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## X-ray Diffraction Study of the Crystal Structure of the $\pi$ -Molecular Compound Pyrene · Pyromellitic Dianhydride at 19 K

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### Abstract

The crystal structure of the pyrene · pyromellitic dianhydride (PMDA)  $\pi$ -molecular compound [(C<sub>16</sub>H<sub>10</sub>:C<sub>10</sub>H<sub>2</sub>O<sub>6</sub>); PYRPMA] has been refined from intensities measured at 19 K using the low-temperature accessory designed by Samson, Goldish & Dick [*J. Appl. Cryst.* (1980), **13**, 425–432] for a four-circle diffractometer. Earlier results for the ordered structure [Herbstein & Snyman (1969). *Philos. Trans. R. Soc. London Ser. A*, **264**, 635–666] are confirmed and extended; at 19 K,  $a = 13.664(3)$ ,  $b = 9.281(2)$ ,  $c = 14.420(3)$  Å,  $\beta = 91.80(2)^\circ$ , space group  $P2_1/n$ ,  $Z = 4$ , with two sets of pyrenes at independent centres of symmetry and the four PMDAs at general positions. The geometrical structures of the two components are in good agreement with quantum mechanical calculations. Analyses of thermal motion and packing show that one set of pyrenes is more

tightly packed than the other; the principal interactions in the crystal are  $\pi$ - $\pi^*$  plane-to-plane interactions between pyrene and PMDA and  $>CH \cdots O=C<$ , between pyrene and PMDA, and between PMDAs.

### 1. Introduction

The mixed-stack  $\pi$ - $\pi^*$  charge-transfer molecular compound pyrene · pyromellitic dianhydride (PMDA) [(C<sub>16</sub>H<sub>10</sub>:C<sub>10</sub>H<sub>2</sub>O<sub>6</sub>); Refcode PYRPMA] undergoes a dis-order-to-order transition at  $\sim 160$  K. Earlier (photographic) X-ray studies (Herbstein & Snyman, 1969) showed that the space group was  $P2_1/a$  ( $Z = 2$ ) above  $\sim 160$  K, with pyrenes and PMDAs at independent centres of symmetry [present measurements give  $a = 13.94(1)$ ,  $b = 9.34(1)$ ,  $c = 7.31(1)$  Å,  $\beta = 93.65(9)^\circ$  at 295 K]. Below  $\sim 160$  K, the  $c$  axis was found to be doubled and the space group changed to  $P2_1/n$  ( $Z = 4$ ), with two pairs of pyrenes at independent centres and the four PMDA molecules in the cell at general

† Experimental work performed while on sabbatical leave at Caltech.

positions, but only slightly displaced from their 295 K positions [present measurements give  $a = 13.664(3)$ ,  $b = 9.281(2)$ ,  $c = 14.420(3)$  Å,  $\beta = 91.80(2)^\circ$  at 19 K]. The transition is single crystal-to-single crystal, with the conservation of axial directions. This enabled us to carry out a refinement of the ordered low-temperature structure, the crystal being held at 19 K (the lowest temperature attainable) in the low-temperature accessory designed by Samson, Goldish & Dick (1980) for a four-circle diffractometer.

The crystal structure of PYRPMA at 295 K has been refined by Allen, Boeyens & Levendis (1989) and described in terms of a model in which the pyrenes are statically disordered over three orientations. The disorder-to-order transition is discussed in a companion paper (Herbstein & Samson, 1994).

## 2. The crystal and molecular structure of PYRPMA at 19 K

### 2.1. Experimental

2.1.1. *General.* Crystals (bright red in colour, elongated along [001] and showing {100} and {110}) were grown from butan-2-one (dried over  $\text{CaCl}_2$ ). After preliminary oscillation and Weissenberg photography (Ni-filtered  $\text{Cu K}\alpha$ ), all measurements were made using a modified Syntex  $P\bar{1}$  four-circle diffractometer (graphite-monochromated  $\text{Mo K}\alpha$ ,  $\langle \lambda \rangle = 0.71069$  Å). The crystal temperature was stable to within 1–2 K at 19 K. One crystal (approximately a cube of 0.3 mm edge) was used for measurements of intensities at 295 K and cell dimensions down to 100 K; it then split and was discarded. A second crystal (same shape as the first but about half its volume) was used for all other measurements.

2.1.2. *Cell dimensions.* These were measured at 19 K using the auto-centring program of the diffractometer based on nine strong reflections in the region  $17 < 2\theta < 25^\circ$ . These results were checked with more precise measurements (slower scan speed, additional reflections, including some at higher angles). The agreement was satisfactory.

2.1.3. *Intensities.* These were measured at 295, 232, 172, 137, 85 and 19 K by the  $\omega/2\theta$  method using a constant angular velocity of  $2^\circ 2\theta \text{ min}^{-1}$ ; background was counted at each extremity ( $2\theta_{K\alpha 1} - 1^\circ$  and  $2\theta_{K\alpha 2} + 1^\circ$ ) for half the scan time. Standard reflections (200,  $0\bar{2}0$ , 004,  $4\bar{4}1$ ,  $5\bar{2}1$ ,  $1\bar{3}1$ ) showed no variation beyond statistical variation over the whole measurement period, during which the crystals were cooled from 295 to 19 K and then returned to 295 K. In all, some 25 000 reflection intensities were measured. Intensities were processed by standard programs to give  $F_o^2$  values and associated weights ( $w = 1/\text{var } F_o^2$ ). Absorption corrections were not applied because of the small size of the crystals used [ $\mu(\text{Mo K}\alpha) = 0.26 \text{ mm}^{-1}$ ;  $(\mu R)_{\text{max}} \simeq 0.08$ ].

We give here details only for the 19 K measurements.\* After reduction, the structure factors of 6643 reflections were obtained (maximum  $\sin\theta/\lambda = 0.7560 \text{ \AA}^{-1}$ ;  $2\theta_{\text{max}} = 65^\circ$ ); 5796 had  $I_{\text{obs}} > 0$  and 3363 had  $F_o^2 > 3\sigma(F_o^2)$ .

2.1.4. *Determination of 19 K crystal structure.* The parameters determined for the ordered structure in 1969 were used as starting points for the refinement of the 19 K structure [CRYM system, full-matrix least squares on  $F_o^2$ , using experimental weights (see Sherfinski & Marsh, 1973, for details)]. Interim convergence was decreed when the largest shift (for a H atom) was  $0.05\sigma$ . At this stage,  $R = 0.123$  for the 5796 positive reflections (goodness-of-fit of 1.41) and for the 3361 reflections with  $F_o^2 > 3\sigma(F_o^2)$   $R = 0.072$ . Difference syntheses in the molecular planes calculated at this stage were rather noisy and the structure was refined further as follows. Keeping hydrogen, extinction and scale parameters fixed, refinement was performed using reflections with  $\sin^2\theta/\lambda^2 > 0.15 \text{ \AA}^{-2}$ . The parameters fixed previously were then refined using reflections with  $\sin^2\theta/\lambda^2 < 0.2 \text{ \AA}^{-2}$ . This was followed by one more cycle based on the high-angle data. Maximum  $\Delta/\sigma$  for the final refinement cycle was less than 0.01. Difference maps in the molecular planes calculated for reflections with  $\sin^2\theta/\lambda^2 < 0.2 \text{ \AA}^{-2}$  showed electron densities of  $\sim 0.3 \text{ e \AA}^{-3}$  near the centres of the bonds and similar negative values at the centres of the six-membered rings; there were also some indications of lone-pair density at the O atoms of the PMDAs. The appearance of these maps indicated that the quality of the intensity measurements would not justify further refinement. The final  $R$  and goodness-of-fit values were hardly changed from the values given above. Atomic parameters are in Table 1 (numbering of atoms shown in Fig. 1). Neglect of the difference-synthesis features presumably partially accounts for the unexpectedly high values of the  $R$  factors, even at 19 K.

### 2.2. Molecular structures of pyrene and PMDA at 19 K

Molecular dimensions for the two crystallographically independent pyrenes are shown in Fig. 1. The averaged bond lengths for pyrene in PYRPMA (m.p. 551 K) at 19 K and in  $\alpha$ -pyrene (m.p. 423 K) at 113 K (Kai, Hama, Yasuoka & Kasai, 1978) are not significantly different (Table 2). The e.s.d.s of individual bond lengths ( $\simeq 0.004$  Å) are too large for effects of temperature or complexation to be discernible. There is also good agreement with MINDO-3 calculations (Apeloig & Danovich,

\* Lists of observed and calculated structure factors and anisotropic thermal parameters, and a comparison of bond lengths and angles and details of data collection and refinement have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71565 (30 pp.). Copies may be obtained through the Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH0039]

Table 1. Atomic parameters for the 19 K structure

The values of  $U_{eq}$  (units of  $10^{-4} \text{ \AA}^2$ ) were calculated following Fischer & Tillmanns (1988) and their e.s.d.'s following the isotropic and orthic approximation of Schomaker & Marsh (1983).

(a) Atomic parameters for pyrene I (e.s.d.'s in parentheses in units of the last significant figure)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
C(A)	0.1761 (2)	0.0129 (3)	0.0656 (2)	94 (5)
C(B)	0.0979 (2)	0.1167 (3)	0.0562 (2)	87 (5)
C(C)	0.1091 (2)	0.2594 (3)	0.0875 (2)	98 (5)
C(D)	0.0310 (2)	0.3567 (3)	0.0794 (2)	103 (5)
C(E)	-0.0587 (2)	0.3134 (3)	0.0397 (2)	101 (5)
C(F)	-0.0724 (2)	0.1728 (3)	0.0069 (2)	91 (5)
C(G)	-0.1637 (2)	0.1253 (3)	-0.0355 (2)	94 (5)
C(H)	0.0063 (2)	0.0726 (3)	0.0156 (2)	89 (5)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{iso}$ ( $\text{\AA}^2$ )
H(CA)	0.2370 (21)	0.0460 (33)	0.0951 (23)	1.2 (8)
H(CC)	0.1712 (22)	0.2950 (33)	0.1174 (22)	1.2 (8)
H(CD)	0.0375 (20)	0.4568 (31)	0.1003 (21)	0.1 (7)
H(CE)	-0.1124 (22)	0.3844 (36)	0.0362 (23)	1.9 (9)
H(CG)	-0.2179 (21)	0.1965 (32)	-0.0443 (22)	1.0 (8)

(b) Atomic parameters for pyrene II (e.s.d.'s in parentheses in units of the last significant figure)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
C(I)	0.1786 (2)	-0.0475 (3)	0.5496 (2)	108 (5)
C(J)	0.1168 (2)	0.0780 (3)	0.5518 (2)	88 (5)
C(K)	0.1499 (2)	0.2106 (3)	0.5880 (2)	106 (5)
C(L)	0.0877 (2)	0.3299 (3)	0.5904 (2)	110 (5)
C(M)	-0.0091 (2)	0.3202 (3)	0.5573 (2)	106 (5)
C(N)	-0.0453 (2)	0.1895 (3)	0.5204 (2)	95 (5)
C(O)	-0.1445 (2)	0.1749 (3)	0.4852 (2)	105 (5)
C(P)	0.0175 (2)	0.0673 (3)	0.5175 (2)	84 (5)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{iso}$ ( $\text{\AA}^2$ )
H(CI)	0.2455 (23)	-0.0432 (34)	0.5731 (24)	1.8 (8)
H(CK)	0.2134 (22)	0.2169 (35)	0.6169 (23)	1.7 (8)
H(CL)	0.1121 (20)	0.4240 (32)	0.6154 (21)	0.4 (7)
H(CM)	-0.0527 (21)	0.4065 (34)	0.5591 (22)	0.9 (8)
H(CO)	-0.1862 (20)	0.2589 (30)	0.4852 (20)	0.1 (7)

(c) Atomic parameters for PMDA (e.s.d.'s in parentheses in units of the last significant figure)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
C(1)	0.1067 (2)	0.0277 (3)	0.2913 (2)	94 (5)
C(2)	0.0413 (2)	0.1423 (3)	0.2918 (2)	75 (5)
C(3)	0.0573 (2)	0.2928 (3)	0.3235 (2)	96 (5)
C(4)	-0.1033 (2)	0.2740 (3)	0.2709 (2)	94 (5)
C(5)	-0.0566 (2)	0.1313 (3)	0.2580 (2)	90 (5)
C(6)	-0.0960 (2)	0.0044 (3)	0.2215 (2)	96 (5)
C(7)	-0.0300 (2)	-0.1107 (3)	0.2212 (2)	80 (5)
C(8)	-0.0447 (2)	-0.2606 (3)	0.1870 (2)	95 (5)
C(9)	0.1135 (2)	-0.2428 (3)	0.2447 (2)	94 (5)
C(10)	0.0666 (2)	-0.0992 (3)	0.2551 (2)	85 (5)
O(1)	0.1273 (2)	0.3504 (2)	0.3564 (2)	126 (4)
O(2)	-0.0321 (2)	0.3664 (2)	0.3100 (2)	102 (4)
O(3)	-0.1844 (2)	0.3143 (3)	0.2546 (2)	122 (4)
O(4)	-0.1140 (2)	-0.3180 (3)	0.1515 (2)	124 (4)
O(5)	0.0440 (2)	-0.3345 (2)	0.2039 (2)	102 (4)
O(6)	0.1941 (2)	-0.2833 (2)	0.2658 (2)	122 (4)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{iso}$ ( $\text{\AA}^2$ )
H(1)	0.1766 (22)	0.0318 (33)	0.3132 (23)	1.3 (8)
H(6)	-0.1682 (22)	0.0008 (32)	0.1999 (22)	1.3 (8)

1990), especially if a small overall scaling factor is introduced.

The two pyrene molecules show similar deviations from planarity (Fig. 2), which can be described as a bending of the groups of three atoms, C, D and

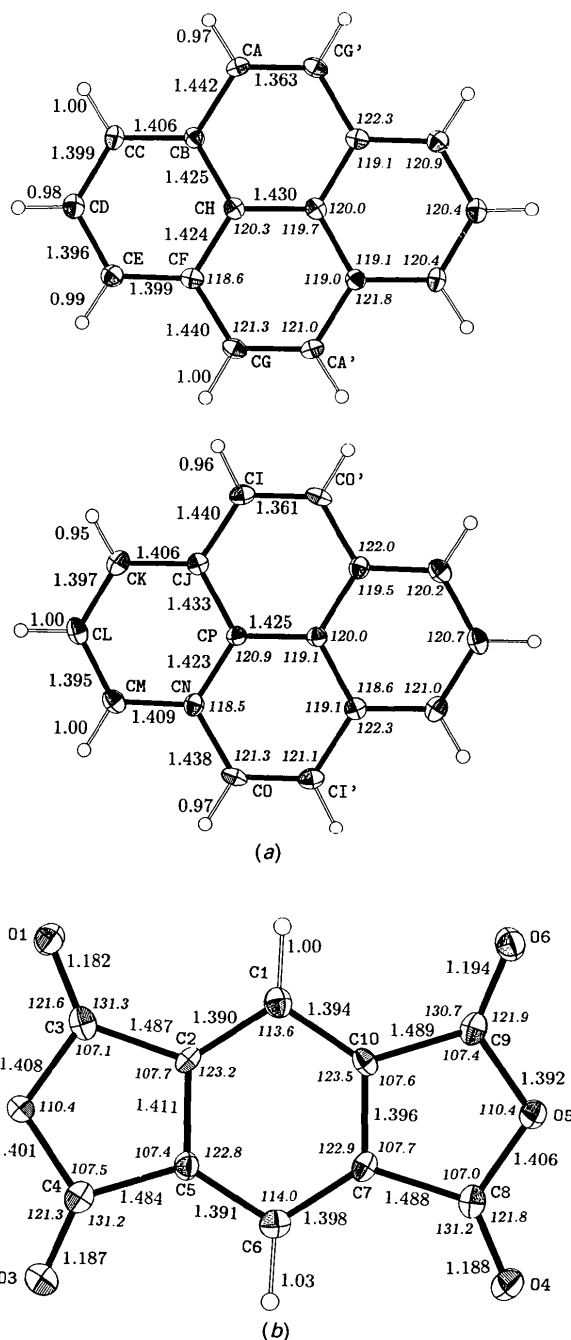


Fig. 1. Molecular nomenclature and detailed results of structure determination: (a) pyrenes I and II - atoms related by crystallographic centres are denoted A' etc.; (b) PMDA. H atoms are numbered as for the C atoms to which they are bonded. The thermal ellipsoids are drawn for 70% probabilities. The inertial systems of axes are defined in accordance with THMA11. Later diagrams giving molecular dimensions are oriented, and thus implicitly numbered, in the same way as the above diagrams. The e.s.d.s of bond lengths are  $\approx 0.004 \text{ \AA}$  and of bond angles  $0.3^\circ$ ; the deviations from the best molecular planes (based on all the atoms of each molecule) are in units of  $10^{-3} \text{ \AA}$ . The mean C—H distance (including the two PMDA values) is  $0.99 (2) \text{ \AA}$ . Librational corrections to C—C bond lengths are  $0.0006\text{--}9 \text{ \AA}$  and have not been included.

Table 2. Comparison of symmetry-averaged C—C bond lengths (Å) in pyrene assuming  $D_{2h}$ -mmm symmetry

The measured values have e.s.d.'s (of individual bond lengths) of  $\sim 0.004$  Å, and  $\sim 0.002$  Å for mean values. The MINDO-3 values in parentheses have been reduced by 1%.

Bond	Present work (at 19 K)*	Pyrene (at 113 K)†	MINDO-3 calculations‡
CD	1.397 (2)	1.387 (1)	1.403 (1.390)
CB	1.405 (4)	1.402 (2)	1.414 (1.401)
BH	1.426 (5)	1.422 (2)	1.436 (1.422)
BA	1.440 (2)	1.436 (1)	1.457 (1.443)
HH'	1.428 (4)	1.427 (—)	1.457 (1.443)
AG'	1.362 (1)	1.353 (0)	1.364 (1.351)

\* Averaged over the two independent molecules; values in parentheses are  $(n-1)$ -weighted sample e.s.d.'s.

† Kai *et al.*, (1978), averaged over one molecule; values in parentheses are  $(n-1)$ -weighted sample e.s.d.'s.

‡ Apeloig & Danovich (1990, unpublished).

*E* (and equivalents), out of the planes of the central 'naphthalene' portions of the molecules. In  $\alpha$ -pyrene, the molecule, which does not have crystallographically imposed symmetry, is slightly folded about the *BB'* line, with a dihedral angle of  $0.9^\circ$  between the best planes of these two 'naphthalene' portions. Thus, the deviations from planarity appear to be caused by intermolecular interactions and are not an inherent property of the pyrene molecule.

Molecular dimensions for PMDA at 19 K are shown in Fig. 1. Measured bond lengths and angles for PMDA in various crystal environments and temperatures are remarkably consistent; it is not possible to discern effects of temperature, complexation or intermolecular interactions at current levels of precision. The present symmetry-averaged 19 K values are compared (Table 3) with calculated values (Apeloig & Danovich, 1990; unpublished) and with the average of the measured values from the structures of PMDA itself (Aravamudhan, Haeberlen, Irgartinger & Krieger, 1979) and its 1:1 charge-transfer molecular compounds

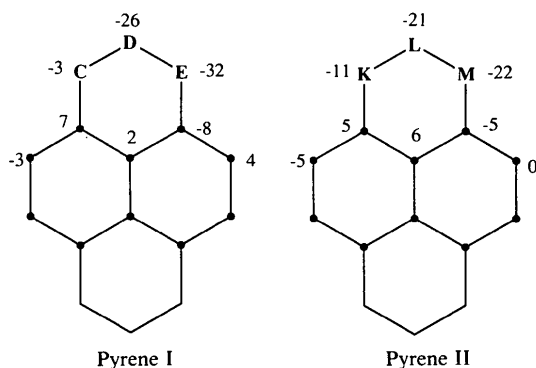


Fig. 2. Deviations (units of  $10^{-3}$  Å) from the best planes through the marked atoms of the two pyrene molecules.

Table 3. Symmetry-averaged C—C and C—O bond lengths (Å) and angles ( $^\circ$ ) of PMDA, assuming  $D_{2h}$ -mmm symmetry — comparison of present 19 K values with average values from other structure determinations (sample e.s.d.'s in parentheses)

Bond lengths	Present results (19 K)	Average values	MNDO (PMDA)	MNDO (maleic anhydride)
1—2	1.393 (4)	1.387 (5)	1.404	1.352
2—5	1.404 (11)	1.391 (6)	1.427	—
2—3	1.487 (2)	1.483 (4)	1.504	1.497
3—O(2)	1.402 (7)	1.395 (7)	1.389	1.409
3—O(1)	1.188 (5)	1.193 (4)	1.215	1.216
Bond angles				
10—1—2	113.8 (3)	114.1 (3)	115.7	—
1—2—5	123.1 (3)	123.0 (2)	122.1	—
5—2—3	107.6 (1)	107.5 (1)	106.5	107.5
2—3—O(1)	131.1 (3)	130.9 (2)	132.5	132.7
2—3—O(2)	107.3 (2)	107.5 (1)	108.1	108.0
3—O(2)—4	110.4 (0)	110.0 (2)	110.6	108.9

with anthracene at 153 K (Robertson & Stezowski, 1978), phenanthrene at 295 K (Evans & Robinson, 1977), acridine at 120 K (Karl, Binder, Kollat & Stezowski, 1982), phenazine at 120 K (Karl, Ketterer & Stezowski, 1982), tetracene at 295 K (Bulgarovskaya, Zavodnik & Vozzhennikov, 1987) and biphenylene at 120 K (both red and black polymorphs; Stezowski, Stigler & Karl, 1986). Details have been deposited (Table B).

The deviations of the atoms of PMDA from the best plane through the benzene ring are shown in Fig. 3. The molecule can be roughly described as having a small twist about the line joining the two furan O atoms.

The PMDA molecules in the various compounds show small but significant differences in deviations from planarity. The benzene rings are planar (indeed, astoundingly so, generally to better than  $0.001$  Å) but atoms of the anhydride portions of the molecules deviate from the benzene ring plane by up to  $0.09$  Å; the pattern varies from crystal to crystal, indicating that this is not an inherent molecular property (as Aravamudhan *et al.*, 1979, inferred) but a consequence of intermolecular interactions.

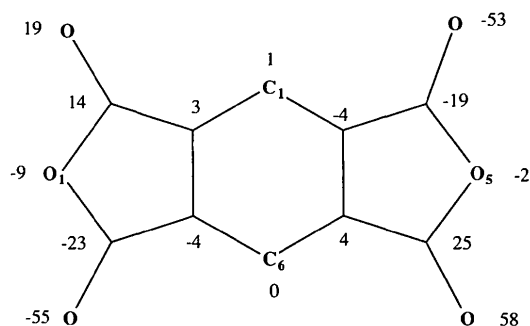


Fig. 3. Deviations (units of  $10^{-3}$  Å) from the best plane of the benzene ring in PMDA at 19 K.

The PMDA molecule can, to a good approximation, be considered to be made up of the fusion of a benzene ring and two maleic anhydride molecules (crystal structure of maleic anhydride by Marsh, Ubell & Wilcox, 1962); the dimensions are compared in Fig. 4. The fusion leads to distortion of the angles in the benzene ring from  $120^\circ$ , which was explained by Herbstein & Snyman (1969) in terms of a simple mechanical model; this feature and the canting of the carbonyl groups towards the furan O atom in both PMDA and MA ( $\angle C2-C3-O^I = 131$  and not  $125^\circ$ ) are both reproduced by quantum mechanics calculations.

We have found only one single-crystal structure analysis of an aromatic hydrocarbon at temperatures below 20 K which can be used for purposes of comparison - anthracene at 16 K by neutron diffraction (Chaplot, Lehner & Pawley, 1982). The  $R$  factor (before correction for multiple scattering) was 6.0% and the nominal e.s.d.s of bond lengths and bond angles are  $\sim 0.003 \text{ \AA}$  and  $0.1^\circ$ , respectively. The magnitudes of the  $U_{ij}$  values and their e.s.d.s are similar to those we have found.

### 2.3. Crystal structures of disordered and ordered phases

The molecular arrangements at 295 and 19 K are not appreciably different from those reported in 1969 and described above (see Figs. 3, 5, 6 and 7 of Herbstein & Snyman, 1969). The projection of the crystal structure down  $[010]$  is shown in Fig. 5, which also serves to introduce the following three figures. The arrangement of pyrenes about the  $(001)$  plane is shown in Fig. 6, that of the PMDAs about the  $(xy\frac{1}{4})$  section in Fig. 7 and that of pyrene I, PMDA and pyrene II about the  $(\bar{1}02)$  plane in Fig. 8; some geometric details are summarized in Table 4.

The packing of the pyrene molecules about the  $(001)$  plane is comparatively loose, with all non-bonded  $H \cdots H$  distances being, at least,  $\sim 0.2 \text{ \AA}$  longer than the van der Waals diameter of hydrogen ( $2.4 \text{ \AA}$ ). Using the facilities of *MacMoMo* (Dobler, 1989) we have rotated pyrene II about the axis ( $N$ ) normal to its plane and followed the changes in non-bonded  $H \cdots H$  distances, keeping the surrounding framework of pyrene I molecules unchanged. Only the boxed values in Fig. 6 change appreciably; the  $2.89 \text{ \AA}$  distance falls to  $2.38 \text{ \AA}$  when pyrene II is rotated

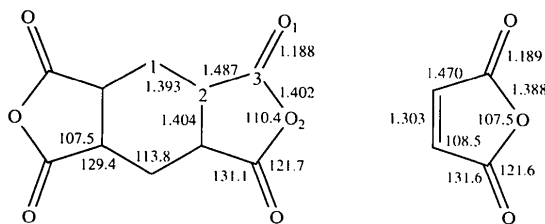


Fig. 4. Comparison of symmetry-averaged dimensions of PMDA ( $D_{2h}$ ) and maleic anhydride ( $C_{2v}$ ).

$12^\circ$  clockwise, while the  $2.61$  and  $3.05 \text{ \AA}$  distances fall to  $2.40 \text{ \AA}$  for  $10$  and  $14^\circ$  anticlockwise rotations. This 'hard-sphere rigid-framework' model is a simple substitute for more sophisticated packing-energy calculations such as have been carried out for the disordered phase of PYRPMA by Allen *et al.* (1989). Using values of  $1.7$  and  $1.2 \text{ \AA}$  for the van der Waals radii of O atoms and H atoms, respectively, one sees that the in-plane packing of the PMDA molecules is quite tight (Fig. 7). Thus, there is no difficulty in accounting for the absence of rotational disorder for the PMDA molecules, although

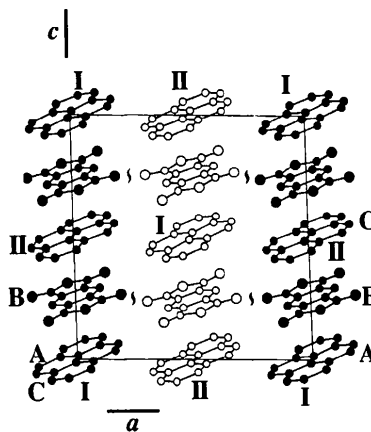


Fig. 5. Crystal structure of PYRPMA at 19 K, projected down  $[010]$  (adapted from Herbstein & Snyman, 1969). The two independent pyrene molecules are designated I and II; there is an  $n$ -glide plane at  $y = \frac{1}{4}$ . Section A-A ( $xy0$ ) is shown in Fig. 6, section B-B ( $xy\frac{1}{4}$ ) in Fig. 7 and section C-C ( $\bar{1}02$ ) in Fig. 8.

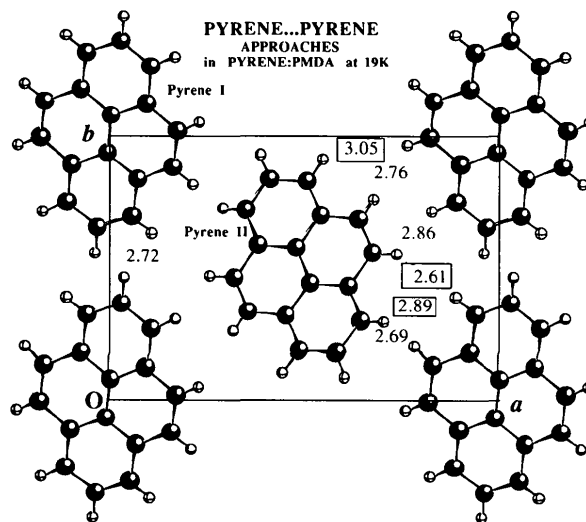


Fig. 6. Arrangement of the crystallographically independent pyrene molecules in the section of the unit cell about the plane  $(xy0)$  in the ordered structure at 19 K. Crystallographically independent distances of less than  $3.05 \text{ \AA}$  between non-bonded H atoms are shown. The significance of the boxed values is described in the text.

the reason for the small displacements of their centres from the  $x = 0, y = 0, z = \frac{1}{4}$  (and related) positions is not clear. The closest intermolecular distances are found between pyrene H atoms and PMDA O atoms in the  $(\bar{1}02)$  plane; in particular, we draw attention to the  $O \cdots H$  distance of 2.48 Å, which is appreciably smaller than the sum of the van der Waals radii. Thus, the ordering results from pyrene  $\cdots$  PMDA interactions, although the details of how the  $O \cdots H$  distances change with temperature are not clear. A decrease in long-range order with increasing temperature (Herbstein & Samson, 1994) would imply that some of the molecules

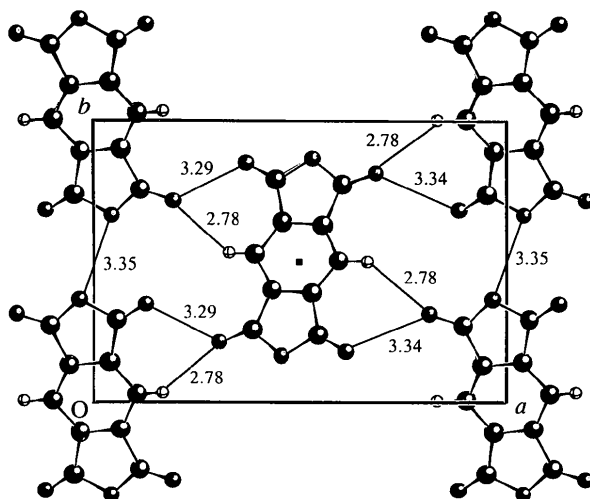


Fig. 7. Arrangement of the PMDA molecules in the section of the unit cell about the plane  $(xy)\frac{1}{4}$ , in the ordered structure at 19 K. Distances of less than 3.4 Å between non-bonded O atoms are shown, as well as the shortest  $O \cdots H$  distances.

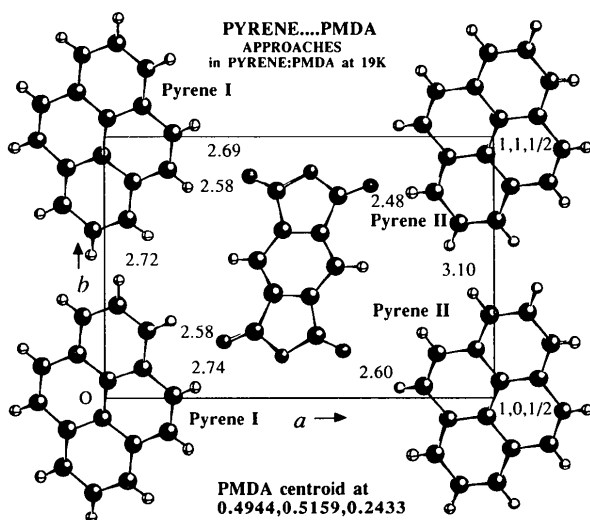


Fig. 8. Arrangement of pyrene I, PMDA and pyrene II molecules in the  $(\bar{1}02)$  plane.

Table 4. *Best planes for pyrene and PMDA molecules at 19 K, and their mutual orientation*

(i) Direction cosines ( $l, m, n$ ) of best planes in the orthogonal system $a, b, c^*$ , and distances from the origin [ $d$ (Å)]				
Molecule	$l$	$m$	$n$	$d$ (Å)
Pyrene I	-0.34871	-0.26964	0.89761	0
Pyrene II	-0.32363	-0.26724	0.90766	6.630
PMDA	-0.31547	-0.26728	0.91052	3.340

(ii) Mutual arrangement of molecules

Molecule I	Molecule II	Angle between best planes ( $^\circ$ )	Angle between $L$ axes ( $^\circ$ )
Pyrene I	Pyrene II	1.55	12.58
Pyrene I	PMDA	2.04	16.75
Pyrene II	PMDA	0.47	29.28

Notes: At 19 K, the centroid of PMDA is at  $x = 0.0056, y = 0.0159, z = 0.2567$  (fractional coordinates in the crystal system).

in pyrene I sites take up the pyrene II orientation, and conversely. We have checked, therefore, what happens to the close intermolecular distances when pyrene I is substituted for pyrene II, and conversely. Referring to Fig. 8, we have replaced the pyrene II molecules on the right-hand side of the diagram by pyrene I molecules; the closer  $O \cdots HC$  distances change (reading from the bottom to the top) from 2.60 to 3.05 Å, > 3.05 to 2.76 Å, 2.48 to 2.95 Å and > 3.05 to 2.85 Å; none of these new distances are too close. When the pyrene I molecules on the left of the diagram are replaced by pyrene II molecules, then (again reading from the bottom to the top) the closer  $O \cdots HC$  distances decrease from 2.58 to 2.16 Å and 2.58 to 2.27 Å; both these new distances are too close. These changes are only approximate because we have not allowed for any relaxation of orientations that may occur as a result of substitution. It seems that, at least in the first stages of the disordering process, the less tightly bound pyrene II molecules can be substituted by 'wrongly oriented' pyrene I molecules, but that the converse process is not possible. Presumably, this asymmetry disappears in the latter stages of the disordering process when both types of substitution become equally probable.

#### 2.4. Analysis of thermal motion at 19 K

The thermal motion has been analysed using the program *THMA11* (version of 15 April, 1987), assuming the molecules behave as rigid bodies (for a summary of recent developments in this area, see Dunitz, Maverick & Trueblood, 1988; Dunitz, Schomaker & Trueblood, 1988). The results of the thermal-motion analysis for the three molecules are summarized in Table 5.

Description of the thermal motion in terms of rigid-body motion is a surprisingly poor approximation. One indication comes from the  $R$  factors (in the Cartesian crystal frame) obtained from the observed and calculated (rigid-body) values of  $U_{ij}$ : 0.127 for pyrene I, 0.133 for pyrene II and 0.201 for PMDA. For comparison, we can note that for 1,2-dinitrobenzene at 298 K (Herbstein &

Table 5. *R.m.s. amplitudes of translation (Å) and libration (°) for pyrene I and II, and PMDA molecules*

The values are given in the inertial (molecular) frames (see Fig. 1 for definition).

(a) (Eigenvalues)<sup>1/2</sup> of L (°) and T (Å) in the inertial frame

	Pyrene I	Pyrene II	PMDA
T1	0.096	0.098	0.098
T2	0.092	0.089	0.094
T3	0.085	0.085	0.073
L1	1.27	1.49	1.41
L2	0.81	1.13	1.15
L3	0.11	0.52	0.80

(b) Angles (°) between the principal axes of translation and libration and the molecular axes (*L*, *M*, *N*) of the pyrene and PMDA molecules

	T1	T2	T3	L1	L2	L3
Pyrene I						
<i>L</i>	17	85	106	99	167	100
<i>M</i>	102	28	115	121	95	32
<i>N</i>	78	62	31	148	79	120
Pyrene II						
<i>L</i>	17	74	98	58	42	65
<i>M</i>	107	18	97	104	110	25
<i>N</i>	84	81	11	35	125	90
PMDA						
<i>L</i>	118	28	90	15	94	75
<i>M</i>	152	118	90	85	7	95
<i>N</i>	90	90	0	104	84	16

Notes: The screw components of PMDA were indistinguishable from zero; for the nine values of  $S(i, j)$ , the r.m.s. value of  $S/\sigma(S)$  was 1.08. The largest value, 0.00018 (8) rad Å, was for  $S(3, 1)$  (Cartesian system).

Kapon, 1990), the *R* value was 0.079 before correcting for torsional librations of the nitro groups and 0.043 after applying such corrections. The same impression is obtained by examining the  $\Delta_{A,B}$  ( $= z_{A,B}^2 - z_{B,A}^2$ ) values, where  $z_{A,B}^2$  is the mean-square displacement of atom *A* in the direction of *B*. For a rigid molecule  $\Delta_{A,B} = 0$ , while Hirshfeld (1976) has suggested that for pairs of bonded atoms as heavy as carbon,  $\Delta_{A,B}$  should be less than  $\sim 10$  (the units of  $\Delta_{A,B}$  are  $10^{-4} \text{Å}^2$ ) for intensity measurements of adequate quality. The mean value of  $\Delta_{A,B}$  for pyrene I is  $10.2 (8.8) \times 10^{-4} \text{Å}^2$ ,  $15.9 (9.6) \times 10^{-4} \text{Å}^2$  for pyrene II and  $31.2 (16.6) \times 10^{-4} \text{Å}^2$  for PMDA and the values in brackets are the population e.s.d.s; the e.s.d.s of the individual  $U_{ij}$  values are also  $\simeq 10$ . The individual  $\Delta_{A,B}$  values in the two pyrene molecules do not show a clear picture but those in PMDA (Fig. 9) suggest that the central benzene ring is rigid but not the two anhydride rings. It is pertinent to note that  $U_{ij}$  is about ten times larger than  $\sigma(U_{ij})$  for PYRPMMA at 19 K, while this ratio is about 40 for 1,2-dinitrobenzene at 298 K.

The values in Table 5 show a familiar picture on the basis of the rigid-body approximation – the translatory motion, which is of much the same magnitude for the three molecules, is fairly closely isotropic and thus the relationship of the principal axes of translation to the

molecular axes is not very precisely defined, whereas the librational motion is quite anisotropic and hence better defined orientationally.

The orientational relationships between librational and molecular axes are not all simple. As pyrene approximates to a circular disk, the in-plane relationships between librational and molecular axes cannot be expected to be well defined. For pyrenes I and II, *L*1, the largest librational amplitude, is roughly about *N*, the normal to the molecular plane, as might be expected. PMDA is anisotropic enough for well-defined relationships to be expected and these are found. The largest librational amplitude is roughly about the long molecular axis *L* (the axis of least inertia) and the smallest about *N*. Presumably, the motion being seen here at 19 K is essentially zero-point motion of the molecules, while at higher temperatures the disorder contribution (to the apparent overall thermal motion) will become increasingly important, and more difficult to disentangle from the true thermal motion.

The librational amplitudes are similar for pyrene II and PMDA, with those for pyrene I somewhat smaller. This confirms that pyrene II is the less tightly bound of the pyrenes, as noted above from the analysis of intermolecular distances.

### 3. Intermolecular cohesion

One major source of intercomponent cohesion is the  $\pi$ - $\pi^*$  interaction between the HOMO of the pyrene molecules and the LUMO of the PMDAs. This is shown by the interplanar distances of *ca* 3.33 and 3.29 Å between pyrenes and PMDAs (Table 2). This is appreciably smaller than the interplanar distance in  $\alpha$ -pyrene [3.53 Å at 295 K (Cameran & Trotter, 1965), 3.475 Å at 113 K]; in PMDA (Aravamudhan *et al.*, 1979) the molecules do not overlap and so an interplanar distance cannot be defined. These interactions are directed approximately along [001]. Perpendicular to this [*i.e.* roughly in (001)], there are CH · · · O distances of 2.48 and 2.60 Å between pyrene II and PMDA, 2.58 ( $\times 2$ ) (Fig. 8), 2.69 and 2.74 Å between pyrene I and PMDA, and 2.78 Å ( $\times 4$ ) between PMDAs (Fig. 7). These are

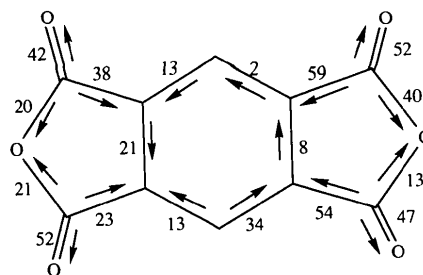


Fig. 9.  $\Delta_{A,B}$  values (units of  $10^{-4} \text{Å}^2$ ) for PMDA. The atom near the arrowhead has the larger mean-square displacement along the interatomic direction.

somewhat longer than values quoted for CH $\cdots$ O hydrogen bonds (2.0–2.4 Å; Jeffrey & Saenger, 1991, see ch. 10) but, as these authors emphasize, weak hydrogen bonds are electrostatic interactions which do not have a sharp cutoff. Thus, we suggest that these interactions should be taken into account in any assessment of the cohesive energy of crystalline PYRPMA.

#### 4. Concluding remarks

The crystal and molecular structure of the ordered phase of PYRPMA has been determined at 19 K, with considerable improvement of detail over that determined at  $\sim$ 110 K by photographic techniques in 1969 but without changing the overall picture. The bond lengths of pyrene and PMDA now have nominal e.s.d.s of  $\sim$ 0.004 Å (more realistic values would be  $\sim$ 0.006 Å). The dimensions reported for these molecules in a variety of chemical environments and temperatures are not significantly different from those found here. Deviations from planarity (up to  $\sim$ 0.01 Å for pyrene and  $\sim$ 0.09 Å for PMDA) do, however, vary from one crystallographic environment to another. The rigid-body model accounts only partially for the anisotropic thermal parameters  $U_{ij}$  determined for PYRPMA at 19 K; these discrepancies are due to errors in the  $U_{ij}$  values and the lack of rigidity, especially in the anhydride rings of PMDA.

We make some remarks, with the benefit of hindsight, about the execution of the present research. It is likely that the effort expended in making full sets of intensity measurements at intermediate temperatures (and their refinement) could have been more profitably directed elsewhere. In regard to the molecular structures, there are indications that systematic errors remain in the 19 K intensity measurements (a referee has correctly noted that 'low-temperature data are not necessarily high-quality data'). If the systematic errors could be substantially reduced using techniques developed by Destro & Marsh (1987, 1993) then more detailed analyses of thermal motion, perhaps on the lines suggested by Hummel, Raselli & Bürgi (1990), and of the distribution of bonding electrons (Destro, Marsh & Bianchi, 1988; Destro, Bianchi & Morosi, 1989) would become possible, with full exploitation of the advantages of the low temperature employed. This may allow determination of the subtle effects of intermolecular interactions on the molecular structures in different chemical environments.

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