

The Crystal Structures at 110 and 300 degrees K of the Equimolar Molecular Compound of Pyrene and Pyromellitic Dianhydride

F. H. Herbststein and J. A. Snyman

Phil. Trans. R. Soc. Lond. A 1969 **264**, 635-662

doi: 10.1098/rsta.1969.0037

Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

THE CRYSTAL STRUCTURES AT 110 AND 300 °K OF THE EQUIMOLAR MOLECULAR COMPOUND OF PYRENE AND PYROMELLITIC DIANHYDRIDE*

BY F. H. HERBSTEIN† AND J. A. SNYMAN‡§

† *Chemical Physics Group of the National Physical and Chemical Research Laboratories, Council for Scientific and Industrial Research, Pretoria, South Africa and Department of Chemistry, Technion—Israel Institute of Technology, Haifa, Israel*

‡ *Chemical Physics Group of the National Physical and Chemical Research Laboratories, Council for Scientific and Industrial Research, Pretoria, South Africa*

(Communicated by H. Lipson F.R.S.—Received 26 July 1968—Revised 6 November 1968)

[Plate 15]

CONTENTS

	PAGE		PAGE
INTRODUCTION	636	INTERMOLECULAR SEPARATIONS	650
PHASE DIAGRAM OF THE SYSTEM PYRENE-PYROMELLITIC DIANHYDRIDE	637	MOLECULAR ARRANGEMENT	651
CRYSTALLOGRAPHIC STUDY	637	DISORDER IN CRYSTALS OF <i>II</i> -MOLECULAR COMPOUNDS	654
(a) Cell dimensions and space groups	637	(a) Demonstration of existence of disorder	654
(b) Measurement and correction of intensities	638	(b) The disorder in pyrene-pyromellitic dianhydride at 300 °K	655
(c) Determination of the structure at 300 °K	639	(c) Comparison with pyrene-1,3,7,9-tetramethyluric acid	656
(d) Determination of the low-temperature structure	640	(d) Indications of different types of disordered structure	657
(e) Summary of computing procedures used	644	NATURE OF THE TRANSFORMATION	658
DESCRIPTION OF THE STRUCTURE	644	CONCLUDING REMARKS	660
MOLECULAR DIMENSIONS	646	APPENDIX	661
(a) Dimensions of pyromellitic dianhydride	647	REFERENCES	661
(b) Pyrene dimensions	648		

The crystal structures of the 1:1 pyrene-pyromellitic dianhydride molecular compound at 110 and at 300 °K have been determined by three-dimensional X-ray diffraction methods (visual intensity measurement, least-squares refinement with isotropic Debye–Waller factors). The component molecules are arranged, plane to plane, in alternating array in mixed stacks. At 110 °K the pyrene molecules in the stacks alternate in two different orientations (about 12° apart) with respect to the interleaving pyromellitic dianhydride molecules, which themselves have small displacements of alternating sign off the stack axis. At about 200 °K this ordered structure changes to a disordered

* This is part IV of the series Molecular Complexes and Compounds; for part III see Boeyens & Herbstein 1965*b*.

§ Present address: South African Atomic Energy Board, Pretoria, South Africa.

structure which has been determined at 300 °K. The component molecules appear in mean positions, abnormally large Debye–Waller factors indicating disorder. The transformation itself has not yet been studied in detail.

Review of the literature suggest that the existence of positional disorder provides an explanation for the widespread reports of high degrees of thermal vibration in crystals of *II*-molecular compounds. Some structure determinations appear to have been of disordered structures without this having been fully appreciated. Analysis of Debye–Waller factors, electron-density and difference syntheses suggests that different types of disorder are found in pyrene-pyromellitic dianhydride and pyrene-1,3,7,9-tetramethyluric acid (Damiani *et al.* 1965) on the one hand and in naphthalene-tetracyanoethylene (Williams & Wallwork 1967) and naphthalene-1,2,4,5-tetracyanobenzene (Kumakura, Iwasaki & Saito 1967) on the other.

The dimensions found for the planar pyrene molecule at 110 °K agree well with those in pyrene itself but are more accurate; the agreement between the present experimental bond lengths and those calculated by the simple valence-bond method is exceptionally good (r.m.s. discrepancy = 0.004 Å). The dimensions of the pyromellitic dianhydride molecule agree well with previous results but are more accurate; the molecule is slightly twisted into a non-centrosymmetric shape.

INTRODUCTION

The highly coloured crystalline charge transfer molecular compounds obtained from aromatic hydrocarbons and various electron acceptors have been the subject of many X-ray diffraction, spectroscopic and theoretical investigations. The theoretical studies are concerned with energies of interaction between the components and thus refer to the structure at absolute zero, while it is also clear that the most fruitful spectroscopic studies are those made on samples at very low temperatures. However, most of the X-ray crystal structure analyses in this field (see Boeyens & Herbstein 1965 *b* for references) have been carried out at room temperature where difficulty has been experienced in obtaining really satisfactory results because of the generally large degree of apparent thermal motion in the crystals. In this paper we report the results of the determination of the crystal structure of the equimolar pyrene-pyromellitic dianhydride molecular compound at 110 and 300 °K, in continuation of earlier work on the structures (at 300 °K) of the equimolar molecular compounds of anthracene and perylene with pyromellitic dianhydride (Boeyens & Herbstein 1965 *a, b*). Comparison of the two pyrene-pyromellitic dianhydride structures has shown that an order–disorder transformation takes place near 200 °K and that much of the apparent thermal motion at 300 °K is in fact due to static, positional disorder of the molecules rather than to dynamic effects. Review of published crystal-structure analyses of other molecular compounds shows that many of these analyses are also of partially disordered crystals.

The results for the low-temperature structure give fairly accurate ($\sigma(\text{C—C}) \sim 0.006 \text{ \AA}$) dimensions for the two component molecules as well as their relative arrangement for comparison with theoretical predictions. No attempt was made to obtain accurate molecular dimensions from the disordered structure.

Intensity measurements from crystals at 110 °K were made at the C.S.I.R., Pretoria, where the low-temperature structure was determined. A preliminary report of this work, which was done in 1964–5, has been published (Herbstein & Snyman 1966). The corresponding work on the structure at 300 °K was done at the Technion, Haifa, in 1966–7. However, the results are presented here in logical rather than chronological order.

PYRENE-PYROMELLITIC DIANHYDRIDE AT 110 AND 300 °K 637

PHASE DIAGRAM OF THE SYSTEM PYRENE-PYROMELLITIC DIANHYDRIDE

Pyromellitic dianhydride was obtained as a gift from E. I. du Pont de Nemours and Co. Inc. (Wilmington, Delaware) and pyrene was purchased commercially. Both materials were purified by recrystallization from glacial acetic acid (Merck, 99 to 100 %) or from methyl ethyl ketone dried over calcium chloride. The pure materials are both colourless, but mixtures in any proportion give bright red melts. Samples were ground together in a mortar, the whole composition range being covered at intervals of 5 mole %. The melting points were determined using sealed tubes in order to avoid differential losses by evaporation. The liquidus for the system (figure 1) shows a 1:1 molecular compound and less definitely two molecular compounds with pyrene:pyromellitic dianhydride ratios of

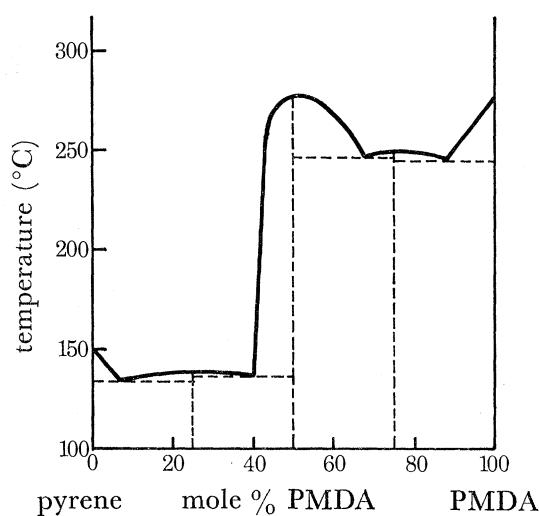


FIGURE 1. Melting-point diagram for the system pyrene-pyromellitic dianhydride. The full lines were determined experimentally, the broken lines were inferred.

3:1 or 2:1 and 1:3 respectively. The flat maxima preclude accurate determination of their compositions but the first of these compounds is presumably (pyrene)₂:pyromellitic dianhydride as a compound of this composition with melting point 120–125 °C (Ilmet, private communication) has been prepared from solution by Ilmet & Kopp (1966). The usual ratio of components in *II*-molecular compounds is 1:1 but many 1:2 and 2:1 compounds are known.

CRYSTALLOGRAPHIC STUDY

(a) Cell dimensions and space groups

Bright-red rod-shaped crystals (m.p. 278 °C) elongated along [001] and showing {110} and {100} faces were obtained by slow cooling of equimolar solutions in dry methyl ethyl ketone. Standard oscillation and Weissenberg techniques were used to determine cell dimensions and space groups of pyrene-pyromellitic dianhydride at 110 and 300 °K (table 1). The crystals were cooled by a stream of dry nitrogen gas passed through liquid nitrogen contained in a Dewar vessel mounted on the Weissenberg camera (details are given by Snyman 1965).

The crystals at 110 and 300 °K differ in the lengths of their [001] axes and in their space groups; the crystal orientation is not changed on cooling through the transformation temperature. A series of oscillation photographs about [001] was then taken at different temperatures, the orientation of the crystal with respect to the X-ray beam, the oscillation range and the exposure being the same for each photograph (figure 2, plate 15). These photographs show two important features:

(a) A set of weak intermediate layer lines (corresponding to [001] ~ 14.4 Å) appears on the photograph taken at 200 °K; there is no marked difference between the mean intensities of the intermediate and original layer lines at 170 or 110 °K.

TABLE 1. CRYSTALLOGRAPHIC RESULTS FOR PYRENE-PYROMELLITIC DIANHYDRIDE

	300 °K	110 °K
<i>a</i>	13.89 Å	13.667 \pm 0.004 Å
<i>b</i>	9.33	9.130 \pm 0.0015
<i>c</i>	7.34	14.404 \pm 0.005
β	93.5°	91° 30' \pm 20'
$\rho_{\text{obs.}}$	1.47 g cm ⁻³	—
$\rho_{\text{calc.}}$	1.47 g cm ⁻³ for 2 molecules of each component per unit cell	1.524 g cm ⁻³ for 4 mole- cules of each component per unit cell
space group	P2 ₁ /a	P2 ₁ /n

Notes. (1) Results at 300 °K determined from oscillation and front-reflexion Weissenberg photographs and agree satisfactorily with earlier results of Boeyens & Herbstein (1965*a*). At 110 °K d_{100} and b were determined from back reflexion Weissenberg photographs (Herbstein 1963) and d_{001} and β from $h0l$ front-reflexion Weissenberg photographs because crystals suitable for back-reflexion could not be obtained.

(2) Wavelengths were taken as Cu $K\alpha_1$, 1.54050 Å; α_2 , 1.54436 Å.

(b) The reflexions on the original layer lines do not undergo *marked* changes in intensity on cooling to 110 °K (apart from a slower decline of intensity with $\sin \theta/\lambda$). This has been checked qualitatively for all layers by comparing appropriate Weissenberg photographs and quantitatively by comparing structure factors measured at 300 and 110 °K.

The interpretation of these results is that a change occurs over the range 170 to 210 °K and that the differences in the molecular arrangements at 110 and 300 °K are such as to affect appreciably only the intensities of the odd layer lines in the unit cell with [001] ~ 14 Å. It was decided that it was necessary to determine both the disordered and ordered structures as ordered structures of this type had not yet been studied in detail; the available evidence showed that 300 and 110 °K were appropriate (and convenient) temperatures for execution of the intensity measurements.

(b) *Measurement and correction of intensities*

The intensities were measured by the standard multiple-film technique (Robertson 1943) using Weissenberg equi-inclination photographs taken with Cu $K\alpha$ (Ni filtered radiation). Some timed precession photographs (Mo $K\alpha$, Zr filter) were also used. An integrating Weissenberg camera was not available when the low-temperature photographs were taken so a visual method (Klein 1963) was used to compensate for poor spot shape due to partial splitting of the crystals that occurred even on slow cooling. This method included allowance for effects of α_1 - α_2 separation and spot-elongation on higher layer-line photographs (Buerger 1942).

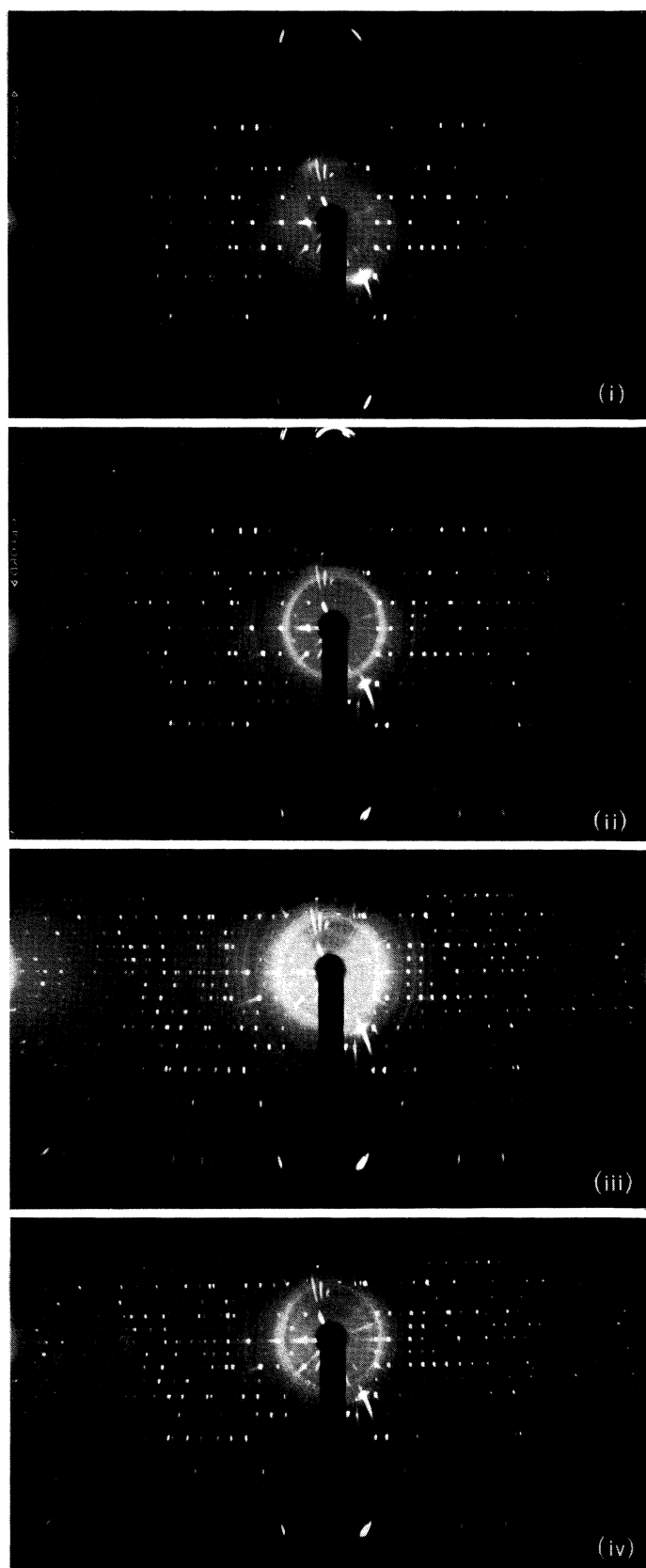


FIGURE 2. Four successive 15° c -axis oscillation photographs of a pyrene-pyromellitic dianhydride single crystal taken at: (i) 293°K , (ii) 200°K , (iii) 170°K , (iv) 110°K respectively. The same oscillation range was used for each photograph. The exposure time for each photograph was 60 min (Cu $K\alpha$, Ni filter, 30 kV, 20 mA). The powder lines on the photographs are due to ice crystals.

PYRENE-PYROMELLITIC DIANHYDRIDE AT 110 AND 300 °K 639

The intensities of 1420 hkl ($0 \leq l \leq 5$) reflexions were measured from Weissenberg photographs and 85 $h0l$ reflexions from precession photographs of crystals at 300 °K. The intensities of 2647 hkl reflexions were measured from [001] ($0 \leq l \leq 8$) and [010] ($h0l$) Weissenberg photographs of crystals at 110 °K. Of these 1341 reflexions were on layer lines with l even and 1306 on layer lines with l odd. All reflexions too weak to be measured were assigned intensities of $\frac{1}{3}I_{\min.}$ (Hamilton 1955). The thinness of the crystal used warranted neglect of absorption corrections. Lorentz and polarization corrections were applied by computer (the computing procedures used in this work are acknowledged on p. 644) and then the structure factors from the various layer lines were placed individually on an approximately absolute scale by use of Wilson's (1942) method. An experimental comparison was made via the common reflexions measured from the [010] photographs; results from the two methods agreed to within about 10% in $|F|$.

(c) Determination of the structure at 300 °K

The presumption that mixed stacks be formed with their axes along [001] and the limitations imposed by the molecular sizes and shapes required that the component molecules be centred at the positions (a) and (b) of space groups $P2_1/a$, e.g. centres of pyrene and pyromellitic dianhydride molecules at $(0\ 0\ 0, \frac{1}{2}\ \frac{1}{2}\ 0)$ and $(0\ 0\ \frac{1}{2}, \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ respectively. The molecular orientations were obtained by use of the Fourier transform method (Knott 1940) and by assuming that the anhydride groups of pyromellitic dianhydride were close to the (pyrene) carbon atoms of highest free valence index, as they are in perylene-pyromellitic dianhydride (Boeyens & Herbstein 1965 *b*). The approximate atomic coordinates derived in this way were refined by least squares on the Elliott 503 computer at the Technion. Towards the end of the refinement separate isotropic Debye-Waller factors were used for all atoms other than hydrogen, which were not included at

TABLE 2. FRACTIONAL ATOMIC COORDINATES (u, v, w) AND INDIVIDUAL ISOTROPIC DEBYE-WALLER FACTORS ($B_j(\text{Å}^2)$) OBTAINED BY REFINEMENT OF THE 300 °K STRUCTURE AND THE QUASI-ROOM TEMPERATURE (q.r.t.) STRUCTURE

(The coordinate standard deviations range from 0.006 to 0.013 Å and those of B_j from 0.11 to 0.26 Å².)

molecule	atom	u		v		w		B_j (Å ²)	
		300 °K	q.r.t.	300 °K	q.r.t.	300 °K	q.r.t.	300 °K	q.r.t.
pyrene	C _A	0.1763	0.1768	-0.0136	-0.0138	0.1211	0.1201	4.65	3.46
	C _B	0.1062	0.1069	0.0998	0.1000	0.1101	0.1104	4.40	2.59
	C _C	0.1269	0.1266	0.2377	0.2374	0.1759	0.1775	6.04	4.47
	C _D	0.0528	0.0512	0.3423	0.3449	0.1654	0.1644	6.90	6.11
	C _E	-0.0340	-0.0364	0.3178	0.3177	0.0936	0.0877	5.96	4.39
	C _F	-0.0596	-0.0606	0.1800	0.1798	0.0257	0.0233	3.96	2.05
	C _G	-0.1557	-0.1553	0.1436	0.1468	-0.0556	-0.0554	4.70	3.24
	C _H	0.0116	0.0121	0.0700	0.0699	0.0322	0.0327	3.17	1.39
pyromellitic dianhydride	C _I	0.1002	0.1021	0.0091	0.0119	0.5704	0.5718	3.42	2.08
	C ₂	0.0340	0.0343	0.1264	0.1262	0.5676	0.5683	3.56	1.85
	C ₃	0.0523	0.0518	0.2715	0.2755	0.6365	0.6351	4.21	2.24
	C ₄	-0.1037	-0.1070	0.2584	0.2580	0.5259	0.5253	4.31	2.05
	C ₅	-0.0601	-0.0605	0.1147	0.1139	0.5025	0.5009	3.08	1.92
	O _I	0.1213	0.1193	0.3305	0.3328	0.7051	0.7043	6.04	2.71
	O _{II}	-0.0361	-0.0372	0.3467	0.3488	0.6033	0.6054	5.01	2.41
	O _{III}	-0.1847	-0.1878	0.2977	0.2982	0.4866	0.4862	5.46	2.22

any stage in the work described in this paper. The Cruickshank–Pilling (1961) weighting scheme was used, i.e.

$$W_{hkl} = (2 + |F_0| + 0.02|F_0|^2)^{-1}.$$

The final R and R_1 values were 0.216 and 0.267. The atomic parameters are given in table 2: the values of the Debye–Waller factors seem rather high for atoms at 300 °K. The values of observed and calculated structure factors are given in table 3, which has been deposited in the Royal Society archives. (Copies of table 3 are obtainable on application to the Executive Secretary, The Royal Society.)

(d) *Determination of the low-temperature structure*

Below about 170 °K the unit-cell volume is approximately double that at 300 °K and thus the unit cell must contain four molecules of each component. The calculated density at 110 °K is 1.524 g cm⁻³; no attempt was made to measure the density at this low temperature. However, the minor changes in density and the non-disruptive nature of the transformation strongly suggest that the structures at 300 and 110 °K must be closely related and that, in particular, mixed stacks of alternating pyrene and pyromellitic dianhydride molecules are retained in the low-temperature structure.

A consequence of these requirements is that it is not possible to arrange all the molecules in the unit cell with their centres at crystallographic centres of symmetry as only four of these are available. The sequence of alternating component molecules in a particular stack can only be preserved if one set of molecules is placed with their centres near $(00\frac{1}{4})$, (which is a general position of space group $P2_1/n$) and symmetry-related positions. Now denote the two types of molecule by A and B respectively. Suppose an A molecule has its centre at approximately $(00\frac{1}{4})$. The symmetry elements generate related A molecules centred at approximately $(00\frac{3}{4})$ in the same stack and at approximately $(\frac{1}{2}\frac{1}{2}\frac{1}{4})$ and $(\frac{1}{2}\frac{1}{2}\frac{3}{4})$ in the other stack in the unit cell. The A molecules near $(00\frac{1}{4})$ and $(00\frac{3}{4})$ are related by the centre of symmetry at $(00\frac{1}{2})$ and thus have identical orientations in space, although the vectorial displacements of their centres with respect to the c -axis have opposite signs. The two distinct arrangements of A in the stack are denoted by A_1 (near $00\frac{1}{4}$) and A_2 (near $00\frac{3}{4}$).

Now consider molecule B. If a molecule is centred at the centre of symmetry at (000) and has orientation ⁽¹⁾ (say), then the unit-cell symmetry elements require further molecules of B having orientations related to ⁽¹⁾ at the centre and the corners of the unit cell. This accounts for only two molecules of B in the unit cell. Another molecule of B must be centred at the centre at $(00\frac{1}{2})$ having an orientation ⁽²⁾, different from ⁽¹⁾. Thus we can conclude that at low temperature B takes on two independent orientations at the two independent symmetry centres available in a particular stack, whereas the A molecules in this stack all have the same orientation but are alternately displaced in opposite directions off the stack axis. This gives rise to the sequence ... B⁽¹⁾, A₁, B⁽²⁾, A₂, B⁽¹⁾ ... down the stack along c . This is illustrated schematically in figure 3.

At this stage it was not known which of A and B represented pyrene and pyromellitic dianhydride. To solve this problem it was necessary to reconcile the room-temperature structure with the low-temperature space group and the general structure of the crystals at low-temperature as outlined above. If the reflexions on the odd layer lines are not taken into

PYRENE-PYROMELLITIC DIANHYDRIDE AT 110 AND 300 °K 641

account, then the c -axis is halved, the space group becomes $P2_1/a$ instead of $P2_1/n$ and a centre of symmetry is introduced at the previous $(0\ 0\ \frac{1}{4})$, now $(0\ 0\ \frac{1}{2})$. In this way one induces an artificially disordered structure, the quasi-room temperature structure, in which molecule B takes on both orientations $B^{(1)}$ and $B^{(2)}$ at centre $(0\ 0\ 0)$ and similarly molecule A takes on both positions A_1 and A_2 centrosymmetrically about (the previous) $(0\ 0\ \frac{1}{4})$. It follows that in the quasi-room temperature structure the positions and orientations of molecules A and B are the averages of A_1 and A_2 and of $B^{(1)}$ and $B^{(2)}$ respectively.

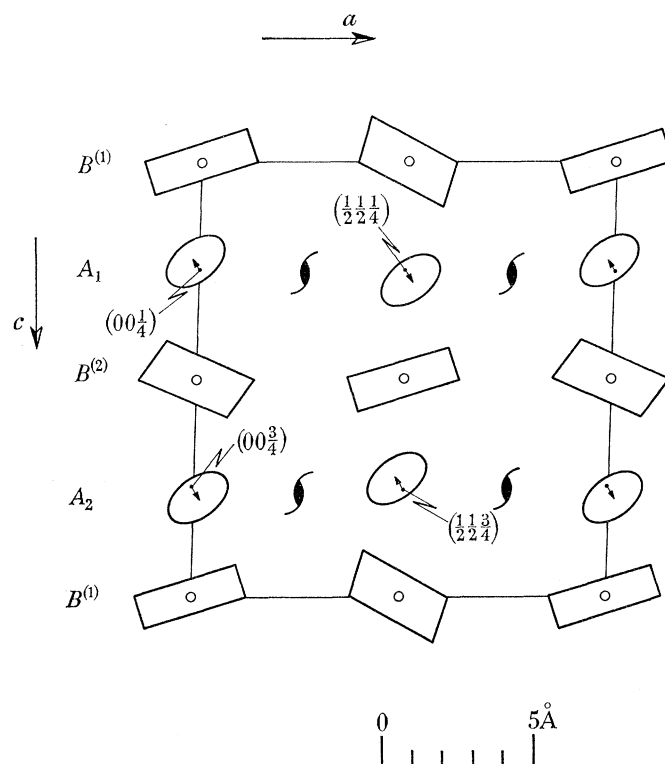


FIGURE 3. Schematic representation of the low-temperature molecular arrangement seen in projection down $[010]$.

One method of identifying molecules A and B is by analysis of the apparent thermal motions of the atoms in the quasi-room temperature structure. In molecule B the separation between equivalent atoms in orientations $B^{(1)}$ and $B^{(2)}$ will give rise to artificially high Debye–Waller factors in the average structure. The Debye–Waller factors of the individual atoms will not be uniform throughout the molecule but will be higher for those atoms furthest away from the molecular centre, since the separation between equivalent atoms in orientations $B^{(1)}$ and $B^{(2)}$ becomes larger the further away they lie from the molecular centre. One would expect a more or less parabolic increase in Debye–Waller factors as the distances of the atoms from the molecular centre increase (Higgs 1955). In the case of molecule A the Debye–Waller factors are also expected to be higher than their thermal values. Since molecule A takes on the average position of two identically oriented molecules, the individual Debye–Waller factors of the atoms are expected to have a more or less uniform value throughout the molecule.

The reflexions with l even from the crystals at 110 °K were used in a least-squares

refinement of the quasi-room temperature structure. This work was done on the IBM 704 computer at the C.S.I.R., Pretoria. The weighting scheme used was

$$W_{hkl} = \left[\frac{10}{|F_{hkl}|} \right]^2 \quad \text{for } |F_{hkl}| > 7|F_{\min.}|,$$

$$= \left[\frac{10}{7|F_{\min.}|} \right]^2 \quad \text{for } |F_{hkl}| < 7|F_{\min.}|.$$

The refinement was stopped at $R = 0.224$ and $R_1 = 0.299$. The results obtained are given in table 2; it will be noticed that the atomic coordinates obtained for the room-temperature structure and the quasi-room temperature structure are very similar. The Debye-Waller factors (B_j) for the quasi-room temperature structure given in table 2 are rather larger than would be expected for the thermal motion of atoms at 110 °K.

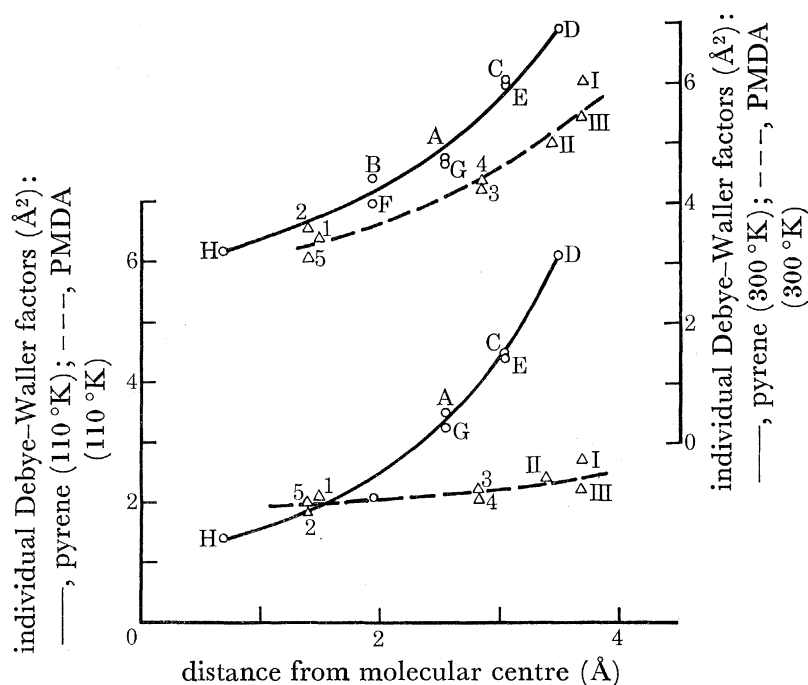


FIGURE 4. The isotropic Debye-Waller factors of the individual atoms in the room-temperature and quasi-room temperature structures plotted against their distances from the molecular centres. Separate curves are shown for pyrene and pyromellitic dianhydride at 110 °K (left-hand scale) and 300 °K (right-hand scale).

The dependence of B_j on distance from the molecular centres is shown in figure 4 for both the quasi-room temperature structure and the structure at 300 °K. In the first of these sets of results the B_j values for the atoms of the pyrene molecule are seen to increase from 1.4 to 6.1 Å² as the distances from the centre increase from 0.7 to 3.5 Å. This is what would be expected of molecule B. The B_j factors of the atoms in pyromellitic dianhydride have a more or less uniform value of 2.0 Å² and this is therefore molecule A. The B_j values at 300 °K are discussed later (p. 655).

At this stage it is clear that in the ordered crystals there are two differently oriented pyrene molecules centred at symmetry centres at (000) and (00½) respectively and that pyromellitic dianhydride molecules occupy general positions, the molecular centres being

PYRENE-PYROMELLITIC DIANHYDRIDE AT 110 AND 300 °K 643

near $(00\frac{1}{4})$, etc. One remaining unknown is the difference between the average orientation of the pyrene molecule in the quasi-room temperature structure and the orientations of the two crystallographically independent pyrene molecules at (000) and $(00\frac{1}{2})$. A second is the displacement of the centre of the pyromellitic dianhydride molecule from $(00\frac{1}{4})$.

The final three-dimensional refinement was carried out by least squares using 2647 reflexions, the quasi-room temperature structure (with an over-all Debye–Waller factor) being taken as starting point. The same weighting scheme was used for the refinements of the quasi-room temperature and low-temperature structures. It was found that the small shifts in atomic positions needed to allow for the different orientations of pyrene molecules and different positions of pyromellitic dianhydride molecules appeared automatically as a result of the refinement process. After the tenth cycle it was decided to introduce separate isotropic Debye–Waller factors for each atom. Since this involved simultaneous adjustment of 138 parameters whereas the 8K IBM 704 at our disposal could handle only 120 parameters at once, it became necessary to split the problem into two. For each cycle two groups of 16 atoms were selected in a random way and for each group the 64 relevant

TABLE 4. PYRENE-PYROMELLITIC DIANHYDRIDE AT 110 °K: FRACTIONAL ATOMIC COORDINATES (u, v, w) AND INDIVIDUAL ISOTROPIC TEMPERATURE FACTORS ($B_j(\text{Å}^2)$) AND THEIR STANDARD DEVIATIONS ($\sigma(x)$, ETC. IN Å)

The final column gives the deviations (in Å) of atoms of the pyrene and pyromellitic dianhydride molecules from their mean planes.

molecule	atom	u	v	w	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)	B_j (Å ²)	Δ (Å)
pyrene ⁽¹⁾	C _A	0.17660	0.01079	0.06448	0.0041	0.0043	0.0055	1.186	0.0014
	C _B	0.09851	0.11592	0.05656	0.0041	0.0042	0.0056	1.089	0.0038
	C _C	0.11043	0.25590	0.08678	0.0043	0.0043	0.0056	1.327	0.0107
	C _D	0.03414	0.35539	0.07968	0.0043	0.0046	0.0056	1.410	-0.0033
	C _E	-0.05728	0.31381	0.03984	0.0042	0.0043	0.0056	1.201	-0.0088
	C _F	-0.07225	0.17239	0.00811	0.0040	0.0041	0.0055	0.969	-0.0136
	C _G	-0.16293	0.12625	-0.03529	0.0041	0.0042	0.0055	1.096	0.0198
	C _H	0.00685	0.07216	0.01545	0.0040	0.0040	0.0048	1.032	0.0085
pyrene ⁽²⁾	C _I	0.17821	-0.04148	0.55156	0.0043	0.0040	0.0058	1.395	0.0002
	C _J	0.11525	0.08280	0.55288	0.0042	0.0045	0.0058	1.293	0.0098
	C _K	0.14656	0.21555	0.58872	0.0044	0.0046	0.0059	1.529	-0.0032
	C _L	0.08282	0.33225	0.58952	0.0048	0.0049	0.0060	1.814	-0.0091
	C _M	-0.01374	0.31837	0.55373	0.0046	0.0047	0.0059	1.618	0.0060
	C _N	-0.04790	0.18812	0.51894	0.0044	0.0045	0.0058	1.417	-0.0019
	C _O	-0.14707	0.16947	0.48230	0.0043	0.0045	0.0058	1.335	0.0013
	C _P	0.01701	0.06796	0.51686	0.0040	0.0041	0.0051	1.096	0.0177
PMDA ₁	C ₁	0.10620	0.02457	0.29044	0.0041	0.0043	0.0054	1.160	0.0049
	C ₂	0.04000	0.13966	0.29011	0.0040	0.0043	0.0056	1.084	0.0046
	C ₃	0.05597	0.28875	0.32221	0.0042	0.0043	0.0056	1.220	0.0165
	C ₄	-0.10296	0.27172	0.26949	0.0042	0.0043	0.0055	1.234	-0.0196
	C ₅	-0.05599	0.12838	0.25593	0.0041	0.0043	0.0055	1.134	0.0114
	C ₆	-0.09690	0.00316	0.21986	0.0042	0.0044	0.0055	1.212	0.0022
	C ₇	-0.03120	-0.11258	0.22008	0.0041	0.0043	0.0056	1.106	0.0003
	C ₈	-0.04619	-0.26113	0.18683	0.0042	0.0045	0.0056	1.277	0.0092
	C ₉	0.11193	-0.24447	0.24352	0.0041	0.0043	0.0055	1.182	-0.0118
	C ₁₀	0.06507	-0.10115	0.25475	0.0041	0.0042	0.0055	1.100	-0.0114
	O _I	0.12705	0.34664	0.35512	0.0030	0.0032	0.0037	1.546	0.0329
	O _{II}	-0.03165	0.36266	0.30829	0.0028	0.0031	0.0036	1.311	0.0013
	O _{III}	-0.18432	0.31251	0.25202	0.0030	0.0032	0.0039	1.584	-0.0422
	O _{IV}	-0.11545	-0.31799	0.15108	0.0031	0.0033	0.0039	1.696	0.0409
	O _V	0.04183	-0.33522	0.20280	0.0029	0.0031	0.0036	1.361	-0.0015
	O _{VI}	0.19225	-0.28480	0.26440	0.0030	0.0032	0.0037	1.550	-0.0379

parameters together with the 10 scale factors were refined. Only two cycles were performed as refinement had clearly ceased at this stage.

The final atomic parameters, together with their standard deviations, are given in table 4. The numbering of the atoms is shown in figures 9 and 10. The final structure factors on an absolute scale are given in table 5, which has been deposited in the archives of the Royal Society. (Copies of table 5 are obtainable on application to the Executive Secretary, The Royal Society.)

(e) *Summary of computing procedures used*

The computing procedures used in the work done in Pretoria have been summarized elsewhere (Boeyens & Herbstein 1965*b*). The computations in Haifa were carried out on an Elliott 503 computer with the integrated set of programmes developed by J. J. Daly, F. S. Stephens & P. J. Wheatley (private communication). The electron density and difference syntheses in the molecular planes were calculated at the Weizmann Institute, Rehovoth.

DESCRIPTION OF THE STRUCTURE

Projections of the final low-temperature structure down the three crystallographic axes are shown in figures 5 to 7. For comparison the projections of the room-temperature structure are also shown in these figures. Detailed calculations of molecular dimensions and intermolecular distances were made only for the low-temperature structure.

The mean molecular planes were calculated for the three independent molecules, pyrene⁽¹⁾, PMDA₁ and pyrene⁽²⁾ as well as the displacements of the atoms from the mean molecular planes. The orthogonalized coordinates (X, Y, Z), are related to the fractional monoclinic coordinates (u, v, w) by the transformations:

$$X = ua + wc \cos \beta, \quad Y = vb, \quad Z = wc \sin \beta.$$

In this set of axes the mean molecular planes of the molecules are described by the following equations:

molecule	
pyrene ⁽¹⁾	$0.3407X + 0.2679Y - 0.9012Z = 0,$
PMDA ₁	$0.3191X + 0.2654Y - 0.9098Z = 3.333,$
pyrene ⁽²⁾	$0.3223X + 0.2630Y - 0.9094Z = 6.629.$

The distances between successive planes are 3.333 and 3.296 Å respectively. The molecules are nearly planar and parallel to each other. The displacements of the atoms from their mean molecular planes are listed in table 5. The actual angles between the mean molecular planes are:

pyrene ⁽¹⁾ and PMDA ₁	1.3°,
pyrene ⁽²⁾ and PMDA ₂	0.0°,
pyrene ⁽¹⁾ and pyrene ⁽²⁾	1.1°.

The distances of the carbon atoms in the pyrene molecules from the mean molecular planes are small and on the basis of the standard deviations the only displacements which may be significant are those of atoms F and G in pyrene⁽¹⁾ and of atom P in pyrene⁽²⁾. If

PYRENE-PYROMELLITIC DIANHYDRIDE AT 110 AND 300 °K 645

these displacements are real, they are probably due to crystal packing forces. The displacements of some atoms in PMDA_1 from the mean molecular plane are comparatively large. The calculated plane through the central benzene ring of the PMDA_1 is given by

$$0.3213X + 0.2599Y - 0.9106Z = 3.335.$$

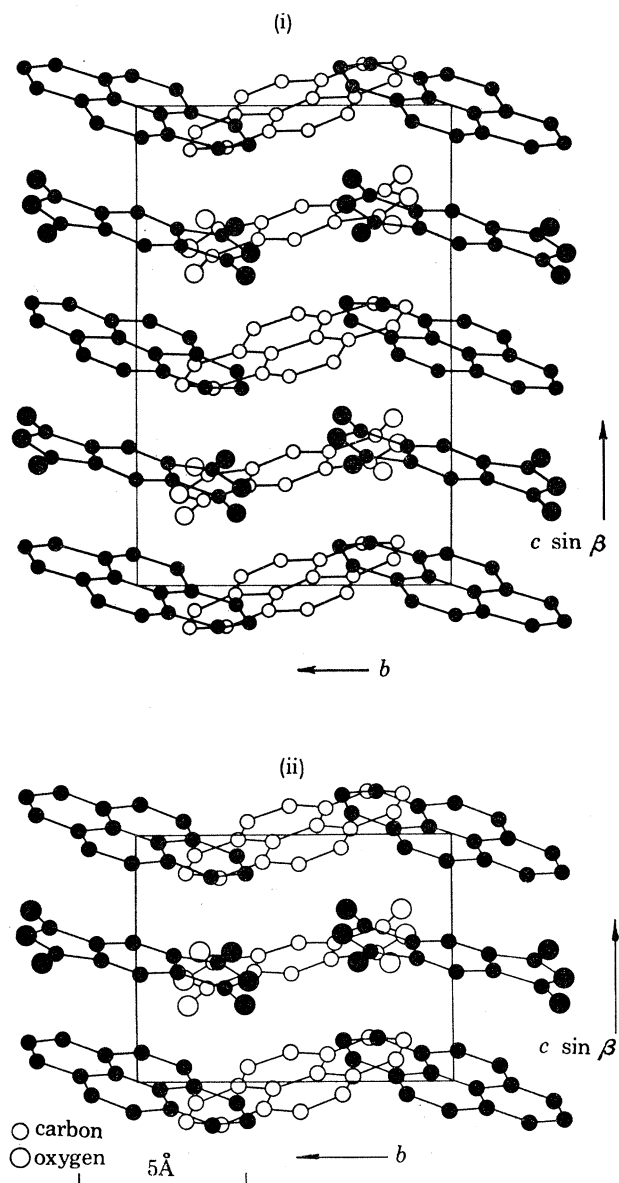


FIGURE 5. The arrangement of pyrene and pyromellitic dianhydride molecules seen in projection down [100] in: (i) the low-temperature structure, (ii) the room temperature structure. In this figure and in figure 6 the molecules whose centres lie at about half-way along the axis of projection are shown by open circles and those whose centres lie in the plane of the diagram by filled circles.

The displacements of the atoms in PMDA_1 from this plane in 10^{-3} \AA are given in figure 8. The figure shows that PMDA_1 is twisted about its long axis and is consequently not centrosymmetric. The possible significance of this twist will be discussed later.

MOLECULAR DIMENSIONS

As anisotropic temperature factors could not be determined because of the limited computing facilities available to us, it was not possible to apply Cruickshank's (1961) correction to the atomic positions due to librations of the molecules. However, the

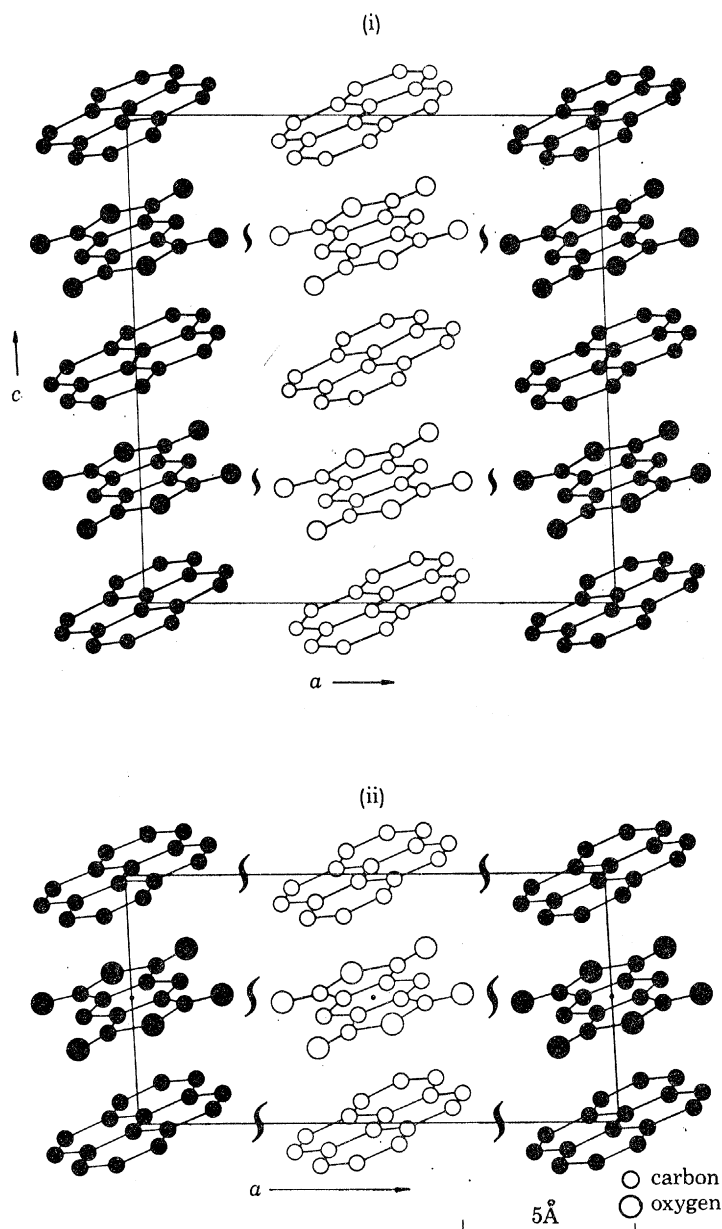


FIGURE 6. The arrangement of pyrene and pyromellitic dianhydride molecules seen in projection down [010] in: (i) the low-temperature structure, (ii) the room temperature structure.

individual isotropic temperature factors (table 4) of the atoms are small so that the systematic increases in bond lengths to be expected from this source are probably smaller than the estimated standard deviations due to random errors. Molecular dimensions were therefore calculated directly from the atomic coordinates of table 4.

PYRENE-PYROMELLITIC DIANHYDRIDE AT 110 AND 300 °K 647

(a) Dimensions of pyromellitic dianhydride

The dimensions of pyromellitic dianhydride obtained in the present study are given in figure 9. The estimated standard deviations in bond lengths are 0.006 Å and in bond angles 0.4°; thus there are no significant differences between chemically equivalent but

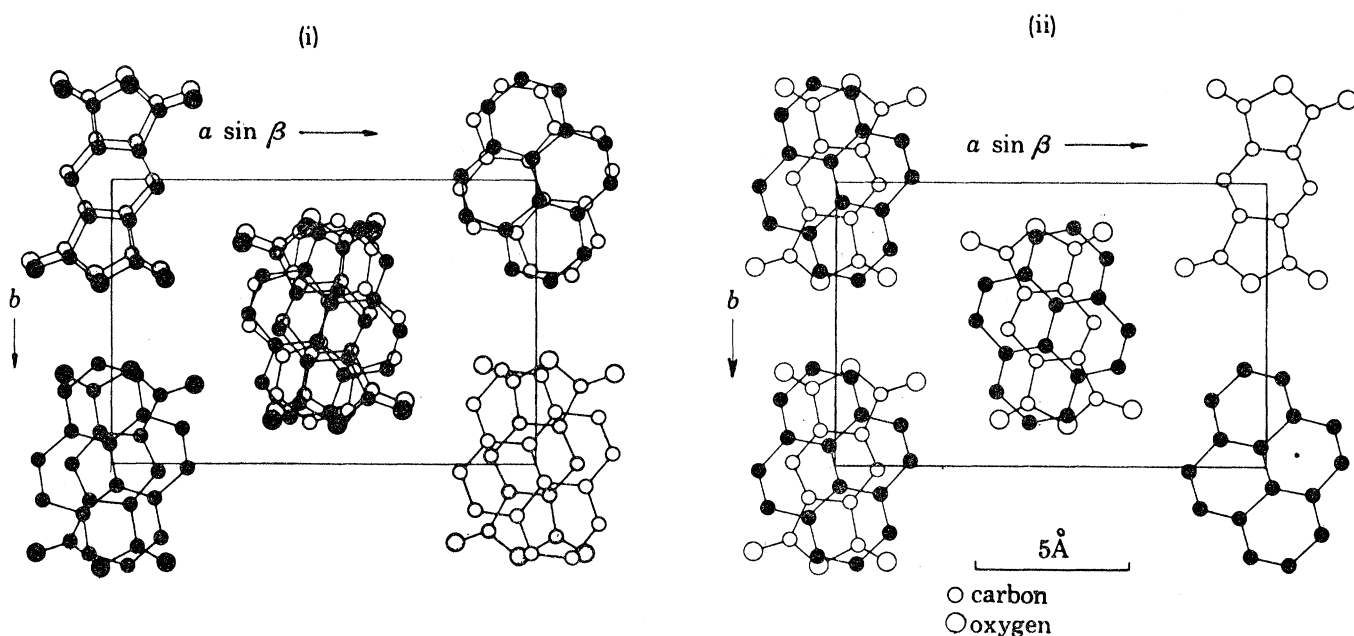


FIGURE 7. The arrangement of pyrene and pyromellitic dianhydride molecules seen in projection down [001] in: (i) the low-temperature structure, (ii) the room-temperature structure. In (i) the pyromellitic dianhydride molecules near $\frac{1}{4}c$ are represented by closed-circle models and those near $\frac{3}{4}c$ by open-circle models. For the sake of clarity two molecules have been left out at each corner of this projection. In (ii) one pyrene and one pyromellitic dianhydride molecule have been left out for clarity.

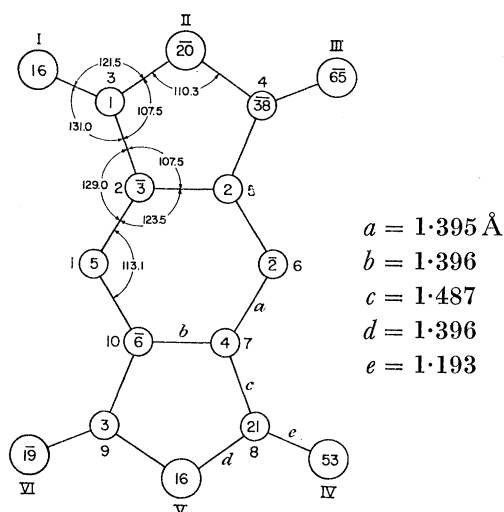


FIGURE 8. The displacements (10^{-3} Å) of the atoms in PMDA_1 from the plane through the central benzene ring, and the averaged molecular dimensions.

crystallographically distinct bond lengths and angles. The pyromellitic dianhydride molecules have no crystallographic symmetry in the present structure but are constrained to be centrosymmetric in perylene-pyromellitic dianhydride (Boeyens & Herbstein 1965*b*). The crystal structure of pyromellitic dianhydride itself has not yet been determined but the molecular symmetry is either $\bar{1}$ or 2 (Boeyens & Herbstein 1967). There are no significant differences between the averaged *dimensions* of the pyromellitic dianhydride molecule in pyrene-pyromellitic dianhydride (see figure 8) and in perylene-pyromellitic dianhydride; however, there are differences in shape which are discussed below.

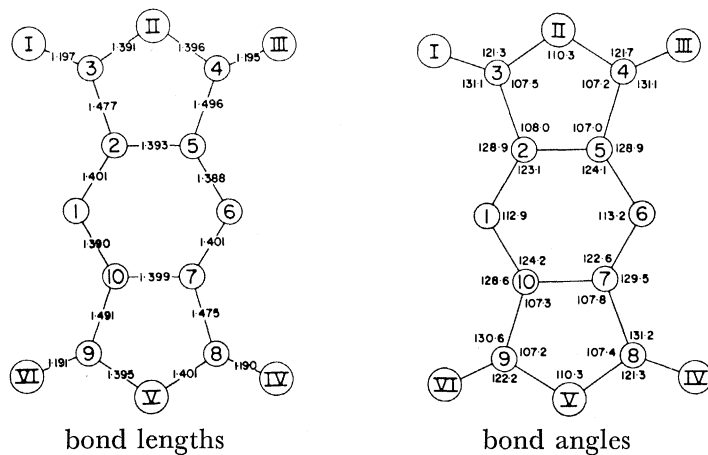


FIGURE 9. The molecular dimensions of PMDA_1 (crystallographic symmetry 1).

The bond lengths in the central benzene ring in pyromellitic dianhydride are very close to those in benzene itself but all the bond angles differ significantly from 120° . The largest differences are at C_1 and C_6 where the angles are 112.9° and 113.2° respectively. A value of 114.3° was obtained for the corresponding angle in the perylene-pyromellitic dianhydride structure. The existence of deviations from 120° of the bond angles in the central benzene ring in pyromellitic dianhydride is therefore definitely established. The dimensions of the five-membered rings in pyromellitic dianhydride are very similar to those in maleic anhydride (Boeyens & Herbstein 1965*b*; Marsh, Ubell & Wilcox 1962). This similarity suggests that angle strain in the pyromellitic dianhydride molecule will show itself only in the central benzene ring. Using the hypotheses that angle strain in the central ring is minimal and that all angle-bending force constants are equal, a simple calculation (Appendix) gives a value of -6° for the deviations of the C_1 , C_6 benzene-ring angles from 120° ; the experimental value is -7° .

The four keto-groups of the pyromellitic dianhydride molecule are all bent away from the centre of the molecule, the mean angles being 131.0° and 121.6° . These deviations from the symmetrical positions are highly significant but we have not been able to explain them.

(b) *Pyrene dimensions*

The present experimental values for the dimensions of the two independent pyrene molecules in pyrene-pyromellitic dianhydride are summarized in figure 10, while various sets of bond lengths and their estimated standard deviations are given in table 6. The latter have been calculated both from the e.s.d.'s of the individual atomic positions

PYRENE-PYROMELLITIC DIANHYDRIDE AT 110 AND 300 °K 649

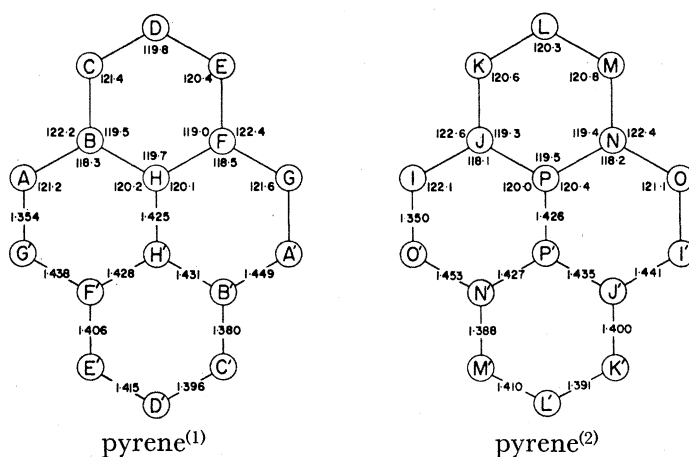


FIGURE 10. The molecular dimensions of the two independent centrosymmetric molecules pyrene⁽¹⁾ and pyrene⁽²⁾.

TABLE 6. COMPARISON OF VARIOUS OBSERVED AND CALCULATED VALUES OF THE BOND LENGTHS IN PYRENE

type of c.e.b.†	experimental bond lengths						
	bonds	lengths and e.s.d.'s (Å)		bonds	lengths and e.s.d.'s (Å)		
<i>a</i>	E—D	1.415	0.005	M—L	1.410	0.005	
	C—D	1.396	0.005	K—N	1.391	0.005	
<i>b</i>	B—C	1.380	0.005	N—M	1.388	0.005	
	F—E	1.406	0.005	J—K	1.400	0.005	
<i>c</i>	H—F	1.428	0.005	P—N	1.427	0.005	
	H—B	1.431	0.005	P—J	1.434	0.005	
<i>d</i>	G—F	1.438	0.005	O—N	1.453	0.005	
	A—B	1.449	0.005	I—J	1.441	0.005	
<i>e</i>	H—H ¹	1.425	0.009	P—P ¹	1.426	0.009	
<i>f</i>	A—G ¹	1.354	0.005	I—O ¹	1.350	0.005	
type of c.e.b.	exptl values of Camerman & Trotter‡			calculated bond lengths			
	average of c.e.b. (Å)	e.s.d. of c.e.b. (Å)	(Å)	valence bond method‡ (Å)	l.c.a.o. m.o. (Å)	s.c.f. m.o.§ (Å)	spin states (Å)
<i>a</i>	1.403	0.006	1.380 ± 0.012	1.397	1.388	1.388	1.380
<i>b</i>	1.394	0.005	1.420 ± 0.009	1.397	1.408	1.395	1.415
<i>c</i>	1.430	0.002	1.417 ± 0.012	1.421	1.427	1.406	1.435
<i>d</i>	1.445	0.003	1.442 ± 0.009	1.448	1.433	1.450	1.415
<i>e</i>	1.426	0.001	1.417 ± 0.014	1.421	1.424	1.436	1.425
<i>f</i>	1.352	0.002	1.320 ± 0.014	1.355	1.360	1.350	1.390
r.m.s. deviation between c.e.b. values and calculated values.				0.004	0.010	0.013	0.024

† Chemically equivalent bonds.

‡ Camerman & Trotter (1965).

§ Pritchard & Sumner (1954).

|| Vroclant & Daudel (1949).

and by taking the deviations of the several chemically equivalent bonds from their mean values. The individual values obtained for the several chemically equivalent bonds do not differ significantly from their mean values.

Three independent sets of pyrene dimensions are available in the literature. Robertson & White (1947) were the first to determine the crystal structure of pyrene itself, but their two-dimensional results have been superseded by the more recent and detailed three-dimensional analysis of Camerman & Trotter (1965). Results of a three-dimensional analysis have also been reported for the pyrene-tetracyanoethylene molecular compound (Ikemoto & Kuroda 1968) (we do not consider here the results for the pyrene-1,3,7,9-tetramethyluric acid molecular compound (Damiani *et al.* 1965) as this appears to be disordered at room temperature). The analysis of Camerman & Trotter (1965) and Ikemoto & Kuroda (1968) were carried out on crystals at room temperature and estimated standard deviations in the range 0.009 to 0.014 Å were reported for the bond lengths. The present results do not differ significantly from those reported earlier but have smaller e.s.d.'s because of the low temperature used in our work. Thus further comparison of our measured bond lengths with calculated values is warranted.

The bond lengths derived from the bond orders calculated by various methods are given in table 6. The correlation curves between bond order and bond length used in these derivations are those given by Cruickshank & Sparks (1960) for the valence-bond and molecular-orbital methods. The r.m.s. deviations between calculated values and the present values for chemically equivalent bonds are included in table 6 and it will be noted that the agreement of the observed values with those predicted by the valence-bond method is very good and much better than that given by any of the other methods. Although the success of the valence-bond method is presumably due as much to fortuitous cancellation of errors as to its intrinsic virtues, it is, nevertheless, striking to note that Cruickshank & Sparks (1960) have already shown that the valence-bond method gives more accurate predictions of bond lengths for a number of aromatic hydrocarbons, including the much-studied naphthalene and anthracene.

The bond angles of the two pyrene molecules are shown in figure 10 and the values found are in reasonable agreement with the other less accurate results.

Deviations of greater than about 1.4 from 120° are very probably significant as the e.s.d. of the bond angles is *ca.* 0.4°. These deviations presumably result from the unequal bond lengths in the molecule.

The available sets of molecular dimensions are not accurate enough to show possible effects of complex formation on the geometry of the pyrene molecule.

INTERMOLECULAR SEPARATIONS

All intermolecular atomic separations less than 4 Å were calculated. The closest intermolecular approaches occur between molecules adjacent to one another within a stack. For clarity two diagrams are shown of the independent molecules projected normal to their molecular planes: (i) the molecular arrangement of pyrene⁽¹⁾ and PMDA₁ projected onto the plane through pyrene⁽¹⁾ (figure 11 (i)); (ii) the molecular arrangement of PMDA₁ and pyrene⁽²⁾ projected onto the plane through pyrene⁽²⁾ (figure 11 (ii)).

PYRENE-PYROMELLITIC DIANHYDRIDE AT 110 AND 300 °K 651

The four closest C...C approaches are (i) between pyrene⁽¹⁾ and PMDA₁:

$$C...2 = 3.290 \text{ \AA}, \quad G'...9 = 3.286 \text{ \AA};$$

and (ii) between pyrene⁽²⁾ and PMDA₁

$$9...M' = 3.319 \text{ \AA}, \quad 4...O = 3.280 \text{ \AA}.$$

These distances are a little smaller than the interlayer separation found in graphite (3.355 Å) and considerably smaller than the normal van der Waals separation of 3.5 Å. If one considers that the interplanar distance between two parallel pyrene molecules in the pyrene crystal (Camerman & Trotter 1965) is 3.53 Å, it can be concluded that the above four contacts definitely do not correspond to the normal van der Waals interaction. The closest C...O distances between overlapping molecules are:

$$I...L = 3.448 \text{ \AA}, \quad V...F' = 3.430 \text{ \AA}.$$

The shortest distances between molecules in different stacks are

$$C...C \ 3.52 \text{ \AA}, \quad C...O \ 3.25 \text{ \AA} \quad \text{and} \quad O...O \ 3.28 \text{ \AA}.$$

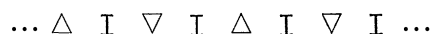
These all correspond to normal van der Waals interactions.

MOLECULAR ARRANGEMENT

In general terms the molecular arrangement is similar to that found in other *II*-molecular compounds (for survey see Boeyens & Herbstein 1965 *b*). The two components are arranged in stacks of almost parallel and almost planar molecules (figures 5 to 7). The stack axes lie along [001] and any one stack (e.g. that at $\frac{1}{2}\frac{1}{2}-$) is surrounded by six others in quasi-hexagonal array. Four of these stacks (those at 00-, 10-, 01-, 11-) are derived from the reference stack by the action of *n*-glide planes perpendicular to [010], i.e. they are displaced by $\frac{1}{2}c$ along the stack axis and differ in orientation. The other two stacks (those at $\frac{1}{2}\frac{1}{2}-$ and $\frac{1}{2}1\frac{1}{2}-$) are identical with the reference stack. It is clear from the closest distances found between atoms in different stacks that only van der Waals interactions operate between stacks. In the disordered phase there are also six stacks surrounding a particular reference stack, two of these being identical to the reference stack and the other four derived from it by the action of the *a*-glide planes perpendicular to [010]. These four stacks differ in orientation from the reference stack but are *not* shifted along [001] with respect to it.

In one respect the molecular arrangement in pyrene-pyromellitic dianhydride differs from that found in almost all the other *II*-molecular compounds examined crystallographically until now—the periodicity along the stack axis is *ca.* 14 Å instead of the *ca.* 7 Å usually found. This is because alternate pyrene molecules in a stack have (slightly) different orientations and the two interleaving pyromellitic dianhydride molecules have (slightly) different positions. (These two pyromellitic dianhydride molecules must be parallel as they are related by a centre of symmetry.) The only other *II*-molecular compound which has a *ca.* 14 Å periodicity along the stack axis and whose structure has been determined is anthracene-1,3,5-trinitrobenzene ([001] = 13.2 Å) (Brown, Wallwork &

Wilson 1964). Here the triangular trinitrobenzene molecules alternately take up opposite orientations in a stack which can thus be represented to a first approximation by



where \triangle is 1,3,5-trinitrobenzene and I is anthracene.

The molecular compounds of hexamethylbenzene with the picryl halides also have 14 Å periodicities along their stack axes, while there are some indications from the diffuse scattering that the a axis may have a 56 Å periodicity at low temperature (Powell & Huse 1943). These structures have not been determined in any detail. The sources of the 14 Å periodicity along the stacks in pyrene-pyromellitic dianhydride and anthracene-trinitrobenzene differ perhaps more in degree than in kind—in the first crystal the two pyrene molecules differ by about 12° in orientation about an axis normal to their planes, while in the second the corresponding difference in orientation is about 60°.

The molecular arrangements in II -molecular compounds can also be described in terms of buckled sheets of molecules. For example in perylene-fluoranil (Hanson 1963) these buckled sheets lie about the (001) planes of the crystal, each sheet containing both perylene and fluoranil molecules. Pyrene-pyromellitic dianhydride is formally similar to perylene-fluoranil in molecular arrangement (both have stack axes along [001], space group $P2_1/n$) but here the different molecules in a particular sheet are the differently oriented pyrene or pyromellitic dianhydride molecules and not molecules of different chemical type: for example, pyrene⁽²⁾ molecule centred at $\frac{1}{2} \frac{1}{2} 0$ is surrounded by four pyrene⁽¹⁾ molecules at 000, etc., and two pyrene⁽²⁾ molecules at $\frac{1}{2} \frac{1}{2} 0$, $\frac{1}{2} 1 \frac{1}{2} 0$. This difference between these two II -compounds is due to the 14 Å periodicity along the stack for pyrene-pyromellitic dianhydride and the 7 Å periodicity for perylene-fluoranil. As the stronger intermolecular interactions are those between adjacent molecules within a stack, it seems to be more realistic physically to describe the molecular arrangement in terms of stacks rather than sheets.

The molecular arrangement seen in projection onto the planes of the pyrene⁽¹⁾ and pyrene⁽²⁾ molecules is shown in figure 11. Each pyrene molecule is sandwiched between two centrosymmetrically related pyromellitic dianhydride molecules but the relative arrangements differ for pyrene⁽¹⁾ and pyrene⁽²⁾. However, in each instance the pyromellitic dianhydride molecule overlaps only one-half of a pyrene molecule, i.e. a naphthalene-like portion and, in this sense, the arrangement resembles that in perylene-pyromellitic dianhydride (see figure 10 of Boeyens & Herbstein 1965*b*). The detailed arrangement is fairly similar for perylene-pyromellitic dianhydride and pyrene⁽¹⁾-PMDA₁ but pyrene⁽²⁾-PMDA₁ resembles perylene-fluoranil more closely and thus deviates considerably from the graphite-like arrangement which has been observed in many, but not all, II -molecular compounds. In addition, it should be noted that the carbonyl group C8-O IV of PMDA₁ overlaps one ring of pyrene⁽¹⁾ and C3-O I overlaps another ring of pyrene⁽²⁾; indeed C8-O IV is bent slightly up towards pyrene⁽¹⁾ above it. Somewhat similar arrangements of carbonyl groups and aromatic rings have been found in other charge-transfer molecular compounds (see Prout & Wallwork (1966) for summary) and it has been inferred that there is a dipole-induced dipole interaction between carbonyl group and aromatic ring which can make an appreciable contribution to the bonding between the

PYRENE-PYROMELLITIC DIANHYDRIDE AT 110 AND 300 °K 653

components. There is little or no similar direct overlap of carbonyl groups and aromatic rings in the other pyromellitic dianhydride molecular compounds whose structures have been determined (with anthracene and perylene (Boeyens & Herbstein 1965*b*)).

The pyromellitic dianhydride molecule is slightly twisted into a non-centrosymmetric shape and some of its atoms make somewhat closer approaches to various atoms of the adjacent pyrene molecules. It is noteworthy that in both perylene-pyromellitic dianhydride and pyrene-pyromellitic dianhydride the pyromellitic dianhydride molecules are significantly distorted from planarity and in the latter molecular compound from being centro-

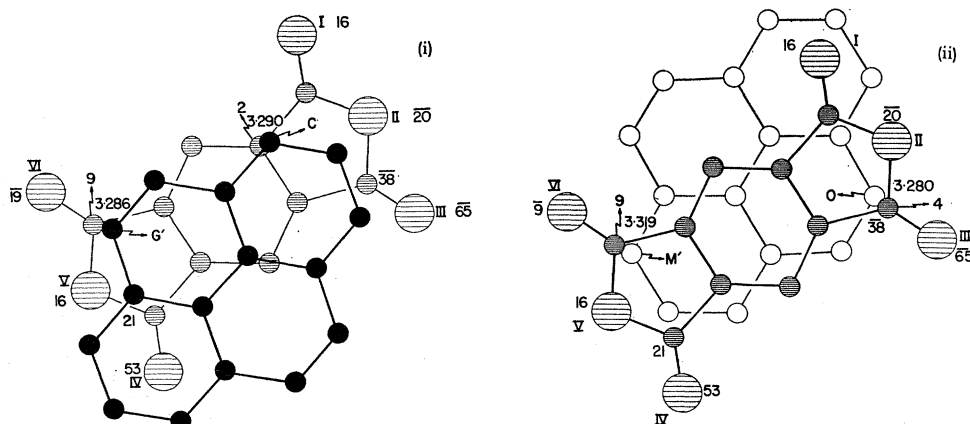


FIGURE 11. The molecular arrangement of the three independent molecules in the low-temperature structure as seen in projection normal to their molecular planes. For clarity two drawings are shown: (i) the molecular arrangement of pyrene⁽¹⁾ and PMDA₁ in projection normal to the plane through pyrene⁽¹⁾, and (ii) the molecular arrangement of PMDA₁ and pyrene⁽²⁾ in projection normal to the plane through pyrene⁽²⁾. The molecule pyrene⁽¹⁾ is 3.333 Å above PMDA₁ and PMDA₁ is 3.296 Å above pyrene⁽²⁾. The shorter distances between various atoms in the pairs of molecules are shown on the diagram as well as the displacements of certain atoms in the pyromellitic dianhydride molecules from the mean planes of their central benzene rings.

symmetric. There are, however, no significant differences between the dimensions of the molecules in their different molecular compounds. Thus the different distortions found in the pyromellitic dianhydride molecules are presumably due to differences in detail between the donor-acceptor interactions in the two molecular compounds. However, the detailed shapes differ by at most a few hundredths of an ångström and these differences are too small to be explained reliably at present. Rather similar differences in detailed shape have been found in the *bis*-8-hydroxyquinolinato-copper (II) molecule which is bow-shaped in its 5-coordinated dimeric form (Palenik 1964), planar in its 1:1 molecular compound with benzotrifuroxan (Prout & Powell 1965), and propeller-shaped in its 1:2 molecular compound with picryl azide (Bailey & Prout 1965).

It may be significant that the pyrene molecules are both oriented so that carbon atoms C, M', which have the highest free valence indices in the pyrene molecule (Brown 1950; Kooyman & Fahrenhorst 1953) both approach the anhydride groups of pyromellitic dianhydride molecules. A similar feature was found in perylene-pyromellitic dianhydride. There is thus a considerable amount of evidence which points to the importance of localized interactions in determining the relative orientations of donor and acceptor molecules, but no single item is particularly convincing.

The interplanar distances between pyrene⁽¹⁾ and PMDA₁ and PMDA₁ and pyrene⁽²⁾ are slightly different at 3.333 and 3.296 Å respectively, but individual distances of closest approach between atoms (see figure 11) do not differ appreciably. Thus it seems unlikely that the intermolecular forces will vary between different pairs of molecules nor can one discern any tendency to the grouping of closer pairs of molecules along the stack.

DISORDER IN CRYSTALS OF *H*-MOLECULAR COMPOUNDS

(a) *Demonstration of existence of disorder*

Most papers on the determination of the crystal structures of *H*-molecular compounds contain a statement about the high degree of thermal motion in the crystals at room temperature. However, as Powell & Huse (1943) pointed out, the melting points of the molecular compounds are not very different from the means of the melting points of their components and thus a much higher degree of thermal vibration than in the components is not to be expected. If, however, the room-temperature structure of the molecular compound lacks long-range order in some respects, then the Debye–Waller factors will be larger than normal because they include a contribution due to static displacements of the atoms from their mean positions. This explanation assumes that the two (or more) possible orientations or positions of the molecules are not too different. The values found here for the Debye–Waller factors of the individual atoms of pyrene-pyromellitic dianhydride illustrate this point.

The only example so far where results are available for both disordered and ordered structures is pyrene-pyromellitic dianhydride. However, many results are available for structure analyses carried out at room temperature only and it is desirable to be able to examine these for evidence of disorder. This is particularly important for crystals where the phase change (or disorder–order transformation) occurs at an inconveniently low temperature. Two methods are available: analysis of the distance-dependence of the Debye–Waller factors of the two components is rapid and requires little extra work whereas computation of electron density and difference syntheses in appropriate molecular planes is more time-consuming but gives more information. The first method can be applied to naphthalene-tetracyanoethylene, where the crystal structure at 300 °K has been determined by Williams & Wallwork (1967). The B_j † values are plotted against distance from the molecular centres in figure 12 and it is clear that the naphthalene molecules are disordered while the Debye–Waller factors of the tetracyanoethylene molecules are close to those expected for a molecular crystal (m.p. 99 °C) at 300 °K. Similar results are obtained from electron-density and difference syntheses in the molecular planes of the two components (figures 13 and 14). Disordered naphthalene molecules have also been detected in naphthalene-1,2,4,5-tetracyanobenzene by use of electron-density syntheses (Kumakura, Iwasaki & Saito 1967).

† These are the equivalent isotropic B_j values calculated from Williams & Wallwork's anisotropic Debye-Waller factors (note erroneous interchange of B_{12} and B_{23} in table 3 of this paper) by Hamilton's (1959) formula. The R-factor obtained by calculating structure factors on the basis of these B_j values and the final atomic co-ordinates is 25.4%, close to the value obtained by Williams & Wallwork (24%) for refinement in terms of individual isotropic Debye-Waller factors.

(b) *The disorder in pyrene-pyromellitic dianhydride at 300 °K*

The Debye–Waller factors obtained from analysis of the structure at 300 °K (table 2) have been plotted against distance from the molecular centres (figure 4). The relatively large values are clear evidence of disorder (for comparison it may be noted that anthracene (m.p. 216 °C) has B_j values at 300 °K which range from 2.83 to 4.00 Å² (Cruickshank 1956)). The B_j values for the atoms of pyrene lie above those for the atoms of pyromellitic dianhydride but the distinction between the two curves is not nearly as clear-cut as it is for the quasi-room temperature structure, or for naphthalene-tetracyanoethylene at 300 °K (figure 12). This suggests that the disordered structure of pyrene-pyromellitic dianhydride at 300 °K cannot simply be equated with that of the averaged ordered structure (i.e. the quasi-room temperature structure).

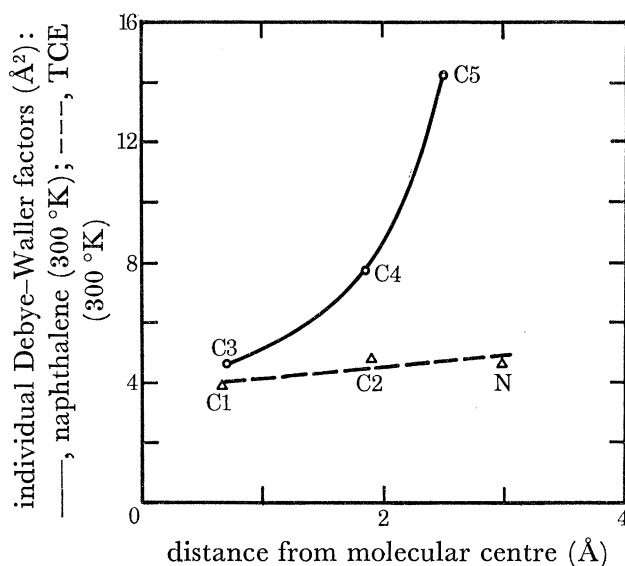


FIGURE 12. The equivalent isotropic Debye–Waller factors of the individual atoms in naphthalene-tetracyanoethylene at room temperature (Williams & Wallwork 1967). Separate curves are shown for the two molecules.

This point has been investigated further by calculation of electron-density and difference syntheses in the molecular planes of pyrene (figure 15) and pyromellitic dianhydride (figure 16), using as input data the $|F_{\text{obs.}}|$ and $F_{\text{calc.}}$ values of table 3 (i.e. those for the structure at 300 °K). The electron-density synthesis of pyrene shows broadened peaks, especially towards the periphery of the molecule, whereas the pyromellitic dianhydride molecule is much better defined. On the other hand, the difference syntheses of the two molecules are surprisingly similar and both can be interpreted in terms of the superposition of two orientations for each of the component molecules, the separation being about 15 to 20°. (However, the angular separations obtained from the difference syntheses appear to be over-estimates when checked against the electron-density syntheses.) Thus the details of the structure at 300 °K are not yet established but the following points seem clear: (a) the structure is disordered, as shown by the values of the Debye–Waller factors; (b) both component molecules appear to be disordered by similar in-plane rotations and

there is little indication of the different arrangements found for the two components in the ordered structure and in naphthalene-tetracyanoethylene and naphthalene-1,2,4,5-tetracyanobenzene.

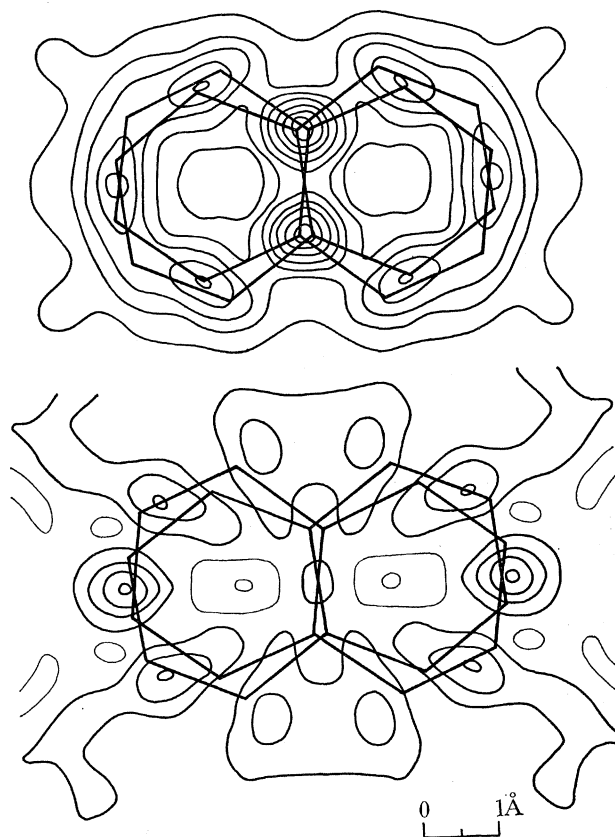


FIGURE 13. Electron-density and difference syntheses in the plane of the naphthalene molecule in naphthalene-tetracyanoethylene at room temperature. This is a more convenient representation of results already given by Williams & Wallwork (1967, their figures 1 and 2). The contours of electron density are at intervals of $1 \text{ e } \text{Å}^{-3}$ and start at $0 \text{ e } \text{Å}^{-3}$, while the contours of difference density are at intervals of $0.5 \text{ e } \text{Å}^{-3}$ (thick lines zero and positive contours, thin lines negative contours).

(c) *Comparison with pyrene-1,3,7,9-tetramethyluric acid*

Pyrene-1,3,7,9-tetramethyluric acid is a molecular compound where there are strong indications of disorder qualitatively similar to that found in pyrene-pyromellitic dianhydride. The crystal structure of pyrene-tetramethyluric acid at 300 °K was determined by Damiani *et al.* (1965) and electron-density syntheses in the molecular planes of the two components have been calculated by Damiani, Giglio & Ripamonti (1967). No difference syntheses have been reported. The electron-density syntheses are very similar to those obtained here for pyrene-pyromellitic dianhydride. Both molecules show evidence of in-plane libration, with rather poor definition of both molecules. It is clearly desirable to analyze as well as the distance-dependence of the Debye-Waller factors and this has been done here by converting the anisotropic Debye-Waller factors given by Damiani *et al.* (1965) to equivalent isotropic Debye-Waller factors using Hamilton's (1959) method. These B_j values are plotted against distance from the molecular centres of gravity in

PYRENE-PYROMELLITIC DIANHYDRIDE AT 110 AND 300 °K 657

figure 17. These results show, as Damiani *et al.* (1965) point out, that both molecules are oscillating about their centres with pyrene oscillating more than tetramethyluric acid. Both the general form of the curves in figure 17 and the actual B_j values are very similar to those found for pyrene-pyromellitic dianhydride at 300 °K. As the melting point of pyrene-tetramethyluric acid is 207 °C (Weil-Malherbe 1946) abnormally large temperature factors would not be expected for this molecular compound. Thus the occurrence of

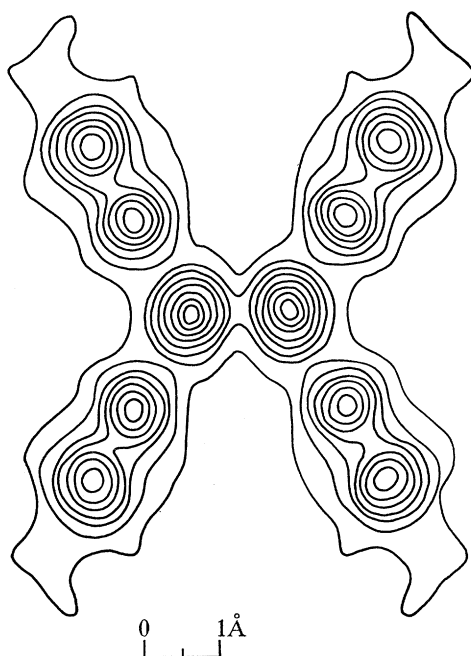


FIGURE 14. Electron-density synthesis in the plane of the tetracyanoethylene molecule in naphthalene-tetracyanoethylene. The difference synthesis is featureless and is not reproduced. For other details see caption to figure 13.

positional disorder is clearly indicated. Any transformation to an ordered structure must take place below about 100 °K as diffraction photographs at this temperature show no evidence of a structure different from that at 300 °K. In contrast to this, it has been found that naphthalene-tetracyanoethylene transforms to a triclinic structure below about 200 °K (Bernstein & Herbstein 1967).

(d) *Indications of different types of disordered structure*

The disordered structures of four molecular compounds have so far been studied in some detail. In two of these (naphthalene-tetracyanoethylene, naphthalene-1,2,4,5-tetracyanobenzene) only the electron-donor molecule is disordered at 300 °K, while in the other two (pyrene-pyromellitic dianhydride, pyrene-tetramethyluric acid) both donor and acceptor molecules appear to be disordered to roughly equal extents at 300 °K. Thus there are at present indications of two rather different types of molecular arrangement in disordered molecular compounds. More detailed analyses of the difference syntheses will require more accurate intensity measurements as both disorder and thermal-libration effects will have to be taken into account.

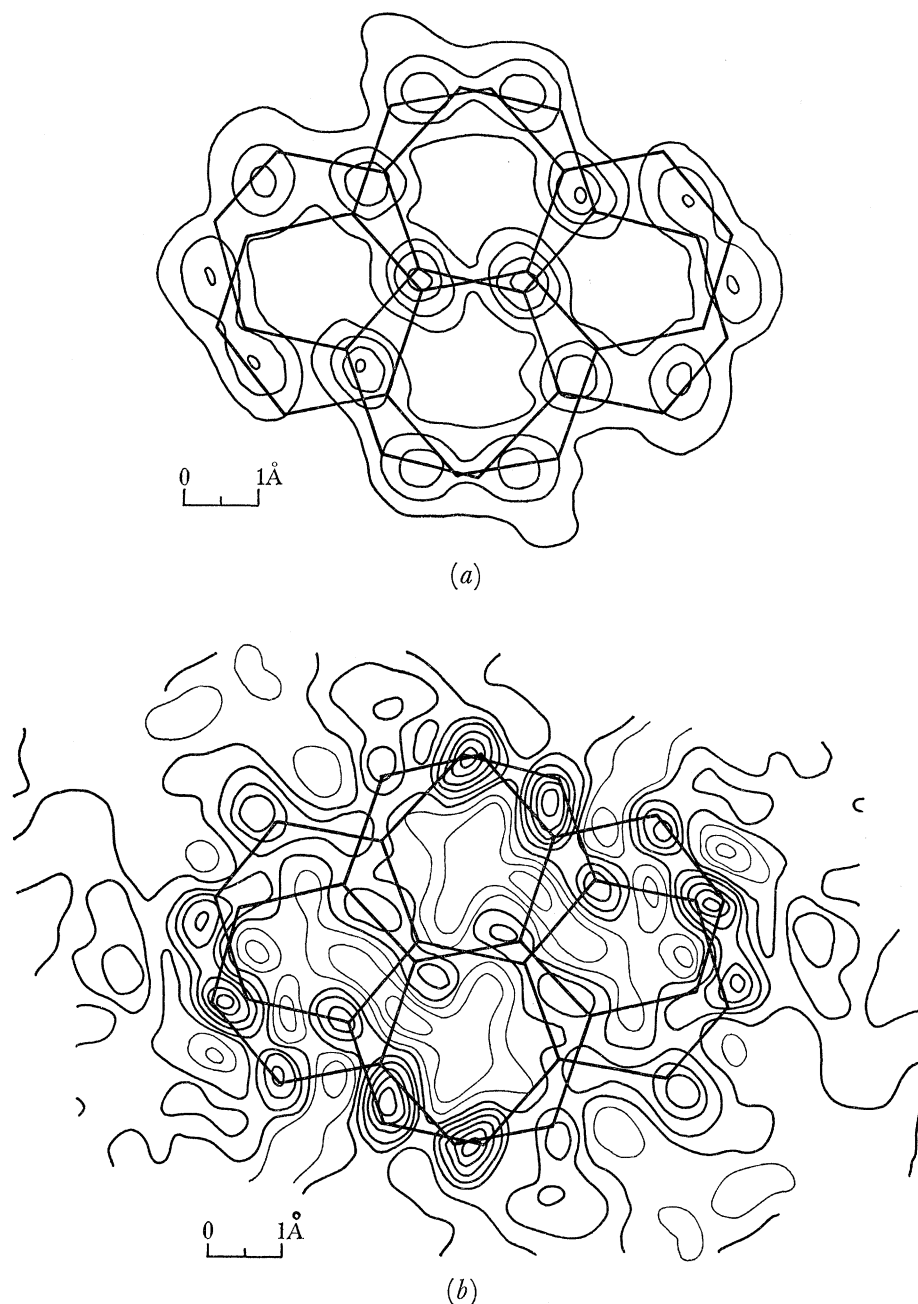


FIGURE 15. Electron-density and difference synthesis in the plane of the pyrene molecule in pyrene-pyromellitic dianhydride at 300 °K. Contour intervals are at $2 \text{ e } \text{Å}^{-3}$, starting at zero in electron-density map and at $0.2 \text{ e } \text{Å}^{-3}$ (thick lines zero and positive contours, thin lines negative contours) in the difference map. The two molecular orientations shown have been chosen to fit the difference map rather than the electron-density map.

NATURE OF THE TRANSFORMATION

Although the transformation between the high- and low-temperature structures has not yet been studied in detail, the available evidence leaves no doubt that it is an order-disorder transformation similar in type to transformations already reported for many one-component crystals (e.g. aniline hydrobromide (Suga 1961; Taguchi 1961; Nitta *et al.*

PYRENE-PYROMELLITIC DIANHYDRIDE AT 110 AND 300 °K 659

1961)). The principal lines of evidence on which this conclusion is based are: (i) the minor differences between the cell dimensions of high and low-temperature phases; (ii) the relatively large temperature interval ($\sim 40^\circ$) over which transformation occurs (see figure 2); (iii) the absence of any sharp peaks in a differential-scanning calorimeter trace

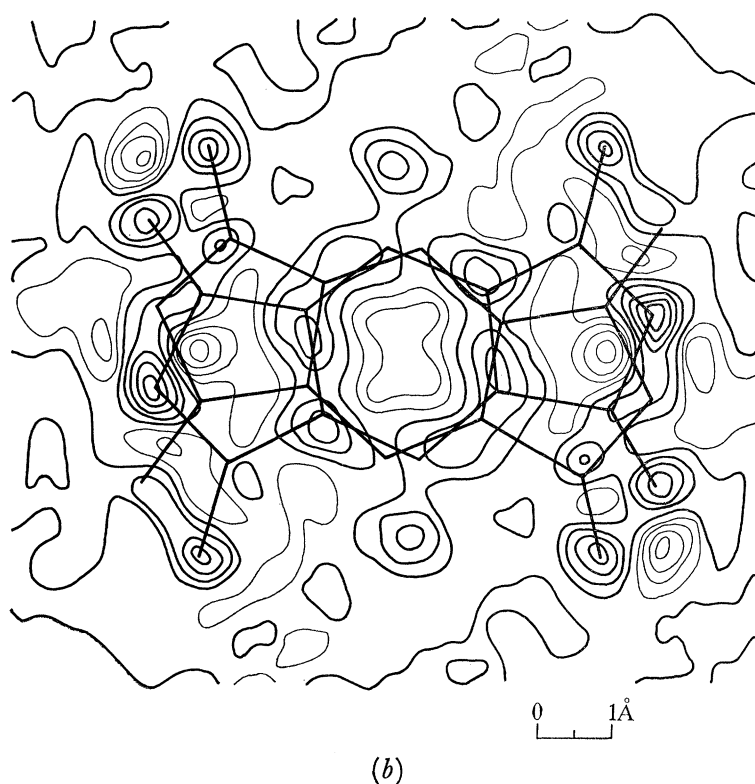
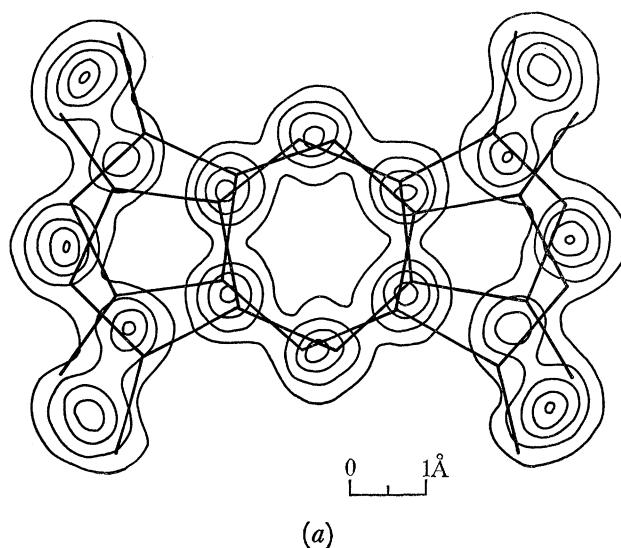


FIGURE 16. Electron-density and difference synthesis in the plane of the pyromellitic dianhydride molecule in pyrene-pyromellitic dianhydride at 300 °K (contour intervals as in figure 15). The two molecular orientations shown have been chosen to fit the difference map rather than the electron-density map.

taken over the temperature interval 150–300 °K; (iv) the present results for the structures of the crystals at 110 and 300 °K.

Much valuable information could be obtained from specific heat–temperature curves for pyrene-pyromellitic dianhydride, and for other analogous molecular compounds.

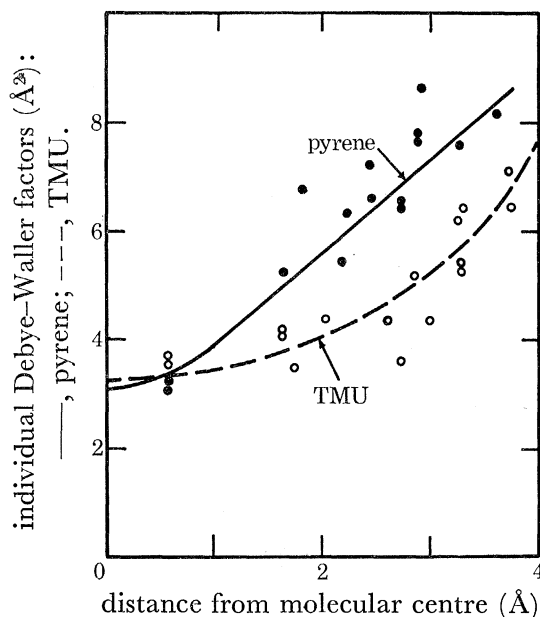


FIGURE 17. The equivalent isotropic Debye-Waller factors of the individual atoms in pyrene-1,3,7,9-tetramethyluric acid at room temperature (Damiani *et al.* 1965). Separate curves are shown for the two molecules.

CONCLUDING REMARKS

In the present paper we have shown that an order–disorder transformation occurs in pyrene-pyromellitic dianhydride at about 200 °K; the existence of disordered high-temperature structures in three other similar molecular compounds suggests that pyrene-pyromellitic dianhydride exemplifies a fairly widespread behaviour. Thus degree of order appears likely to play an important role in the crystal chemistry of *H*-molecular compounds. However the order–disorder transformation temperature will probably vary widely among the molecular compounds and has been determined only for isolated examples. Consequently there is little evidence available about the physical (thermodynamic) condition of those materials whose crystal structures have been determined apart from what can be inferred from the diffraction pattern. An immediate conclusion is that it is desirable to first determine the thermal properties as a function of temperature of any crystal whose structure is of interest and where the possibility of a temperature-dependent degree of order is suspected. Then the crystal structure can be determined at a strategically chosen rather than an essentially arbitrary temperature and will refer to a material in a defined thermodynamic condition.

We are grateful to all those workers who have given us copies of their various computer programs (see p. 644), to Dr D. Rabinovich (Weizmann Institute) for the electron-density calculations in the molecular planes, and to Professor B. L. van Duuren (New York) for a sample of pyrene-tetramethyluric acid.

APPENDIX—CALCULATION OF BOND-ANGLES IN THE CENTRAL RING OF THE
PYROMELLITIC DIANHYDRIDE MOLECULE

A simple calculation gives the values of the bond angles expected in the central ring of the pyromellitic dianhydride molecule on the hypothesis that the angle strain energy at the atoms of this ring is minimal. We assume that the molecule has $m m m$ symmetry, that the internal angles in the five-membered rings are 108.0° and that the unstrained values of the bond angles at the carbon atoms of the six-membered ring are 120° . Let the angle strains (in degrees) be noted $\delta\alpha$, $\delta\beta$ and $\delta\gamma$; k is the angle-bending force constant and is assumed to be equal for all angles.

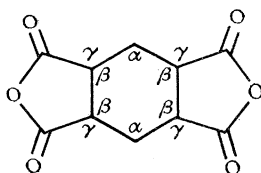


FIGURE A1.

The angle strain energy is

$$E = \frac{1}{2}k \{2(\delta\alpha)^2 + 4(\delta\beta)^2 + 4(\delta\gamma)^2\}. \quad (\text{A } 1)$$

Furthermore

$$2(\delta\alpha) = -4(\delta\beta),$$

$$\delta\beta = \delta\gamma = 120 - 108.0 = 12.0^\circ.$$

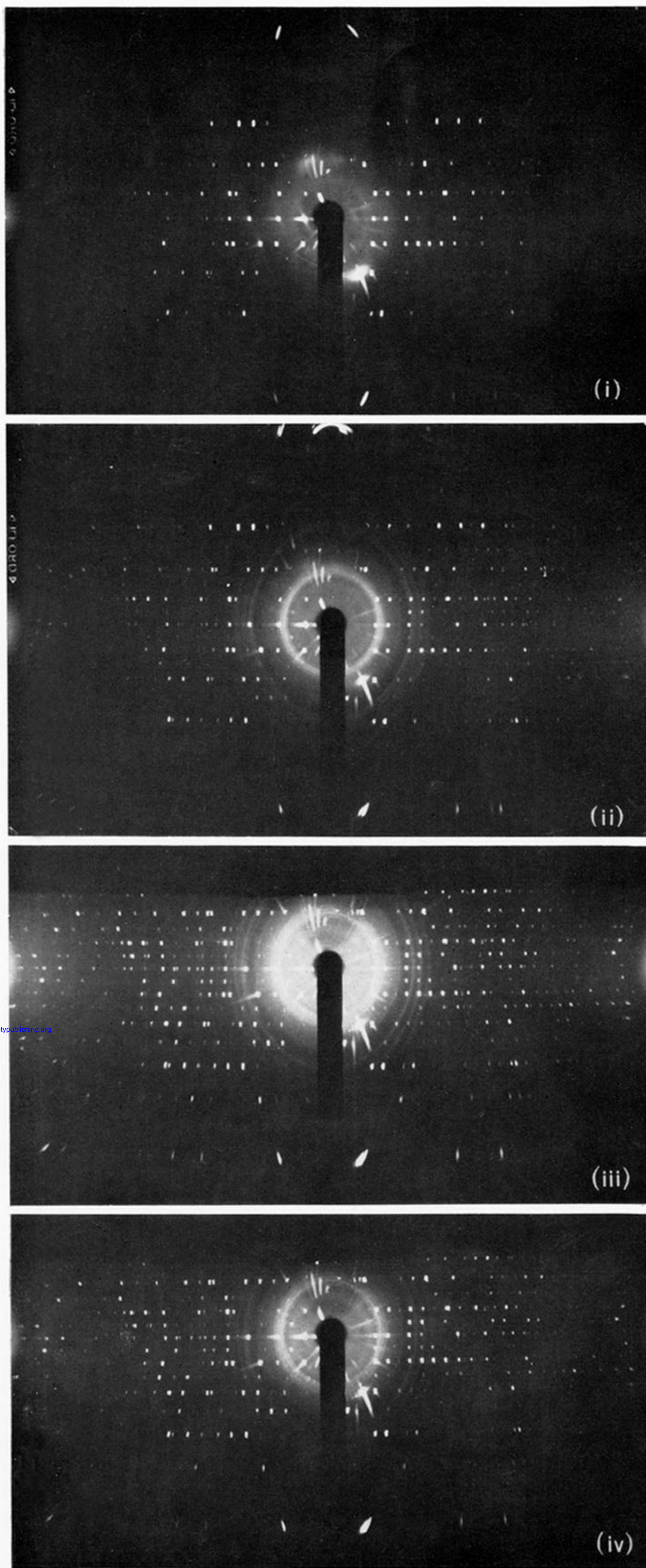
Substituting in (A 1) we obtain $E = k\{8(\delta\beta)^2 - 48(\delta\beta) + 288\}$.

For minimal strain energy $\partial E/\partial(\delta\beta) = 0 = 16(\delta\beta) - 48$, whence $\delta\beta = 3.0^\circ$.
The experimental value is 3.5° .

REFERENCES

- Bailey, A. S. & Prout, C. K. 1965 *J. Chem. Soc.* p. 4867.
 Bernstein, T. & Herbstein, F. H. 1967 Unpublished results.
 Boeyens, J. C. A. & Herbstein, F. H. 1965a *J. Phys. Chem.* **69**, 2153.
 Boeyens, J. C. A. & Herbstein, F. H. 1965b *J. Phys. Chem.* **69**, 2160.
 Boeyens, J. C. A. & Herbstein, F. H. 1967 *J. Phys. Chem.* **71**, 4587.
 Brown, D. S., Wallwork, S. C. & Wilson, A. 1964 *Acta Crystallogr.* **17**, 168.
 Brown, R. D. 1950 *J. Chem. Soc.* p. 691.
 Buerger, M. J. 1942 *X-ray crystallography*, p. 229. New York: Wiley.
 Camerman, A. & Trotter, J. 1965 *Acta Crystallogr.* **18**, 636.
 Cruickshank, D. W. J. 1956 *Acta Crystallogr.* **9**, 915.
 Cruickshank, D. W. J. 1961 *Acta Crystallogr.* **14**, 896.
 Cruickshank, D. W. J. & Pilling, D. E. 1961 In *Computing methods and the phase problem*, p. 32. Oxford: Pergamon Press.
 Cruickshank, D. W. J. & Sparks, R. A. 1960 *Proc. Roy. Soc. A* **258**, 270.
 Damiani, A., DeSantis, P., Giglio, E., Liquori, A. M., Puliti, R. & Ripamonti, A. 1965 *Acta Crystallogr.* **19**, 340.
 Damiani, A., Giglio, E. & Ripamonti, A. 1967 *Acta Crystallogr.* **22**, 692.
 Hamilton, W. C. 1955 *Acta Crystallogr.* **8**, 185.
 Hamilton, W. C. 1959 *Acta Crystallogr.* **12**, 609.
 Hanson, A. W. 1963 *Acta Crystallogr.* **16**, 1147.
 Herbstein, F. H. 1963 *Acta Crystallogr.* **16**, 255.

- Herbstein, F. H. & Snyman, J. A. 1966 *Acta Crystallogr.* **21**, A 115.
- Higgs, P. W. 1955 *Acta Crystallogr.* **8**, 99.
- Ikemoto, I. & Kuroda, H. 1968 *Acta Crystallogr.* B **24**, 383.
- Ilmet, I. & Kopp, L. 1966 *J. Phys. Chem.* **70**, 3371.
- Klein, K. P. 1963 M.Sc. thesis, University of Cape Town.
- Knott, G. 1940 *Proc. Phys. Soc. Lond.* **52**, 229.
- Kooyman, E. C. & Fahrenhorst, E. 1953 *Trans. Faraday Soc.* **49**, 58.
- Kumakura, S., Iwasaki, F. & Saito, Y. 1967 *Bull. Chem. Soc. Japan* **40**, 1826.
- Marsh, R. E., Ubell, E. & Wilcox, H. E. 1962 *Acta Crystallogr.* **15**, 35.
- Nitta, I., Watanabe, T. & Taguchi, I. 1961 *Bull. Chem. Soc. Japan* **34**, 1405.
- Palenik, G. J. 1964 *Acta Crystallogr.* **17**, 687.
- Powell, H. M. & Huse, G. 1943 *J. Chem. Soc.* p. 435.
- Pritchard, H. O. & Sumner, F. H. 1954 *Proc. Roy. Soc. A* **226**, 128.
- Prout, C. K. & Powell, H. M. 1965 *J. Chem. Soc.* p. 4882.
- Prout, C. K. & Wallwork, S. C. 1966 *Acta Crystallogr.* **21**, 449.
- Robertson, J. M. 1943 *J. Sci. Instrum.* **20**, 175.
- Robertson, J. M. & White, J. G. 1947 *J. Chem. Soc.* p. 358.
- Snyman, J. A. 1965 M.Sc. thesis, University of South Africa, Pretoria.
- Suga, H. 1961 *Bull. Chem. Soc. Japan* **34**, 426.
- Taguchi, I. 1961 *Bull. Chem. Soc. Japan* **34**, 392.
- Vroelant, C. & Daudel, R. 1949 *C. r. hebd. Séanc. Acad. Sci., Paris* **228**, 399.
- Weil-Malherbe, H. 1946 *Biochem. J.* **40**, 351.
- Williams, R. M. & Wallwork, S. C. 1967 *Acta Crystallogr.* **22**, 899.
- Wilson, A. J. C. 1942 *Nature, Lond.* **150**, 152.



Downloaded from rsta.royalsocietypublishing.org

FIGURE 2. Four successive 15° c -axis oscillation photographs of a pyrene-pyromellitic dianhydride single crystal taken at: (i) 293°K , (ii) 200°K , (iii) 170°K , (iv) 110°K respectively. The same oscillation range was used for each photograph. The exposure time for each photograph was 60 min ($\text{Cu } K\alpha$, Ni filter, 30 kV, 20 mA). The powder lines on the photographs are due to ice crystals.