

Molecular Complexes. Part XXI.¹ Crystal and Molecular Structure of Pyrene-1,3,5-Trinitrobenzene

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Crystals of the title 1:1 molecular complex are triclinic, $a = 6.77$, $b = 16.35$, $c = 8.55$ Å, $\alpha = 93.0$, $\beta = 101.3$, $\gamma = 95.6^\circ$, space group $P\bar{1}$, $Z = 2$. The structure has been determined by direct methods from diffractometer data with a novel modification of the $|E|$ values and refined by least-squares to R 0.094 for 3232 reflections. The dimensions of the component molecules have been corrected for rigid-body thermal motion and are in agreement with those from previous work. The mode of donor-acceptor overlap of the molecules in the alternate plane-to-plane stacks parallel to the a axis of the crystal gives near maximisation of the donor-acceptor charge-transfer interaction.

CONTINUING our investigations into the structures of π - π^* electron-donor-acceptor complexes of pyrene^{2,3} the crystal and molecular structure of a 1:1 molecular complex between pyrene and 1,3,5-trinitrobenzene has been determined.

EXPERIMENTAL

Preparation.—Laboratory-grade trinitrobenzene was recrystallised from ethanol. The complex was prepared as

¹ Part XX, I. J. Tickle and C. K. Prout, preceding paper.

² Part XVI, I. J. Tickle and C. K. Prout, *J.C.S. Perkin II*, 1973, 528.

large orange needles by slow evaporation of an equimolar solution of pyrene and trinitrobenzene in ethanol.

Crystal Data.— $C_{22}H_{13}N_3O_6$, $M = 415.4$. Triclinic, $a = 6.77 \pm 0.01$, $b = 16.35 \pm 0.01$, $c = 8.55 \pm 0.01$ Å, $\alpha = 93.0 \pm 0.1$, $\beta = 101.3 \pm 0.1$, $\gamma = 95.6 \pm 0.1^\circ$, $U = 921.7$ Å³, $D_m = 1.49$ (by flotation), $Z = 2$, $D_c = 1.50$. Space group $P\bar{1}$ (C_1^1 , No. 2). Cu- K_α radiation, $\lambda = 1.5418$ Å, $\mu = 9.4$ cm⁻¹. Crystal size $0.45 \times 0.45 \times 0.25$ mm.

Unit-cell dimensions were measured and three-dimensional intensity data collected on a Hilger and Watts four-circle diffractometer with an ω -2 θ scan. Balanced filters were

³ Part XV, I. J. Tickle and C. K. Prout, *J.C.S. Perkin II*, 1973, 523.

used for $\theta < 25^\circ$. There was no significant drift in the intensities of the reference reflections during data collection. 3614 independent reflections were observed with $\theta < 75^\circ$, of which 3239 were taken as significantly (3σ) above background. Lorentz, polarisation, and an empirical absorption correction were applied.⁴

The normalised structure amplitudes $|E|$ were computed and had a distribution that corresponded to that of a hypercentrosymmetric crystal ($\langle |E| \rangle$, 0.69; $\langle |E^2 - 1| \rangle$, 1.201; $\%|E| > 1$, 23.4; $\%|E| > 2$, 6.2; $\%|E| > 3$, 1.40; all for $\langle |E^2| \rangle$ scaled to unity). All attempts to solve the structure by direct methods with unmodified $|E|$ values failed. The sharpened Patterson function indicated that the planes of all the molecules in the unit cell were parallel and coincided with the rational plane (4, $\bar{1}$, $\bar{1}$) and it was sought to derive a trial structure by a method analogous to that used in ref. 1. The locations of the centres of the two molecules were determined correctly and six feasible models set up. While these models were being tested the structure was solved by direct methods in the following manner. The reciprocal lattice, weighted according to normalised structure amplitude, showed an interference fringe bounded approximately by planes for which $4h-k-l = \pm 4$ and containing very few E values > 1 . This was crossed by several less obvious fringes. These fringes arise from the regular repeating nature of the contents of the unit cell. It was thought possible that some modification functions applied to the E values might compensate for the non-random distribution. Several functions based on the value of the scalar product $A = 4h-k-l$, between the diffraction vector and the vector normal to the molecular plane were tried and the function $f = 1 - \sin(\pi A/9)/(\pi A/9)$ which represents a damped oscillation (Bessel function) reducing those E values within the major interference fringe led to a correct solution which was one of the possible models deduced from the Patterson function.

In a symbolic-addition⁵ calculation on the modified E values, 380 reflections were signed, compared with 450 for the unmodified data, and the fifth solution in order of probability gave an interpretable E map. The low probability of the correct solution arises because there is a strong indication that the first symbolic reflection (2,0,0) is positive whereas it is actually negative. This is related to the fact that the (4, $\bar{1}$, $\bar{1}$) planes of the Patterson function are close to the (2,0,0) planes, whereas in real space alternate (4, $\bar{1}$, $\bar{1}$) planes contain atoms and these interleave the (2,0,0) planes giving a phase difference of π .

It was later found that 23 E values had been incorrectly signed, compared with 87 for the original data, so that the effect of the modification was to remove a large number of incorrectly signed reflections. Unfortunately the method described does not appear to be generally useful for systems containing co-planar planar molecules. Attempts to apply the method to 8-hydroxyquinoline-trinitrobenzene⁶ and acenaphthene-tetracyanoquinodimethane¹ were unsuccessful. In neither case, however, are there interference fringes in the weighted reciprocal lattice parallel to the molecular planes.

The atomic co-ordinates derived from the E map were first refined with isotropic temperature factors, unit weights,

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

⁴ A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Cryst.*, 1968, *A*, **24**, 351.

⁵ J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

and a three-block approximation to the normal matrix. Then followed anisotropic refinement for which the normal matrix was subdivided into five blocks, one for the scale factor and overall U_{iso} , and two each for the pyrene and trinitrobenzene space and thermal parameters. Two cycles were computed with unit weights and two further cycles with the weighting scheme $w = |1 + (F_o/p)^2|^{-1}$, where $p = 3.9$.

Examination of a number of intense reflections (> 34) with $\theta < 18^\circ$ and poor agreement between F_o and F_c revealed a systematic correlation between the ratio $r = |F_o|/|F_c|$ and the measured integrated count, I . The correlation is approximately represented by $r = 1 - gI$ where g is a constant (0.46×10^{-6}). Even for the highest count observed, 1.46×10^6 , [(200), peak height 0.175×10^6 c.p.s.; $|F_o|$, 76.4; $|F_c|$, 205.2, $r = 0.37$] the dead-time correction for the counter could not account for $r < 0.8$. Therefore the effect must be attributed largely to secondary extinction, despite the large numbers of reflections (*ca.* 50) involved. The reflections were given zero weight in the subsequent refinement.

After a further cycle, a difference-Fourier synthesis was computed and the hydrogen atoms were located and included. Further refinement was attempted with a weighting scheme according to ref. 7 (individual weights) but this was unsatisfactory and the previous weighting scheme with $p = 7.5$ was re-applied. After four more cycles the refinement converged with R 0.094 for 3239 reflections. In the final difference-Fourier synthesis the estimated standard deviation of the electron density was $0.2 \text{ e } \text{ \AA}^{-3}$ and all peaks and troughs were within $\pm 2.5\sigma$.

The observed structure amplitudes and structure factors calculated from the final atomic co-ordinates in Table 1 are given in Supplementary Publication No. SUP 20632 (18 pp., 1 microfiche).^{*} The estimated standard deviations in Table 1 were obtained from the inverse of the normal matrix. Rollett's NOVTAPE system as modified by Hodder and Rollett and Ford's ALGOL system were used for calculations. Atomic scattering factors were those for neutral atoms from ref. 8.

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, centres of libration, which do not necessarily coincide with the molecular centroids, and deviations from the weighted least-squares best planes are shown in Figure 2 for both component molecules. In the case of trinitrobenzene the assumption of rigid-body motion is probably not entirely justified since the nitro-groups undoubtedly undergo libration about the C-N bonds. The in-plane libration of the pyrene molecule is much greater, presumably because the trinitrobenzene molecules are constrained by dipole-dipole interactions. Bond lengths corrected for libration are shown in Table 3.

The dimensions of the trinitrobenzene agree well with

⁶ E. E. Castellano and C. K. Prout, *J. Chem. Soc. (A)*, 1971, 550.

⁷ D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Cryst.*, 1969, *B*, **25**, 374.

⁸ 'International Table 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 atoms 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)	0.7284(3)	0.8416(1)	0.2051(2)	0.0486(8)	0.0496(8)	0.0536(8)	0.0148(13)	0.0310(13)	0.0187(13)
C(2)	0.7731(2)	0.8461(1)	0.3692(2)	0.0427(8)	0.0536(8)	0.0554(9)	0.0007(13)	0.0267(13)	0.0124(13)
C(3)	0.7820(2)	0.7724(1)	0.4414(2)	0.0393(7)	0.0610(9)	0.0478(7)	0.0091(13)	0.0160(11)	0.0114(12)
C(4)	0.7501(2)	0.6966(1)	0.3549(2)	0.0389(7)	0.0519(8)	0.0607(9)	0.0192(14)	0.0190(13)	0.0086(12)
C(5)	0.7081(2)	0.6968(1)	0.1912(2)	0.0419(7)	0.0477(8)	0.0565(9)	-0.0047(13)	0.0242(13)	0.0059(12)
C(6)	0.6952(3)	0.7677(1)	0.1112(2)	0.0494(8)	0.0558(9)	0.0481(8)	0.0088(13)	0.0249(13)	0.0144(13)
N(1)	0.7164(3)	0.9185(1)	0.1225(2)	0.0757(10)	0.0576(9)	0.0683(10)	0.0343(14)	0.0507(16)	0.0327(15)
N(2)	0.8276(2)	0.7740(1)	0.6170(2)	0.0510(8)	0.0808(11)	0.0510(8)	0.0129(15)	0.0083(12)	0.0168(14)
N(3)	0.6750(2)	0.6176(1)	0.0938(2)	0.0534(8)	0.0508(8)	0.0733(10)	-0.0115(14)	0.0310(14)	0.0041(12)
O(1)	0.6605(4)	0.9125(1)	-0.0212(2)	0.1536(18)	0.0801(11)	0.0664(9)	0.0515(16)	0.0556(21)	0.0501(23)
O(2)	0.7612(3)	0.9835(1)	0.2045(2)	0.1105(13)	0.0494(7)	0.0956(11)	0.0154(15)	0.0482(20)	0.0245(16)
O(3)	0.8624(3)	0.8408(1)	0.6913(2)	0.1063(13)	0.0969(12)	0.0552(8)	-0.0219(16)	0.0059(17)	0.0456(20)
O(4)	0.8296(3)	0.7093(1)	0.6784(2)	0.0940(12)	0.0998(12)	0.0603(8)	0.0551(17)	-0.0039(16)	-0.0041(19)
O(5)	0.7048(3)	0.5559(1)	0.1641(2)	0.0948(11)	0.0498(7)	0.1061(13)	-0.0022(15)	0.0379(19)	0.0053(15)
O(6)	0.6228(3)	0.6182(1)	-0.0503(2)	0.1074(13)	0.0758(10)	0.0686(9)	-0.0400(15)	0.0284(17)	0.0111(18)
C(7)	0.1679(3)	0.7470(2)	0.0275(2)	0.0538(10)	0.1127(18)	0.0406(8)	0.0007(19)	0.0121(14)	0.0110(21)
C(8)	0.2112(3)	0.8050(1)	0.1638(2)	0.0401(8)	0.0716(11)	0.0479(8)	0.0284(15)	0.0198(13)	0.0112(14)
C(9)	0.2177(4)	0.8911(2)	0.1506(4)	0.0587(11)	0.0830(15)	0.0955(16)	0.0899(26)	0.0442(21)	0.0240(20)
C(10)	0.2598(4)	0.9441(2)	0.2836(4)	0.0865(15)	0.0581(12)	0.1331(24)	0.0415(27)	0.0678(31)	0.0109(21)
C(11)	0.2955(3)	0.9158(1)	0.4333(4)	0.0612(12)	0.0560(11)	0.1141(20)	-0.0515(23)	0.0521(24)	-0.0120(18)
C(12)	0.2918(3)	0.8319(1)	0.4535(2)	0.0415(8)	0.0613(10)	0.0553(9)	-0.0205(15)	0.0221(13)	0.0004(14)
C(13)	0.3313(3)	0.8003(2)	0.6089(2)	0.0595(11)	0.1110(18)	0.0407(8)	-0.0255(19)	0.0209(15)	0.0085(21)
C(14)	0.2497(2)	0.7747(1)	0.3172(2)	0.0336(7)	0.0474(8)	0.0442(7)	0.0036(12)	0.0191(11)	0.0061(11)
C(15)	0.3272(4)	0.7192(2)	0.6250(3)	0.0625(12)	0.1389(23)	0.0457(9)	0.0526(23)	0.0282(17)	0.0416(26)
C(16)	0.2849(3)	0.6601(1)	0.4904(3)	0.0502(10)	0.0764(12)	0.0770(13)	0.0648(21)	0.0368(18)	0.0296(17)
C(17)	0.2814(5)	0.5740(2)	0.5006(5)	0.0911(18)	0.0924(19)	0.1411(27)	0.1372(39)	0.0665(36)	0.0645(31)
C(18)	0.2452(6)	0.5212(2)	0.3682(7)	0.0991(21)	0.0545(14)	0.2228(50)	0.0618(40)	0.0850(51)	0.0410(27)
C(19)	0.2067(4)	0.5496(2)	0.2161(5)	0.0729(15)	0.0574(12)	0.1593(30)	-0.0454(30)	0.0491(32)	0.0189(21)
C(20)	0.2049(3)	0.6332(1)	0.1965(3)	0.0411(8)	0.0588(10)	0.0889(14)	-0.0392(19)	0.0336(17)	0.0054(14)
C(21)	0.1642(3)	0.6671(2)	0.0409(3)	0.0527(10)	0.1075(18)	0.0537(10)	-0.0639(21)	0.0163(16)	0.0024(20)
C(22)	0.2462(2)	0.6895(1)	0.3355(2)	0.0345(7)	0.0479(8)	0.0575(9)	0.0097(13)	0.0243(12)	0.0120(12)

	x/a	y/b	z/c	U_{iso}		x/a	y/b	z/c	U_{iso}
H(2)	0.805(4)	0.900(2)	0.439(3)	0.050(7)	H(13)	0.370(6)	0.834(3)	0.694(5)	0.097(13)
H(4)	0.758(3)	0.653(1)	0.400(3)	0.037(6)	H(15)	0.351(6)	0.691(2)	0.723(5)	0.087(10)
H(6)	0.684(4)	0.766(2)	0.002(4)	0.054(8)	H(17)	0.311(5)	0.569(2)	0.604(5)	0.083(11)
H(7)	0.134(5)	0.770(2)	-0.087(4)	0.073(9)	H(18)	0.281(8)	0.460(3)	0.329(7)	0.151(19)
H(9)	0.182(6)	0.903(2)	0.037(5)	0.088(11)	H(19)	0.178(6)	0.519(3)	0.106(5)	0.091(11)
H(10)	0.259(7)	1.005(3)	0.294(6)	0.118(15)	H(21)	0.137(4)	0.628(2)	-0.049(3)	0.051(7)
H(11)	0.346(4)	0.949(2)	0.548(4)	0.059(7)					

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

TABLE 2

Analysis of rigid-body thermal motion

Principal axes	Directional cosines relative to:					
	Inertial axes			Orthogonal crystal axes		
(a) Pyrene						
T Tensor/ \AA^2						
0.0512(11)	0.999	0.025	-0.031	0.093	-0.988	0.124
0.0387(13)	-0.027	0.995	-0.094	0.100	0.133	0.986
0.0292(22)	0.028	0.095	0.995	-0.991	-0.080	0.111
ω Tensor/deg. ²						
11(1)	0.774	0.631	0.049	0.004	-0.708	0.706
15(1)	-0.630	0.776	-0.029	-0.004	0.706	0.708
37(1)	-0.056	-0.008	0.998	-1.000	-0.006	0.000
(b) Trinitrobenzene						
T Tensor/ \AA^2						
0.050(2)	0.997	0.034	0.065	-0.047	-0.080	0.996
0.049(2)	-0.034	0.999	-0.005	-0.045	0.996	0.078
0.026(4)	-0.065	0.003	0.998	-0.998	-0.041	-0.051
ω Tensor/deg. ²						
17(2)	0.874	-0.402	0.274	-0.236	-0.509	0.828
26(2)	0.386	0.916	0.110	-0.148	0.861	0.487
13(1)	-0.295	0.010	0.956	-0.960	-0.007	-0.279

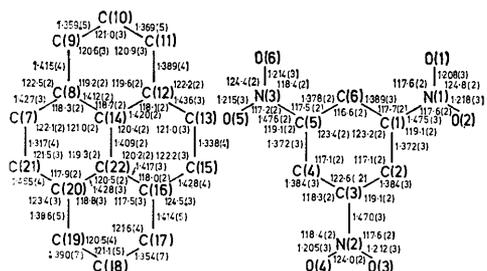


FIGURE 1 Interatomic distances (Å) before libration correction and interbond angles (deg.) with standard deviations in parentheses

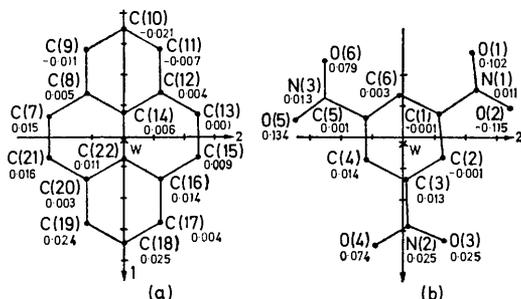


FIGURE 2 Molecular inertial axes of (a) pyrene and (b) trinitrobenzene showing the centres of libration *w* and deviations from the mean molecular planes

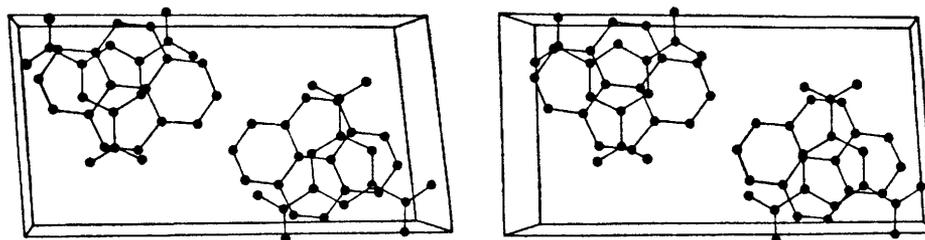


FIGURE 3 Stereoscopic view of the crystal-packing (along the *a* axis)

those from previous determinations.^{6,9,10} The nitro-groups are twisted out of the mean plane in typical fashion; the angles between the NO₂ planes and the plane of the benzene nucleus are 6.0, 2.6, and 6.3°.

TABLE 3

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

(a) Pyrene	(b) Trinitrobenzene	
C(7)–C(8)	C(1)–C(2)	1.379
C(7)–C(21)	C(1)–C(6)	1.396
C(8)–C(9)	C(1)–N(1)	1.480
C(8)–C(14)	C(2)–C(3)	1.391
C(9)–C(10)	C(3)–C(4)	1.391
C(10)–C(11)	C(3)–N(2)	1.475
C(11)–C(12)	C(4)–C(5)	1.379
C(12)–C(13)	C(5)–C(6)	1.384
C(12)–C(14)	C(5)–N(3)	1.480
C(13)–C(15)	N(1)–O(1)	1.212
C(14)–C(22)	N(1)–O(2)	1.222
C(15)–C(16)	N(2)–O(3)	1.216
C(16)–C(17)	N(2)–O(4)	1.209
C(16)–C(22)	N(3)–O(5)	1.218
C(17)–C(18)	N(3)–O(6)	1.218
C(18)–C(19)		
C(19)–C(20)		
C(20)–C(21)		
C(20)–C(22)		

There are no significantly short oxygen–oxygen intermolecular contacts, the shortest being O(3) ··· O(1) 3.26, and O(4) ··· O(6) 3.28 Å (the second atom in each case is in the molecule displaced by unit translation along the +*z* axis). The dimensions of the pyrene molecule are somewhat anomalous; in particular the bonds C(9)–C(10) (1.365) and C(17)–C(18) (1.359 Å) are too short, but it may be that the libration corrections for these outermost atoms have been underestimated.

Figure 3 shows a stereoscopic projection of the unit cell. The structure consists of stacks of alternate donor and acceptor components with the stacking axis parallel to the crystallographic *a* axis. The planes of all the molecules are parallel; the angle between the normals of the pyrene and trinitrobenzene is 0.5° and the separation within a stack is 3.38 Å. Since the molecules are in general positions the overlap orientation between any particular molecule and the two adjacent molecules are slightly different (Figure 4).

There is a region near the centre-on-centre position in which stabilisation is maximised and the observed orientations lie in this region, with an energy of almost 100% of the maximum. The centre-on-centre orientation has a stabilisation of *ca.* 95% of the maximum.¹¹ The energy depends mainly on the relative positions of

the centroids of the component molecules and is not very sensitive to rotation of one component relative to the other.

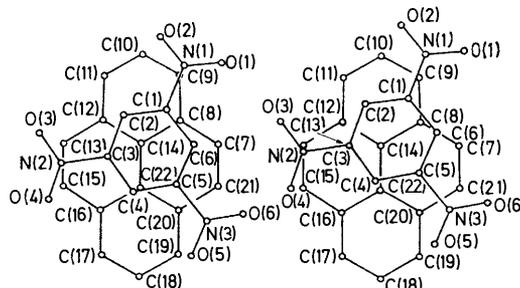


FIGURE 4 Projection of the 1,3,5-trinitrobenzene on the least-squares best plane of the pyrene molecule at (a) *x, y, z* and (b) 1 + *x, y, z*

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¹⁰ Chang Sun Choi and J. E. Abel, *Acta Cryst.*, 1972, **B**, **28**, 193.

¹¹ B. Mayoh and C. K. Prout, *J.C.S. Faraday II*, 1972, 1072.