Molecular Complexes. Part XV.[1] Crystal Structure of the 1 : 1 Molecular Complex of Pyrene and 1,2,4,5-Tetracyanobenzene at 290 and 178 K

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The crystal and molecular structure of the title complex has been determined at 290 and 178 K by three-dimensional *X*-ray diffraction methods. Crystals are monoclinic, unit cell dimensions (290 K) a = 7·27, b = 15·57, c = 8·44 Å, γ = 93·6°; (178 K) a = 7·27, b = 15·36, c = 8·38 Å, γ = 94·0°; space group $P2_1/b$, Z = 2. The structure was determined by Patterson and Fourier methods from visually estimated photographic data and refined by full matrix least-squares techniques to R 0·101 (290 K, 1367 independent reflections) and 0·110 (178 K, 767 independent reflections). In the crystal alternate pyrene and tetracyanobenzene molecules form stacks along the a axis. The mean separation of the molecular planes, which are inclined at an angle of 4·4°, is 3·50 Å at both temperatures. 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 between tetracyanobenzene molecules. A detailed analysis of the anisotropic temperature factors suggests that there is a large in-plane angular oscillation of the pyrene molecule, together with a co-operative translational and rocking motion of the complex as a whole.

SYSTEMATIC theoretical interpretation[2] of the relative orientations of electron donor and acceptor molecules in crystalline molecular complexes must be founded on structural data for series of complexes of a given electron donor with various types of electron acceptor. The structures of eight complexes in which the donor is 8-hydroxyquinoline or its copper or palladium complex have been determined,[3-10] but the presence of heavy-metal atoms and strongly dipolar bonds in these molecules complicates the interpretation of observed relative orientations. A donor whose interactions with electron acceptors are simpler is pyrene, which has high symmetry, no heavy atoms, and no strongly dipolar bonds. The structures of its complexes with tetracyanoethylene,[11] 1,3,7,9-tetramethyluric acid,[12] and pyromellitic dianhydride[13] have been determined, and the structure of the 1,2,4,5-tetracyanobenzene complex is now reported.

EXPERIMENTAL

Slow evaporation of a solution of pyrene and tetracyanobenzene in glacial acetic acid yielded orange crystals of the complex, elongated along a, with the (010) faces well developed. At 290 K multiple-film equi-inclination Weissenberg photographs were taken about the a (layers 0—6) and c (layers 0—7) axes. Intensities were measured visually, giving totals of 1054 and 1040 reflections, respectively. Lorentz and polarisation corrections were applied, and the two sets of data were scaled and merged, using a weighting scheme, to give a set of 1367 independent reflections. The merging R value was 0·092. The technique used to collect the low-temperature photographic data on a Weissenberg camera was that of Viswamitra.[14]

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[13] F. H. Herbstein and J. A. Snyman, *Phil. Trans.* 1969, **A264**, 635.

[14] M. Viswamitra, University of Bangalore, personal communication.

Accurate temperature control was essential because the crystal shatters at 171 K. This temperature is quite reproducible and is independent of the rate of cooling of the specimen. At 171 K the colour of a powdered sample changes reversibly from orange above this temperature to yellow below. Data collection was carried out at 178 ± 2 K. At the low temperature, small shifts in crystal orientation occurred and it was necessary to limit exposure time to 8 h. 767 reflections of the layers 0—6*kl* were estimated visually from multiple-film Weissenberg photographs. The results from individual layers were placed on a common scale by using the exposure time to *X*-rays from a stabilised source and standardised development conditions. Lorentz and polarisation corrections were applied.

Crystal Data.—$C_{26}H_{12}N_4$, $M = 380{\cdot}1$. Monoclinic, (i) 290 K: $a = 7{\cdot}27 \pm 0{\cdot}01$, $b = 15{\cdot}57 \pm 0{\cdot}02$, $c = 8{\cdot}44 \pm 0{\cdot}01$ Å, $\gamma = 93{\cdot}6 \pm 0{\cdot}1°$, $U = 961{\cdot}4$ Å^3, $D_m = 1{\cdot}33$, $Z = 2$; $D_c = 1{\cdot}313$; (ii) 178 K: $a = 7{\cdot}27 \pm 0{\cdot}03$, $b = 15{\cdot}36 \pm 0{\cdot}05$, $c = 8{\cdot}38 \pm 0{\cdot}03$ Å, $\gamma = 94 \pm 0{\cdot}4°$. Space group $P2_1/b$ (C^5_{2h}, No. 14, 1st setting) Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 6·4 cm^{-1}.

Structure Determination.—The unit cell contains two pyrene and two tetracyanobenzene molecules. The space group $P2_1/b$ requires that these lie about centres of symmetry.

A three-dimensional sharpened Patterson function calculated from the data collected at 290 K showed the planes and approximate orientations of both molecules. A three-dimensional Fourier synthesis, phased on an idealised pyrene molecule at the origin and lying in the plane and orientation indicated by the Patterson function, revealed the tetracyanobenzene molecule. Six cycles of full-matrix least-squares refinement of this trial structure, varying all atomic co-ordinates and individual isotropic temperature factors, reduced *R* to 0·23 when the refinement converged. At this point, the dimensions of the tetracyanobenzene molecule were in good agreement with previous results,[1,5,6,15–17] but the dimensions of the pyrene molecule, and the temperature factors of some of its atoms, were unsatisfactory. A second Fourier synthesis was therefore calculated, phased on the final co-ordinates for the tetracyanobenzene molecule. This showed that, in the pyrene molecule, only the three carbon atoms lying nearest to the centre of symmetry were well defined. The electron density contours in the region of the outer atoms were smeared out in the plane of the molecule, and not localised as distinct peaks.

Notwithstanding these difficulties, four further full-matrix anisotropic least-squares refinement cycles were calculated with a weighting scheme $w = [1 + (F_o/3{\cdot}8)^2]^{-1}$. The refinement converged and *R* was 0·101.

As an alternative, a trial disordered structure was postulated, containing two pyrene molecules (each with half-occupancy) fitted to the electron density distribution of the F_o syntheses (Figure 1). The close proximity of pairs of carbon atoms in this trial structure leads to an ill-conditioned normal matrix in the least-squares refinement and hence to unrealistic shifts and variances. To reduce the false correlations between the parameters, subsidiary conditions (in effect, bond-length information) were introduced by the method developed by Rollett and Ford [18] from a suggestion of Waser.[19] The function minimised was $\Sigma w^1(d - d^1)^2 + R^1$ where R^1 is the main condition $\Sigma(wF_o - F_c)^2$, d is the distance between the *i*th and *j*th atoms calculated from present best parameters and d^1 is the expected distance. This refinement, with isotropic temperature factors, which converged after eight cycles at an *R* value of 0·152, was significantly better than the initial isotropic refinement, but not significantly better than the anisotropic refinement.

The trial structure at 178 K with the atomic co-ordinates and individual isotropic temperature factors obtained from the initial refinement of the 290 K data was refined by full-matrix anisotropic least-squares. The refinement converged after six cycles at *R* 0·110.

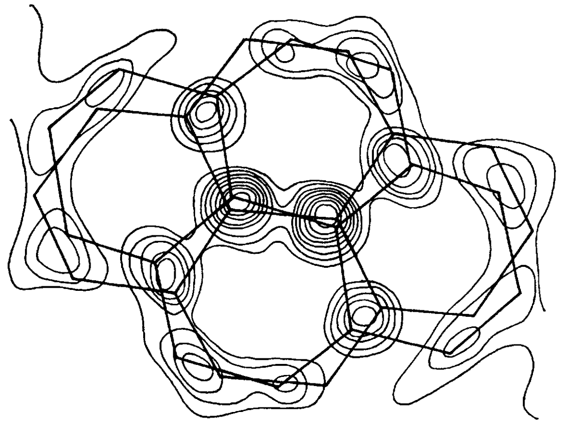

FIGURE 1 The disordered trial pyrene positions superimposed on the electron density contour map in the plane of the pyrene molecule

In order to check that the differences in temperature factors at 290 and 178 K were not due merely to the difference in the quantity of the data, the refinement at 290 K was repeated with only those reflections observed at 178 K. The temperature factors obtained from this restricted 290 K data were not significantly different from those obtained from the full data.

The observed structure amplitudes at 290 and 178 K and the structure factors calculated from the final atomic parameters in Table 1 are listed in Supplementary Publication SUP 20596 (18 pp., 1 microfiche).*

All calculations were carried out on the Oxford University English Electric KDF 9 computer. Rollett's NOVTAPE system,[20] modified by Hodder, was used for all calculations assuming isotropic thermal motion, except for the constrained refinement of the disordered model. This, and all calculations assuming anisotropic thermal motion, used Rollett and Ford's ALGOL system.[21] Atomic scattering factors for neutral atoms were taken from ref. 22, and corrected for the real part of the anomalous dispersion.

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

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RESULTS AND DISCUSSION

The Crystal Structure.—The crystal structure is built up from isolated pyrene and tetracyanobenzene molecules alternating in plane-to-plane stacks which are characteristic of π–π* electron-donor–acceptor complexes.

TABLE 1

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

(*a*) At 290 K

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	474(5)	306(3)	1506(5)	46(2)	53(2)	59(2)	10(4)	7(3)	5(3)
C(2)	567(5)	859(3)	193(5)	47(2)	49(2)	66(3)	2(4)	16(3)	7(3)
C(3)	97(6)	558(3)	−1308(5)	51(2)	53(2)	63(2)	10(4)	12(4)	7(3)
C(4)	947(6)	634(3)	3067(6)	60(2)	61(2)	68(3)	0(4)	−9(4)	5(4)
C(5)	1190(6)	1761(3)	420(6)	61(2)	56(2)	71(3)	9(4)	−4(4)	−8(4)
N(1)	1323(7)	897(3)	4278(6)	106(4)	84(3)	69(3)	−14(5)	−31(5)	22(5)
N(2)	1673(7)	2462(3)	624(7)	87(3)	59(2)	103(4)	22(5)	−19(5)	−31(4)
C(6)	5043(9)	893(6)	−2536(8)	76(3)	132(5)	78(4)	119(8)	38(6)	68(7)
C(7)	5607(6)	1097(3)	−876(7)	50(2)	55(2)	111(4)	34(5)	43(5)	21(3)
C(8)	6323(10)	1897(4)	−435(16)	72(4)	53(3)	224(10)	41(10)	66(11)	13(5)
C(9)	6784(9)	2045(5)	1060(18)	63(3)	87(4)	241(11)	−100(12)	50(10)	21(6)
C(10)	6632(8)	1418(7)	2311(11)	57(3)	159(7)	149(7)	−208(12)	−15(7)	43(7)
C(11)	5866(6)	555(4)	1843(6)	51(2)	113(4)	69(3)	−79(6)	−16(4)	45(5)
C(12)	5647(9)	−133(7)	2934(6)	79(4)	192(8)	43(3)	44(8)	17(5)	98(9)
C(13)	5372(5)	411(2)	255(5)	40(2)	49(2)	53(2)	−14(3)	12(3)	12(3)

(*b*) At 178 K

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	478(12)	312(6)	1520(12)	22(4)	34(5)	45(6)	7(9)	3(8)	11(6)
C(2)	584(11)	859(6)	200(15)	19(5)	32(5)	58(7)	−7(9)	11(7)	8(6)
C(3)	131(12)	561(6)	−1330(12)	19(4)	38(5)	47(6)	6(8)	17(7)	4(7)
C(4)	941(14)	639(6)	3079(13)	40(6)	34(5)	43(6)	5(9)	6(8)	20(7)
C(5)	1206(13)	1765(7)	415(15)	23(5)	36(6)	52(7)	8(9)	−5(8)	−5(7)
N(1)	1263(14)	903(6)	4320(12)	70(6)	40(5)	55(6)	−4(9)	−15(9)	23(7)
N(2)	1730(12)	2469(6)	613(13)	46(5)	38(5)	78(6)	17(9)	−11(8)	−5(7)
C(6)	5006(16)	846(10)	−2605(15)	39(6)	105(10)	47(7)	81(14)	32(10)	74(12)
C(7)	5581(12)	1077(7)	−985(14)	14(5)	35(5)	95(8)	34(10)	29(9)	12(6)
C(8)	6328(15)	1898(8)	−560(23)	27(6)	46(7)	138(13)	9(15)	29(13)	25(8)
C(9)	6788(16)	2069(9)	953(23)	33(7)	47(7)	145(14)	−33(17)	39(14)	23(9)
C(10)	6619(15)	1472(11)	2247(20)	25(6)	95(9)	100(9)	−110(16)	5(11)	37(11)
C(11)	5870(13)	609(8)	1801(13)	17(5)	68(7)	47(7)	−37(11)	3(7)	25(8)
C(12)	5719(16)	−41(10)	2958(14)	35(7)	106(10)	45(7)	−1(14)	19(9)	37(12)
C(13)	5364(11)	418(6)	232(12)	8(4)	31(4)	44(5)	−1(8)	8(6)	13(5)

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

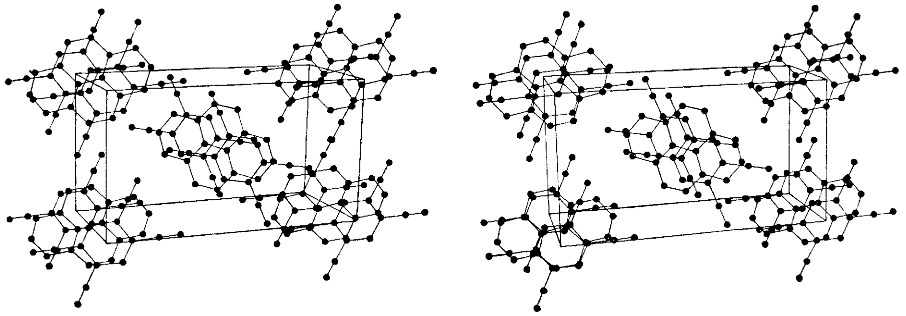

FIGURE 2 Pyrene–1,2,4,5-tetracyanobenzene: generalised stereoscopic projection. The transformation matrix from the orthogonal crystal axes a, b', c to a set of orthogonal axes X, Y, Z, with Z perpendicular to the plane of the paper, is:

$$\begin{array}{rrr} 0{\cdot}186 & -0{\cdot}054 & -0{\cdot}981 \\ 0{\cdot}281 & 0{\cdot}960 & 0{\cdot}000 \\ 0{\cdot}942 & -0{\cdot}276 & 0{\cdot}194 \end{array}$$

This is shown in stereoscopic projection in Figure 2, for the structure at 178 K. The pyrene position is much less well-defined than that of the tetracyanobenzene.

Bonded distances and interbond angles, with their standard deviations are shown in Figure 3(a) for the structure at 290 K and Figure 3(b) for that at 178 K.

The dimensions of the tetracyanobenzene molecule are the same as those observed for the uncomplexed molecule[1] and in other electron-donor–acceptor complexes.[5,6,15-17] The dimensions of the pyrene molecule are in relatively poor agreement with those from other determinations[11-13,23] and the expected values obtained from extended Hückel calculations.[24] The dimensions observed at 178 K are, in general, in better agreement with expected values than those found at 290 K. The

[23] J. M. Robertson and J. G. White, *J. Chem. Soc.*, 1947, 358.

[24] B. Pullman and A. Pullman, 'Quantum Biochemistry,' Interscience, New York, 1963.

relatively poor dimensions are due to the large thermal motion of the pyrene molecule.

The overlap diagram, the projection of the tetracyanobenzene acceptor on the least-squares best plane of the pyrene donor, is shown in Figure 4. MO Calculations[2] predict that the charge-transfer interaction would be maximised for a centre-on-centre superposition, and is only 60% of the likely maximum value in the observed orientation.

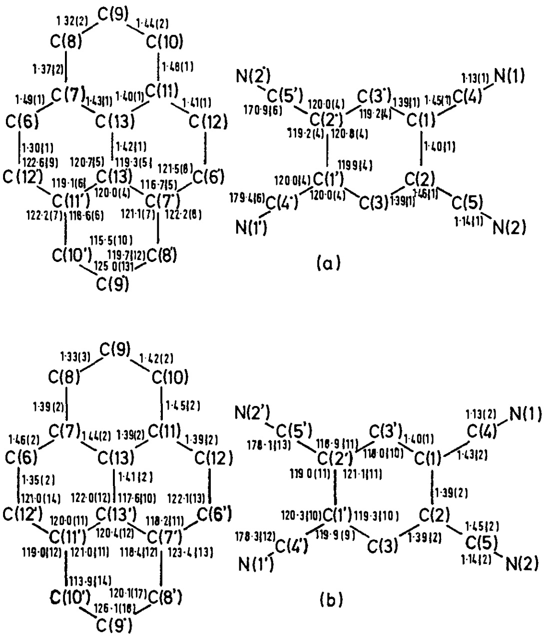

FIGURE 3 Bond lengths and interbond angles with standard deviations at (a) 290, and (b) 178 K

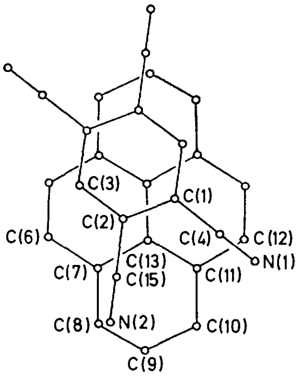

FIGURE 4 The projection of the tetracyanobenzene molecule on the least-squares best plane of the pyrene molecule (at 178 K)

With molecules of similar size yet dissimilar shape, as in this case, lattice arrangements required for good lattice packing and centre-on-centre overlap are not the same. The former requires that the normal to the molecular planes is inclined to the stacking axis, while the latter requires that it is coincident with this. In these circumstances, factors other than charge-transfer interactions and lattice packing may determine the final compromise orientation adopted. In the present structure, this deciding factor is probably the dipole–dipole attractions between neighbouring tetracyanobenzene molecules. This interpretation is consistent with the observation that it is the pyrene molecules which show large thermal motions in this structure, while the tetracyanobenzene molecules are relatively firmly held in the lattice and show no excessive vibration. At both temperatures the mean interplanar separation is 3·50 Å and the molecular planes are inclined at an angle of 4·4°. It is commonly observed that the donor and acceptor molecules are not parallel in cases where one molecule is not completely covered by the second.[25] There are eight contact distances <3·5 Å between the atoms of pyrene and tetracyanobenzene within the electron-donor–acceptor stack, but only one contact <3·5 Å from a nitrogen atom [N(2) · · · C(10)] of a pyrene molecule in an adjacent stack (see Table 2).

TABLE 2

Intermolecular contacts (Å) <3·5 Å between the pyrene and tetracyanobenzene molecules at 178 K

$C(1) \cdots C(10^{I})$	3·45	$C(4) \cdots C(10^{I})$	3·50
$C(1) \cdots C(11^{I})$	3·41	$C(5) \cdots C(9^{I})$	3·30
$C(2) \cdots C(9^{I})$	3·48	$N(1) \cdots C(12^{III})$	3·48
$C(3) \cdots C(7^{I})$	3·44	$N(2) \cdots C(10^{IV})$	3·48
$C(3) \cdots C(12^{II})$	3·49		

Roman numerals refer to the following equivalent positions relative to the reference atom at x, y, z:

I $x - 1, y, z$
III $1 - x, y, 1 - z$
II $-x, -y, -z$
IV $1 - x, \frac{1}{2} - y, z - \frac{1}{2}$

There are no contacts <3·5 Å between the atoms of one tetracyanobenzene molecule and a second such molecule, and none between pairs of pyrene molecules.

Thermal Analysis.—The electron-density distribution at 290 K (Figure 1) might represent either an arrangement of disordered pyrene molecules or a pyrene molecule executing large thermal oscillation. Attempts to refine a disordered model for the structure at 290 K were relatively unsuccessful. The disorder corresponds to a W-shaped potential well within a barrier large compared with kT at room temperature and the oscillation to a flat-bottomed potential well. The third possibility, a W-shaped well with a barrier lower than kT at room temperature, would lead to a dynamic situation at high temperature which could be frozen in at low temperatures. If the crystal were cooled to 178 K the first case would lead to approximately the same apparent oscillation as at room temperature, but the second case would show a considerable reduction in the molecular oscillation. The third case might or might not lead to a significant reduction in thermal motion.

The thermal ellipsoids demonstrate that the in-plane atomic vibration, whether real or apparent, is considerably reduced at the lower temperature. For the pyrene and TCNB molecules, with their skeletal atoms of similar mass, it is reasonable to assume that at both temperatures the internal vibrations are small

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[25] C. K. Prout and J. D. Wright, *Angew. Chem. Internat. Edn.*, 1968, **7**, 659.

compared with the rigid-body vibrations, and to attempt to interpret the atomic vibrational ellipsoids solely in terms of the latter. The motion of these molecules at crystallographic symmetry centres can then be expressed in terms of two symmetric tensors; the T tensor describing the linear oscillation of the centre of gravity of the molecule, and the ω tensor describing the angular oscillations of the molecule about this centre.[26] Table 3 gives the principal axes of the T tensors (in Å^2) and the ω tensors (in deg^2) for pyrene and tetracyanobenzene at 290 and 178 K together with their direction cosines with respect to the inertial axes of the molecule and the orthogonal crystal axes (*a*, *b**, and *c*).

TABLE 3

Analysis of rigid-body thermal motion

	Vectors of the T or ω matrix relative to:					
Principal axes	Inertial axes			Orthogonal crystal axes		
T Tensors/Å^2						
(*a*) Pyrene at (i) 290 K						
0·064(4)	0·9878	0·0495	−0·1479	0·4482	0·8741	0·1871
0·046(4)	−0·0170	0·9769	0·2130	−0·3145	0·3501	−0·8823
0·033(7)	0·1550	−0·2097	0·9658	−0·8368	0·3366	0·4318
(ii) 178 K						
0·047(4)	0·9282	−0·3717	−0·0195	0·3571	0·7272	0·5862
0·038(4)	0·3716	0·9284	−0·0071	0·0265	0·6195	−0·7845
0·006(7)	0·0208	−0·0007	0·9998	−0·9337	0·2957	0·2020
(*b*) Tetracyanobenzene at (i) 290 K						
0·063(2)	0·8917	−0·4474	0·0692	0·1625	0·4147	0·8953
0·050(2)	0·3908	0·8378	0·3813	−0·2448	0·8960	−0·3706
0·033(3)	−0·2285	−0·3129	0·9219	−0·9559	−0·1589	0·2471
(ii) 178 K						
0·050(2)	0·7811	−0·6237	−0·0302	0·2142	0·1943	0·9573
0·033(2)	0·6131	0·7568	0·2267	−0·0210	0·9807	−0·1944
0·011(3)	−0·1185	−0·1956	0·9735	−0·9766	0·0215	0·2142
ω Tensors/deg.^{2}						
(*a*) Pyrene at (i) 290 K						
16(6)	0·9630	−0·2439	0·1143	0·2261	0·8300	0·5098
5(3)	0·2451	0·9695	0·0035	−0·0330	0·5296	−0·8476
64(2)	−0·1116	0·0246	0·9934	−0·9735	0·1749	0·1471
(ii) 178 K						
10(5)	0·9787	−0·0320	0·2026	0·1279	0·9383	0·3214
4(3)	0·0373	0·9991	−0·0223	−0·0744	0·3322	−0·9403
36(2)	−0·2017	0·0294	0·9790	−0·9890	0·0963	0·1123
(*b*) Tetracyanobenzene at (i) 290 K						
25(8)	0·9931	0·0503	0·1056	0·1652	0·8056	0·5690
12(2)	−0·1028	0·8062	0·5827	−0·5716	0·5483	−0·6104
5(1)	−0·0558	−0·5895	0·8058	−0·8037	−0·2244	0·5511
(ii) 178 K						
9(5)	0·7157	−0·6203	−0·3210	0·4764	0·0783	0·8757
13(4)	0·6971	0·6069	0·3817	−0·1536	0·9881	−0·0048
1(1)	−0·0419	−0·4970	0·8668	−0·8657	−0·1322	0·4828

For both molecules the in-plane linear oscillation is greater than the out-of-plane oscillation. The amplitudes of the oscillations are the same for both molecules, and the amplitude is only slightly reduced on cooling from 290 to 178 K. The principal axes of the T tensor of the pyrene molecule lie along the inertial axes, but the principal axes of that of the tetracyanobenzene molecule lie between its inertial axes, approximately parallel to the principal axes of the T tensor of the pyrene.

The principal axes of the ω tensor of the pyrene molecule are approximately coincident with the inertial axes, and show as expected that the mean square in-plane libration is very much greater than the out-of-plane rocking. On cooling from 298 to 178 K, the mean square librational amplitudes in the principal directions are approximately halved. This suggests that on cooling, the in-plane libration apparent from the electron-density synthesis is damped rather than frozen in, indicating a potential well, with an energy barrier much less than ***k****T* at 178 K. The libration of the tetracyanobenzene molecule is similarly reduced on cooling. The out-of-plane rocking motion is comparable to, but the in-plane libration is substantially less than that found for the pyrene. The thermal motion within the crystal is consistent with a large in-plane libration of the pyrene molecule, together with a co-operative translational and rocking motion of the complex as a whole. Specific-heat studies will give further information about the thermal motion and the probable phase-change at 171 K.

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[26] J. S. Rollett, 'Computing Methods in Crystallography,' Pergamon, Oxford, 1965, p. 66 ff.