisotropic temperature factors, gave the final parameters of Table 1, with R 0·104 (0·092 excluding unobserved reflections).

The observed structure amplitudes, together with the structure factors calculated from the final atomic parameters, are presented in Supplementary Publication No. SUP 21059 (8 pp.).*

All calculations used the '*X*-Ray ' program system [4] either on the University of London CDC 6600 and 7600 computers or (for diffractometer settings and cell parameter refinement) on the University of Kent ICL 4130 computer. Atomic scattering factors for neutral atoms were taken from ref. 5.

RESULTS AND DISCUSSION

The crystal structure is shown in Figure 1, and the bond lengths and interbond angles, with their standard deviations (estimated by the BONDLA link of the '*X*-Ray ' program system, from the diagonal elements from the least-squares refinement), are in Figure 2. Table 2 compares the dimensions of the chrysene molecule with the data from *X*-ray diffraction [1] and MO calculations [6] for chrysene itself. The dimensions

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

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

[4] ' X-Ray '67 ' Program System, 1970 version, J. M. Stewart, F. A. Kundell, and J. C. Baldwin, Computer Science Centre, University of Maryland Technical Report TR 67 58.

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

[6] H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc.*, 1954, *A*, **226**, 138.

from the present work agree rather more closely with calculated values than do the results from ref. 1. The dimensions of the tcnq molecule are in good agreement with those from previous determinations [7-16] and MO calculations [17,18] for the neutral molecule. Both molecules are planar, the mean deviation from the least-squares best plane through the molecule (excluding hydrogen atoms) being 0·007 Å for chrysene and 0·009 Å for tcnq. The angle between the two planes is 3·4°. Figure 1 (b) shows the tcnq molecule projected on the least-squares best plane of the chrysene molecule. The tcnq molecule is not completely covered by the chrysene molecule, and it is commonly observed that the donor and acceptor molecules are not parallel in such cases.[19] The observed relative orientation of the molecules does not maximise overlap of the highest-filled-donor and lowest-vacant-acceptor orbitals, and

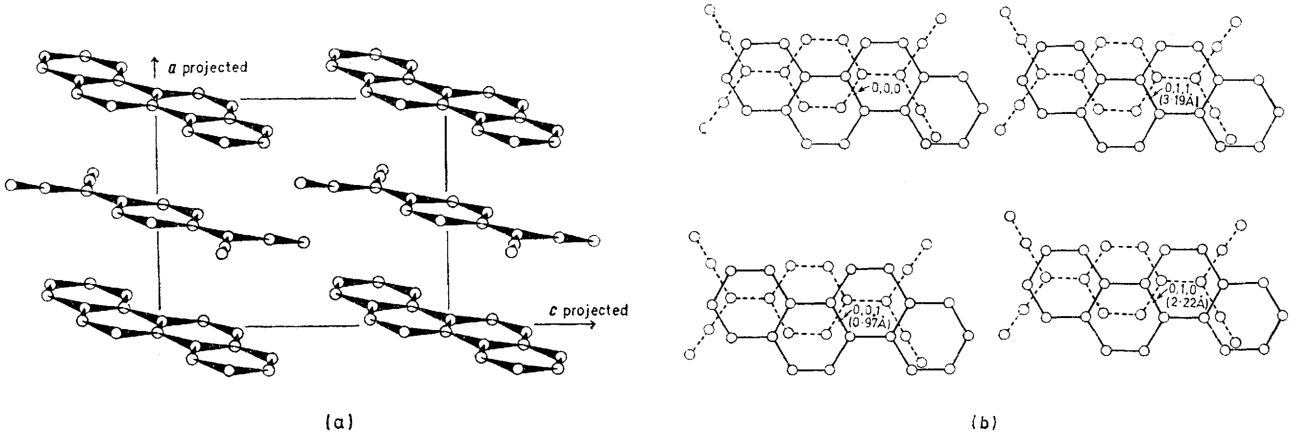

FIGURE 1 The molecular arrangement in the crystal of chrysene–7,7,8,8-tetracyanoquinodimethane, projected down (a) the *b* axis, and (b) on the plane of the chrysene molecule at 0,0,0. [In (b), the positions and relative heights of the centres of the chrysene molecules are marked. The tcnq molecules lie above the respective chrysene molecules by a mean separation of 3·37 Å. The transformation matrix from the fractional atomic co-ordinates of the triclinic unit cell to the orthogonal (Å) best plane co-ordinates *X*, *Y*, and *Z* (with *Z* perpendicular to the molecular plane), is:

$$\begin{matrix} -2{\cdot}4257 & 4{\cdot}9127 & 5{\cdot}6547 \\ 1{\cdot}0972 & -5{\cdot}8785 & 7{\cdot}2123 \\ 6{\cdot}7489 & 2{\cdot}2866 & 0{\cdot}9117 \end{matrix}]$$

TABLE 2

Comparison of observed and calculated bond lengths (Å) in the chrysene molecule

	Obs.		Calc.[c]	
Bond	(1)[a]	(2)[b]	MO	SCMO
C(1)–C(1′)	1·414	1·402	1·413	1·438
C(1)–C(2)	1·461	1·409	1·426	1·438
C(2)–C(3)	1·403	1·390	1·414	1·388
C(3)–C(4)	1·418	1·410	1·417	1·439
C(4)–C(5)	1·535	1·403	1·372	1·355
C(1′)–C(5)	1·409	1·410	1·406	1·380
C(2)–C(6)	1·412	1·433	1·404	1·423
C(6)–C(7)	1·369	1·423	1·381	1·363
C(7)–C(8)	1·386	1·387	1·398	1·423
C(8)–C(9)	1·363	1·392	1·380	1·363
C(3)–C(9)	1·421	1·435	1·407	1·424

[a] This work. [b] Ref. 1. [c] Ref. 6.

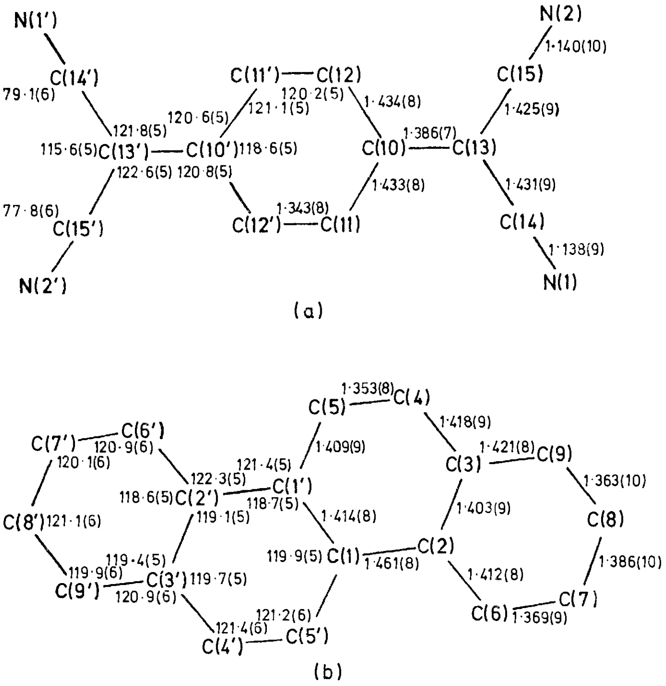

FIGURE 2 Bond lengths (Å) and interbond angles (deg.), with standard deviations in parentheses

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

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

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

[12] I. J. Tickle and C. K. Prout, *J.C.S. Perkin II*, 1973, 724.

[13] C. K. Prout and I. J. Tickle, *J.C.S. Perkin II*, 1973, 727.

[14] I. Goldberg and U. Shmueli, *Acta Cryst.*, 1973, **B29**, 421.

[15] I. Goldberg and U. Shmueli, *Acta Cryst.*, 1973, **B29**, 432.

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[17] D. A. Lowitz, *J. Chem. Phys.*, 1967, **46**, 4698.

[18] H. T. Jonkman and J. Kommandeur, *Chem. Phys. Letters*, 1972, **15**, 496.

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is probably determined in part by the dipole–induced-dipole interactions, between donor and acceptor, which are favoured in this orientation. Charge-transfer interactions involving other orbitals of the molecules may also contribute to the stability of the observed orientation, although no molecular orbital calculations have been performed to investigate this possibility.[20]

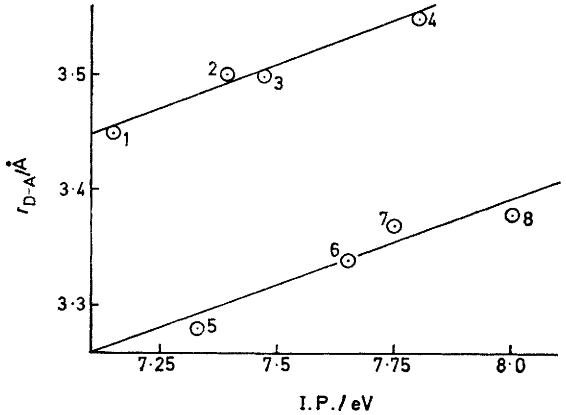

FIGURE 3 Dependence of donor–acceptor interplanar distance (r_{DA}) on donor ionisation potential, for some tcnq complexes. The upper and lower lines are for complexes with monoclinic and triclinic lattices, respectively. (1) Perylene, (2) anthracene, (3) pyrene, (4) hexamethylbenzene, (5) bis-(8-hydroxyquinolinato)copper(II), (6) acenaphthene, (7) chrysene, (8) phenazine

The mean interplanar spacing is 3·37 Å. It has recently been suggested[15] that there is a correlation between the interplanar spacings in tcnq complexes of different donors and the orbital energies of these donors. Figure 3 shows the interplanar spacings in some tcnq complexes as a function of the donor ionisation potential. Clearly, no overall correlation exists, although if the complexes are divided into monoclinic and triclinic types, two roughly linear relationships appear, as expected from perturbation theory considerations. The differences between interplanar spacings in complexes with different lattice types are larger than those due to orbital energy differences, and thus in general the correlation of interplanar spacing and orbital energy may be obscured by the more important lattice packing effects.

The crystal structure is built up of the stacks of alternating donor and acceptor molecules characteristic of π–π* electron-donor–acceptor complexes. The stacking axis is the *a* axis. There are no short contacts between tcnq molecules in adjacent stacks, and the relative positions of the closest tcnq molecules in adjacent stacks are virtually identical with those found in the anthracene–tcnq complex.[8] However, there is a region of possible π overlap between chrysene molecules in adjacent stacks [C(8) and C(9) of that at 0,0,0 overlapping with C(8′) and C(9′) of that at 0,1,1], the shortest contact being between C(8) of the molecule at 0,0,0 and C(8′) of the molecule at 0,1,1 (3·65 Å). This feature is believed to be important in its influence on the charge-carrier generation step in photoconductivity of the complex.[2]

The values of the anisotropic temperature factors, together with the good agreement between the bond lengths in both molecules and those of previous determinations, show that, unlike many other molecular complex crystals,[21] the crystals of this complex are not disordered. This may be due to the elongated nature of both component molecules, leading to large energy barriers for in-plane oscillation or rotation.

[4/385 *Received, 26th February,* 1974]

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