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

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Crystals of the title 1 : 1 molecular complex are triclinic, $a = 6{\cdot}74$, $b = 16{\cdot}88$, $c = 8{\cdot}26$ Å, $\alpha = 94{\cdot}8$, $\beta = 92{\cdot}0$, $\gamma = 95{\cdot}3°$, space group $P\bar{1}$, $Z = 2$. The structure has been determined by Patterson methods from diffractometer data and refined by least squares to R 0·063 for 2290 independent reflections. The dimensions of the component molecules have been corrected for rigid-body motion. 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 XVIII[1] the crystal and molecular complex of acenaphthene (I) and chloranil was described. This complex was chosen because a solid-state complex between naphthalene and a *p*-benzoquinone derivative could not be prepared. In acenaphthene–chloranil maximisation of the charge-transfer interaction was not achieved[2] probably owing to repulsion between the hydrogen atoms of the *peri*-dimethylene group of the acenaphthene and the peripheral atoms at the electron acceptor, and the complex may or may not be representative of the complexes of naphthalenes with *p*-benzoquinones.

Although it was possible to prepare a crystalline complex of naphthalene and 7,7,8,8-tetracyanoquinodimethane (cyclohexa-2,5-diene-1,4-diylidenedimalononitrile) (II) crystals suitable for *X*-ray work could not

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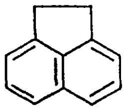
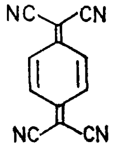
[1] Part XVIII, I. J. Tickle and C. K. Prout, preceding paper.

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

be obtained. However for a hypothetical naphthalene–(II) system [2] the π–π^* overlap is maximised at such a donor–acceptor orientation that it is unlikely to be affected by hydrogen repulsion effects if naphthalene is replaced by acenaphthene. Therefore, the crystal structure of the acenaphthene–(II) complex was determined.



(I)



(II)

EXPERIMENTAL

Laboratory-grade acenaphthene was recrystallised from ethanol. (II) Was prepared according to method (B) in ref. 3, and was recrystallised several times, first from ethyl acetate and then from acetonitrile. The complex was prepared by the same method as for acenaphthene–chloranil,[1] but with ethyl acetate as solvent. Large black needles were obtained from the deep violet solution (Found: C, 80·1; H, 3·6; N, 15·7. $C_{24}H_{14}N_4$ requires C, 80·4; H, 3·9; N, 15·6%).

In the absence of free acenaphthene, single crystals decomposed quite rapidly (within 48 h), even when sealed in a glass capillary, apparently owing to sublimation of the acenaphthene, but it was found possible to preserve a crystal for *X*-ray data collection by coating it with a thin film of Durafix cement.

Crystal Data.—$C_{24}H_{14}N_4$, $M = 358{\cdot}4$. Triclinic pinacoidal, $a = 6{\cdot}74 \pm 0{\cdot}01$, $b = 16{\cdot}88 \pm 0{\cdot}01$, $c = 8{\cdot}26 \pm 0{\cdot}01$ Å, $\alpha = 94{\cdot}8 \pm 0{\cdot}1$, $\beta = 92{\cdot}0 \pm 0{\cdot}1$, $\gamma = 95{\cdot}3 \pm 0{\cdot}1°$, $U = 931{\cdot}0$ Å^3, $D_m = 1{\cdot}285$ (by flotation), $Z = 2$, $D_c = 1{\cdot}278$. Space group $P\bar{1}$ (C_i^1, No. 2). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, μ(Cu-K_α) = 6·25 cm^{-1}.

Unit-cell dimensions were measured and three-dimensional intensity data collected on a Hilger and Watts four-circle diffractometer, with a ω—2θ step-scan. Balanced filters were used for $\theta < 15°$. The absence of any gross or systematic change in the intensities of the reference reflections during the course of the data collection confirmed that no significant decomposition of the crystal recurred. Of the 3279 reflections ($\theta < 75°$) of net positive intensity, 2290 were taken as significantly (4σ) above background. Lorentz, polarisation, and empirical absorption [4] corrections were applied.

The overall temperature factor (*B* 4·4) was estimated from a Wilson plot [5] which exhibited a damped oscillatory behaviour at low Bragg angle.

The distribution of normalised structure factors (E) ($\langle|E|\rangle$, 0·722; $\langle|E^2 - 1|\rangle$, 1·135; $\%|E| < 1$, 23·2; $\%|E| < 2$, 5·4; $\%|E| < 3$, 1·65 when $\langle E^2\rangle$ set equal to 1) indicated a hypercentrosymmetric (centrosymmetric with possible additional non-space-group symmetry elements) unit-cell. Attempts to determine the structure with the Oxford CSSA [6] direct methods system failed, possibly owing to the non-random atomic distribution leading to a partial breakdown of the Cochran–Woolfson probability formula.[7]

In the Patterson function (sharpened to ' point atoms at rest ') all significant maxima lay close to the $(4,\bar{1},0)$ plane in an extensive isometric array of 1·4 Å spacing. The short *c* axis repeat restricted the molecules of (II) to two possible orientations consistent with the Patterson function. Intermolecular vectors between two centrosymmetric 16 'heavy' atom molecules of (II) related by a centre of symmetry include a 16-fold vector defining the centroid-to-centroid separation of these molecules. This vector was identified at 0·38, 0·52, and 0·295. An F_o synthesis with phases calculated from one of the two possible positions for (II) showed the carbon skeleton of the acenaphthene.

The atomic co-ordinates were refined by the least-squares method, initially with unit weights for all reflections and isotropic temperature factors, and then with anisotropic temperature factors and a weighting function for individual reflections.[8] The seven intense reflections $(0,1,1,\ 1,1,\bar{3},\ 2,\bar{2},0,\ 2,1,0,\ 2,0,0,\ 2,1,0\ 4,\bar{1},0)$ appeared to suffer from extinction effects and were given zero weight. Hydrogen atoms were located from a difference-Fourier synthesis and their space parameters included in the following refinement with the C–H bond length constrained to $1{\cdot}05 \pm 0{\cdot}02$ Å by Waser's [9] method as implemented by Rollett and Ford.[10] The normal matrix was divided into five blocks, one for derivatives containing the F_c scale factor and a dummy overall U_{iso}, and two each for the acenaphthene and molecules of (II), containing the derivatives of the space and thermal parameters respectively. The refinement converged at R 0·063 after eight cycles. The final difference-Fourier map with an estimated standard deviation of electron density of 0·06 e Å^{-3} had no significant (3σ) features.

The observed structure amplitudes and structure factors calculated from the final atomic parameters in Table 1 are given in Supplementary Publication No. SUP No. 20630 (14 pp, 1 microfiche).* The estimated standard deviations in Table 1 were obtained from the diagonal elements of the inverse of the normal matrix. Rollett's NOVTAPE system as modified by Hodder [11] and Rollett and Ford's ALGOL system [10] were used for calculations. Atomic scattering factors used were those for neutral atoms taken from ref. 12.

RESULTS AND DISCUSSION

Interatomic distances and interbond angles derived from the atomic parameters in Table 1 are shown in Figure 1. Table 2 details the rigid-body thermal motion analysis. The inertial axes, the centres of libration which in this crystal do not necessarily coincide with the molecular centroids, and deviations from the weighted least-squares best planes are shown for both component

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

[3] D. S. Asker and W. R. Hertler, *J. Amer. Chem. Soc.*, 1962, **84**, 3370.

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[5] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

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

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[8] D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Cryst.*, 1969, *B*, **25**, 374.

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[10] J. S. Rollett and G. Ford, unpublished work; J. S. Rollett in ' Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, p. 117.

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

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

TABLE 1

Atomic parameters * with standard deviations in parentheses. Hydrogen atoms are numbered according to the carbon atom 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)	0·2042(4)	0·8293(1)	0·0621(3)	0·0582(13)	0·0403(11)	0·0541(12)	−0·0019(18)	0·0049(20)	0·0076(18)
C(2)	0·2066(4)	0·8348(1)	0·2383(3)	0·0644(15)	0·0392(10)	0·0531(12)	−0·0080(18)	0·0050(21)	0·0066(19)
C(3)	0·1932(4)	0·7686(1)	0·3178(3)	0·0607(14)	0·0433(11)	0·0511(12)	−0·0039(18)	0·0049(21)	0·0061(19)
C(4)	0·1734(4)	0·6902(1)	0·2310(3)	0·0550(13)	0·0429(11)	0·0512(11)	0·0007(18)	0·0072(19)	0·0087(18)
C(5)	0·1673(4)	0·6850(1)	0·0554(3)	0·0676(15)	0·0389(11)	0·0517(11)	−0·0091(17)	0·0022(21)	0·0057(20)
C(6)	0·1811(4)	0·7506(1)	−0·0244(3)	0·0685(15)	0·0465(11)	0·0468(11)	−0·0018(18)	0·0021(21)	0·0086(21)
C(7)	0·2210(4)	0·8968(1)	−0·0202(3)	0·0669(15)	0·0415(11)	0·0564(12)	0·0015(19)	0·0043(19)	0·0048(20)
C(8)	0·2215(5)	0·8934(1)	−0·1944(3)	0·0882(19)	0·0460(12)	0·0638(15)	0·0139(22)	0·0081(27)	0·0086(24)
C(9)	0·2439(5)	0·9754(1)	0·0620(3)	0·0969(20)	0·0393(12)	0·0617(14)	0·0080)20)	0·0032(28)	0·0079(24)
C(10)	0·1660(4)	0·6231(1)	0·3140(3)	0·0605(14)	0·0427(11)	0·0520(11)	−0·0014(18)	0·0097(21)	0·0051(19)
C(11)	0·1486(4)	0·5441(1)	0·2320(3)	0·0751(17)	0·0413(11)	0·0570(13)	0·0113(19)	0·0051(24)	0·0075(21)
C(12)	0·1762(4)	0·6276(1)	0·4879(3)	0·0669(16)	0·0493(12)	0·0556(13)	0·0089(20)	0·0142(23)	0·0064(21)
C(13)	0·6758(4)	0·6561(2)	0·4627(3)	0·0575(14)	0·0576(13)	0·0524(12)	0·0183(20)	0·0128(21)	0·0171(21)
C(14)	0·6622(4)	0·5842(2)	0·3721(4)	0·0663(16)	0·0529(14)	0·0812(18)	0·0180(25)	0·0184(27)	0·0124(23)
C(15)	0·6588(4)	0·5837(2)	0·1995(4)	0·0670(17)	0·0671(16)	0·0749(17)	−0·0321(27)	0·0186(27)	0·0087(26)
C(16)	0·6688(4)	0·6522(2)	0·1227(3)	0·0634(16)	0·0839(19)	0·0523(13)	−0·0141(25)	0·0091(23)	0·0172(27)
C(17)	0·6830(4)	0·7278(2)	0·2128(3)	0·0533(14)	0·0687(15)	0·0472(11)	0·0129(21)	0·0057(20)	0·0076(22)
C(18)	0·6964(4)	0·8040(2)	0·1542(4)	0·0676(17)	0·0795(18)	0·0633(14)	0·0483(26)	0·0153(26)	0·0198(27)
C(19)	0·7122(5)	0·8712(2)	0·2603(4)	0·0833(20)	0·0613(15)	0·0873(20)	0·0543(28)	0·0154(32)	0·0152(28)
C(20)	0·7138(5)	0·8690(2)	0·4303(4)	0·0800(19)	0·0534(14)	0·0830(18)	0·0081(25)	−0·0009(31)	0·0156(26)
C(21)	0·7010(4)	0·7960(2)	0·4914(3)	0·0651(15)	0·0543(13)	0·0577(13)	0·0043(20)	0·0001(23)	0·0178(22)
C(22)	0·6867(3)	0·7264(1)	0·3826(3)	0·0531(13)	0·0531(12)	0·0493(11)	0·0114(19)	0·0065(20)	0·0157(20)
C(23)	0·6885(5)	0·6793(2)	0·6455(3)	0·0705(17)	0·0714(16)	0·0516(12)	0·0241(23)	0·0125(23)	0·0220(25)
C(24)	0·6972(5)	0·7714(2)	0·6638(3)	0·0867(20)	0·0701(17)	0·0538(13)	−0·0089(24)	0·0026(26)	0·0239(28)
N(1)	0·2221(5)	0·8913(2)	−0·3329(3)	0·1241(23)	0·0722(16)	0·0648(14)	0·0087(24)	0·0101(30)	0·0179(31)
N(2)	0·2601(5)	1·0386(1)	0·1258(3)	0·1622(29)	0·0484(12)	0·0788(16)	−0·0013(23)	0·0027(35)	0·0084(30)
N(3)	0·1376(4)	0·4812(1)	0·1685(3)	0·1104(19)	0·0433(11)	0·0726(14)	0·0031(19)	0·0160(27)	0·0046(23)
N(4)	0·1846(4)	0·6323(2)	0·6277(3)	0·0847(17)	0·0780(15)	0·0599(13)	0·0106(22)	0·0155(23)	0·0086(25)

	x/a	y/b	z/c	U_{iso}		x/a	y/b	z/c	U_{iso}
H(2)	0·220(4)	0·890(2)	0·290(3)	0·045(8)	H(18)	0·685(4)	0·810(2)	0·030(3)	0·045(7)
H(3)	0·202(4)	0·774(2)	0·447(3)	0·043(8)	H(19)	0·720(4)	0·929(2)	0·226(4)	0·047(7)
H(5)	0·148(4)	0·630(1)	−0·004(3)	0·031(7)	H(20)	0·731(4)	0·916(2)	0·499(4)	0·051(8)
H(6)	0·172(4)	0·746(2)	−0·143(4)	0·048(8)	H(231)	0·807(4)	0·661(2)	0·697(3)	0·033(7)
H(14)	0·649(4)	0·530(2)	0·421(3)	0·046(8)	H(232)	0·562(5)	0·658(2)	0·693(4)	0·059(10)
H(15)	0·648(5)	0·527(2)	0·144(4)	0·069(11)	H(241)	0·807(5)	0·797(2)	0·729(4)	0·055(10)
H(16)	0·657(5)	0·651(2)	0·001(4)	0·060(9)	H(242)	0·561(5)	0·786(2)	0·717(4)	0·069(11)

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

TABLE 2

Analysis of rigid-body thermal motion

	Direction cosines relative to:					
Principal axes	Inertial axes			Orthogonal crystal axes		
(*a*) Acenaphthene						
T Tensor/Å^2						
0·0513(20)	0·762	−0·328	0·559	0·571	−0·782	0·249
0·0480(17)	0·150	0·928	0·340	0·360	−0·034	−0·932
0·0547(23)	−0·630	−0·175	0·756	0·738	0·622	0·262
ω Tensor/deg.^{2}						
10(2)	0·965	0·260	−0·030	−0·003	−0·929	−0·370
11(2)	−0·261	0·964	−0·045	−0·034	0·370	−0·928
19(1)	0·018	0·051	0·998	0·999	0·010	−0·033
(*b*) Molecule (II)						
T Tensor/Å^2						
0·0556(16)	0·851	−0·448	−0·274	−0·261	0·518	−0·815
0·0393(17)	0·464	0·886	−0·007	−0·018	0·841	0·540
0·0482(20)	0·246	−0·121	0·962	0·965	0·156	−0·210
ω Tensor/deg.^{2}						
26(3)	0·990	−0·136	−0·027	−0·018	0·794	−0·608
6(1)	0·137	0·990	0·030	0·015	0·608	0·794
3·3(0·3)	0·022	−0·033	0·999	1·000	0·005	−0·023

molecules in Figure 2. The libration of the acenaphthene is isotropic as it is in its chloranil complex but for the molecule of (II) the librational amplitude about the long axis is several times greater than about the other two. However, these amplitudes are clearly related to the molecular shape and have no other significance. Bond lengths, corrected for rigid-body motion, are given in Table 3.

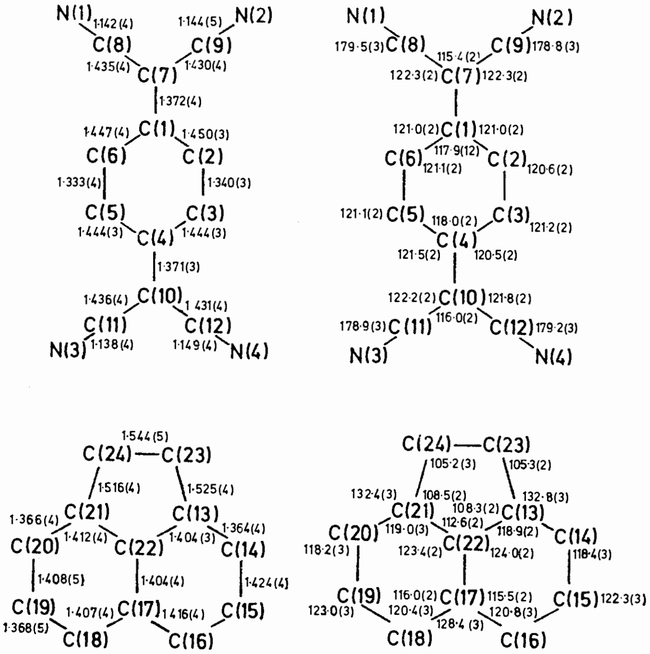

FIGURE 1 Interatomic distances (Å) before libration correction and interbond angles (deg.) with standard deviations in parentheses

The crystal structure shown in stereoscopic projection in Figure 3, is built up from the alternate donor–acceptor stacks characteristic of the π–π^* electron-donor–acceptor complexes. Because the donor- and acceptor-molecules lie at general positions in the unit-cell the relationships between any one molecule in the stack and those immediately above and below it are not necessarily equivalent but in this complex the differences are not significant. Thus the mean spacing between the best plane of the donor and the C_6 ring of either neighbouring acceptor in the donor acceptor stack is 3·37 Å and these planes are very nearly parallel with an inclination of 1·4°. Figure 4 shows the projection of the molecule of (II) at *x,y,z* (with respect to Table 1) projected on the least-squares best plane of the acenaphthene molecule at *x,y,z*. The projection of (II) at 1 + *x,y,z* on the plane of the acenaphthene at *x,y,z* does not differ significantly. The acenaphthene and (II) molecules are therefore at pseudo-inversion centres giving rise to the hypercentricity, revealed by the intensity statistics, which is essential if the infinite donor–acceptor stacks are to be formed. The orientation of donor and acceptor in Figure 1 is not significantly different from that suggested[2] for maximum π–π^* overlap, which requires the long axis of the (II) to lie along the C(14) · · · C(17) vector with the C(10)–C(4) bond midway along the C(14) · · · C(17) vector.

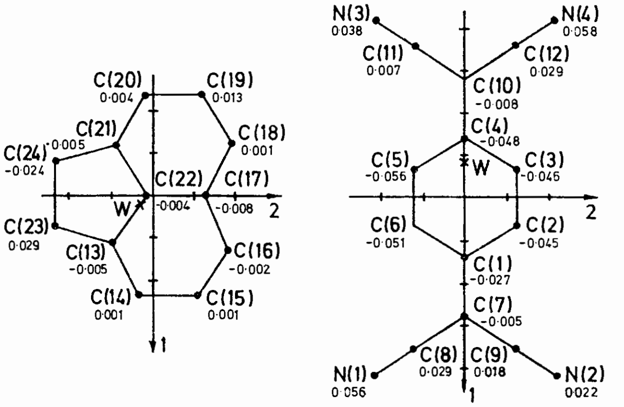

FIGURE 2 Inertial axes of the component molecules, with the centres of libration indicated by w, and deviations from the weighted least-squares best planes

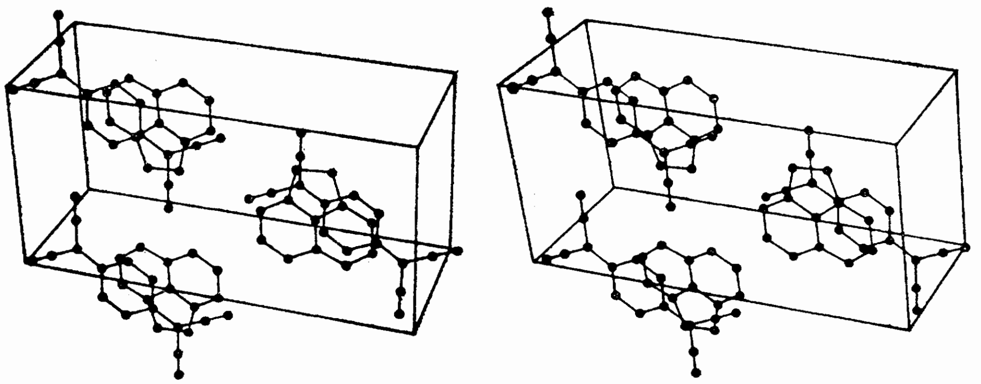

FIGURE 3 Stereoscopic projection. Rotation matrix (for conversion from crystal co-ordinates referred to the orthogonal axes, *a*, *b'*, *c** to plotter co-ordinates):

0·462	0·198	−0·864
−0·394	0·919	0·000
0·794	0·341	0·503

The dimensions of the molecules are in good agreement with those found in the crystals of the two pure substances [13,14] and there is no observable significant change in bond length on complex formation. This must cast further doubt on the significance of the short bonds observed in acenaphthene in its chloranil complex.[1] The acenaphthene molecule is slightly but significantly buckled with one of the two methylene carbon atoms [C(23)] being 0·029 above the best plane of the molecule and the other [C(24)] 0·024 Å below. The molecule of (II) is significantly 'bowed.' All the nitrile groups are displaced in the same direction out of the plane of the C_6 ring so that the nitrogen atoms are 0·07—0·13 Å from the ring plane. The displacements are in the $\pm x$ crystal direction and might arise from the mutual intermolecular repulsion of groups of CN dipoles of pairs of molecules of (II) in neighbouring stacks and related by crystallographic inversion centres. The intermolecular contacts from N(3) at x, y, z to N(3) at $x, 1 - y, \bar{z}$ and N(4) at $x, 1 - y, 1 - \bar{z}$ (3·43 and 3·35 Å) are among the shortest such contacts in the crystal.

TABLE 3

Bond-lengths (A) after correction for rigid-body thermal motion

(*a*) In acenaphthene

C(13)–C(14)	1·369 Å
C(13)–C(22)	1·410
C(13)–C(23)	1·530
C(14)–C(15)	1·429
C(15)–C(16)	1·367
C(16)–C(17)	1·421
C(17)–C(18)	1·411
C(17)–C(22)	1·409
C(18)–C(19)	1·372
C(19)–C(20)	1·412
C(20)–C(21)	1·370
C(21)–C(22)	1·418
C(21)–C(24)	1·522
C(23)–C(24)	1·550

(*b*) In molecule (II)

C(1)–C(2)	1·452
C(1)–C(6)	1·449
C(1)–C(7)	1·374
C(2)–C(3)	1·343
C(3)–C(4)	1·449
C(4)–C(5)	1·449
C(4)–C(10)	1·372
C(5)–C(6)	1·335
C(7)–C(8)	1·436
C(7)–C(9)	1·432
C(8)–N(1)	1·143
C(9)–N(2)	1·146
C(10)–C(11)	1·439
C(10)–C(12)	1·433
C(11)–N(3)	1·140
C(12)–N(4)	1·151

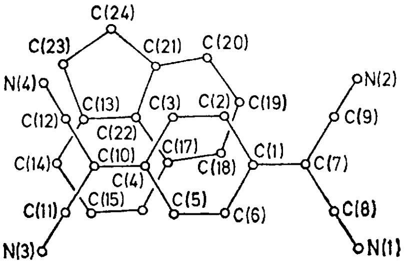

FIGURE 4 Projection of the molecule of (II) at x,y,z on the least-squares best plane of the acenaphthene molecule at x,y,z

We thank the S.R.C. for a studentship (to I. J. T.).

[2/2367 *Received*, 16*th October*, 1972]

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