their standard deviations. The lengths of principal axes of the L tensor were 16, 7, and $4(°)^2$, and implied corrections to the interatomic distances were in the range 0·002–0·004 Å. We have ignored these corrections.

While the relatively large standard deviations in the anisotropic temperature parameters of the hydrogen atoms preclude detailed discussion of their significance, we are comforted to note that the implied libration ellipsoids (Fig. 2) are not totally unreasonable.

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A Neutron Diffraction Study of the Crystal Structure of Pyrene, $C_{16}H_{10}$

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The crystal structure of pyrene, $C_{16}H_{10}$, has been redetermined at room temperature by means of neutron diffraction. Least-squares refinement of positional, thermal, scale, and extinction parameters gave an R value of 0·034 for 1008 reflexions [with $F^2 > 2\sigma(F^2)$] and 236 parameters; the weighted R value is 0·032. The bond distances agree with those predicted by molecular orbital calculations; the discrepancy between earlier observations and the theoretical values stems from the fact that the earlier values were determined by X-ray diffraction, which locates the centre of the charge cloud rather than the centre of the atom. A correlation has been found for the differences between bond distances determined by X-rays and by neutrons with a function of the bond orders.

Introduction

The crystal structure of pyrene has been previously determined by Robertson & White (1947) from two-dimensional data, and by Camerman & Trotter (1965), henceforth referred to as C & T, from three-dimensional data. Both studies were made by means of X-ray diffraction.

The bond distances obtained by C & T differ considerably from those calculated by SCF-LCAO-Π-MO methods [*e.g.* Warren & Yandle (1968)]. We have therefore determined the structure yet again, this time by means of neutron diffraction so as to obtain more accurate measurements of the bond lengths. The present determination was carried out at room temperature.

Whilst this work was being carried out we learnt from Allmann (1970) that he had repeated the X-ray work on pyrene. There are marked differences between the X-ray results and those obtained by neutron

diffraction. We attribute the difference to the non-sphericity of the electron clouds and correlate the differences between the bond distances as obtained by the two methods with a function of the bond order.

Crystal data

Pyrene, $C_{16}H_{10}$; $M = 202·2$; m.p. 150°C. Monoclinic, $a = 13·649 \pm 0·01$, $b = 9·256 \pm 0·01$, $c = 8·470 \pm 0·01$ Å, $\beta = 100·28° \pm 0·04°$, $U = 1052·9$ Å^3. The cell dimensions are those of C & T. $D_M = 1·27$, $Z = 4$. The linear absorption coefficient for neutrons ($\lambda = 1·025$ Å) $= 1·55$ cm^{-1}. The systematic absences are: $h0l$ with h odd, $0k0$ with k odd; the space group is $P2_1/a$ (C_{2h}^5, No. 14).

Experimental

The crystal used for data collection was approximately cylindrical, with the cylinder axis along the [001] direc-

CRYSTAL STRUCTURE OF PYRENE, $C_{16}H_{10}$

Table 1. *Observed and calculated structure factors* ($\times 10$)

Table 2. *Atomic coordinates* ($\times 10^5$) *expressed as fractions of the cell edges*

The estimated standard deviations (in fractions of cell edges $\times 10^5$) are given in parentheses.

	x/a	y/b	z/c
C(1)	28146 (18)	−4125 (25)	41456 (29)
C(2)	29365 (15)	2457 (22)	27270 (29)
C(3)	22965 (13)	−771 (18)	12844 (24)
C(4)	24096 (15)	5720 (21)	−1973 (27)
C(5)	17783 (16)	2502 (22)	−15876 (26)
C(6)	9800 (14)	−7557 (19)	−16095 (23)
C(7)	3315 (17)	−10959 (26)	−30127 (26)
C(8)	−4367 (17)	−20713 (27)	−30042 (30)
C(9)	−5747 (15)	−27280 (24)	−15874 (31)
C(10)	682 (13)	−24163 (18)	−1365 (25)
C(11)	−398 (15)	−30658 (22)	13503 (29)
C(12)	5839 (16)	−27524 (21)	27387 (27)
C(13)	13914 (14)	−17466 (18)	27559 (23)
C(14)	20577 (18)	−14134 (24)	41660 (25)
C(15)	15091 (12)	−10765 (17)	13034 (21)
C(16)	8484 (12)	−14100 (17)	−1484 (21)
H(1)	33033 (42)	−1684 (63)	52300 (69)
H(2)	35285 (35)	10229 (56)	27111 (69)
H(4)	30123 (37)	13070 (52)	−1986 (71)
H(5)	18702 (42)	7616 (56)	−26842 (62)
H(7)	4394 (43)	−5841 (65)	−41017 (57)
H(8)	−9439 (42)	−23365 (73)	−40938 (71)
H(9)	−11709 (37)	−34934 (62)	−15871 (82)
H(11)	−6478 (38)	−38321 (57)	13549 (77)
H(12)	4891 (43)	−32458 (57)	38439 (69)
H(14)	19801 (46)	−19427 (62)	52686 (61)

tion. The mean diameter was $4\cdot15\pm0\cdot15$ mm and the length $5\cdot45\pm0\cdot15$ mm.

Three-dimensional neutron data were collected on an automatic Hilger–Ferranti four-circle diffractom-

eter located at the DR3 reactor of the Danish Atomic Energy Commission Research Establishment Risø.

The wavelength of the monochromatic neutron beam was $1\cdot025\pm0\cdot001$ Å and the flux at the specimen was $0\cdot9\times10^6$ n.cm^{-2} sec^{-1}. That part of the beam imping-ing on the crystal was uniform to $\pm5\%$. The reflexions were measured in the symmetrical A setting (Furnas & Harker, 1955) with the crystal's c^* axis parallel to the φ axis. The ω–2θ scan technique was used and counts for each step were recorded. The total range of measurement for a reflexion was $2\cdot88°$. Within $\pm0\cdot96°$ of the expected centre of the peak the step size was $0\cdot04°$; elsewhere a step of $0\cdot08°$ was used.

For $\sin\theta/\lambda\leq0\cdot30$, all four symmetry-related reflex-ions were recorded. For $0\cdot30<\sin\theta/\lambda\leq0\cdot555$, only reflexions with $l\geq0$ were measured. This gave a total of 3500 reflexions. A standard reflexion (240) was meas-ured every 16 reflexions.

Intensity data were reduced to structure factors using the program *DRAM* (Krebs Larsen & Leh-mann, 1970) which determines the limits of the peak so that $\sigma_c(I)/I$ is as small as possible, where I is the integrated intensity and $\sigma_c(I)$ is the standard devia-tion based on the counting statistics. For the 812 weakest reflexions [those for which $F^2<3\sigma(F^2)$ and $|F|<9\cdot3$] it was found to be better to use fixed posi-tions for the limits of the peak.

After averaging symmetry-related reflexions, the number of independent reflexions was 1492, of which 484 had $I<2\sigma_c(I)$ and were excluded from the final refinement.

The variation of the intensity of the standard reflex-ion was of the order of 2% during a reactor operation

Table 3. *Thermal parameters and their estimated standard deviations* (*in* Å$^2\times10^{-4}$)

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
C(1)	841 (15)	768 (14)	824 (16)	93 (12)	−15 (13)	−149 (12)
C(2)	571 (12)	647 (12)	1010 (17)	−38 (10)	22 (12)	−230 (12)
C(3)	498 (10)	452 (10)	803 (15)	−12 (8)	183 (10)	−64 (9)
C(4)	656 (13)	535 (11)	996 (17)	−69 (10)	332 (12)	100 (11)
C(5)	761 (13)	653 (12)	851 (16)	60 (10)	384 (12)	185 (11)
C(6)	602 (12)	575 (11)	579 (12)	160 (9)	166 (9)	77 (9)
C(7)	782 (15)	910 (16)	618 (13)	286 (12)	17 (11)	−5 (12)
C(8)	694 (14)	967 (17)	859 (17)	182 (13)	−50 (13)	−167 (13)
C(9)	506 (12)	744 (14)	1119 (20)	−16 (10)	9 (12)	−223 (13)
C(10)	445 (10)	458 (10)	888 (15)	−2 (8)	152 (10)	−21 (10)
C(11)	615 (12)	572 (12)	1118 (19)	−99 (10)	316 (13)	103 (12)
C(12)	765 (14)	616 (12)	856 (16)	47 (10)	341 (12)	212 (11)
C(13)	612 (12)	501 (10)	604 (13)	95 (9)	197 (10)	68 (9)
C(14)	922 (16)	785 (14)	537 (13)	219 (12)	68 (12)	−25 (10)
C(15)	443 (10)	360 (8)	598 (11)	32 (7)	158 (8)	−1 (8)
C(16)	429 (9)	391 (9)	600 (11)	53 (7)	138 (8)	6 (8)
H(1)	1164 (41)	1211 (42)	1207 (45)	118 (34)	−224 (34)	−335 (35)
H(2)	859 (33)	980 (34)	1538 (49)	−327 (27)	85 (32)	−300 (32)
H(4)	942 (34)	875 (31)	1625 (50)	−359 (26)	409 (33)	122 (31)
H(5)	1247 (40)	1125 (37)	1064 (37)	13 (31)	494 (31)	447 (30)
H(7)	1363 (45)	1453 (47)	747 (32)	433 (40)	189 (29)	228 (30)
H(8)	991 (39)	1628 (55)	1177 (47)	167 (38)	−282 (35)	−328 (39)
H(9)	732 (31)	1183 (41)	1827 (58)	−275 (29)	172 (34)	−294 (38)
H(11)	913 (34)	1026 (35)	1803 (55)	−375 (28)	439 (35)	223 (34)
H(12)	1229 (42)	1074 (36)	1220 (42)	−34 (31)	511 (34)	391 (32)
H(14)	1398 (46)	1244 (40)	765 (32)	198 (35)	183 (31)	193 (28)

Table 4. **T, L,** *and* **S** *and their estimated standard deviations, relative to an orthogonal axial system with* **A** *parallel to* **a** *and* **C** *parallel to* **c***

T′, L′, and S′ are T, L, and S referred to the molecules inertial axes, the first axis along the molecule and the third perpendicular to the molecule. T is in $Å \times 10^{-4}$, L in $(°)^2$, and S in $(°)$ $Å \times 10^{-4}$.

Carbon atoms only

Arbitrary orthogonal system

$$T = \begin{pmatrix} 387 & 48 & 63 \\ & 357 & 10 \\ & & 603 \end{pmatrix} \quad \sigma(T) = \begin{pmatrix} 10 & 11 & 7 \\ & 12 & 8 \\ & & 8 \end{pmatrix}$$

Inertial axial system

$$T' = \begin{pmatrix} 321 & -9 & 20 \\ & 415 & -50 \\ & & 610 \end{pmatrix}$$

$$L = \begin{pmatrix} 17·86 & -6·34 & 2·48 \\ & 17·15 & 2·42 \\ & & 15·70 \end{pmatrix} \quad \sigma(L) = \begin{pmatrix} 0·74 & 0·55 & 0·57 \\ & 0·57 & 0·54 \\ & & 1·17 \end{pmatrix} \quad L' = \begin{pmatrix} 23·56 & 0·01 & -1·33 \\ & 9·29 & -0·23 \\ & & 17·86 \end{pmatrix}$$

$$S = \begin{pmatrix} 625 & 567 & -155 \\ 453 & 32 & 550 \\ -327 & -327 & -659 \end{pmatrix} \quad \sigma(S) = \begin{pmatrix} 269 & 103 & 166 \\ 92 & 252 & 138 \\ 155 & 143 & 1507* \end{pmatrix} \quad S' = \begin{pmatrix} -151 & -519 & 194 \\ -39 & 528 & 1001 \\ -165 & 329 & -379 \end{pmatrix}$$

R.m.s. delta = 0·0023 (for carbon atoms only).

All atoms

$$T = \begin{pmatrix} 329 & 115 & 84 \\ & 281 & 10 \\ & & 666 \end{pmatrix} \quad \sigma(T) = \begin{pmatrix} 40 & 41 & 28 \\ & 46 & 29 \\ & & 30 \end{pmatrix} \quad T' = \begin{pmatrix} 186 & -13 & 34 \\ & 424 & -73 \\ & & 666 \end{pmatrix}$$

$$L = \begin{pmatrix} 22·99 & -4·04 & 5·31 \\ & 20·21 & 2·38 \\ & & 26·84 \end{pmatrix} \quad \sigma(L) = \begin{pmatrix} 1·56 & 1·19 & 1·16 \\ & 1·28 & 1·10 \\ & & 2·39 \end{pmatrix} \quad L' = \begin{pmatrix} 24·87 & -·19 & -1·64 \\ & 15·16 & -1·32 \\ & & 30·00 \end{pmatrix}$$

$$S = \begin{pmatrix} 670 & 727 & -275 \\ 355 & 46 & 556 \\ -487 & -693 & -716 \end{pmatrix} \quad \sigma(S) = \begin{pmatrix} 727 & 292 & 470 \\ 275 & 693 & 401 \\ 430 & 390 & 319* \end{pmatrix} \quad S' = \begin{pmatrix} -171 & -729 & 159 \\ 139 & 755 & 1053 \\ -268 & 155 & -583 \end{pmatrix}$$

R.m.s. delta = 0·0052 (all atoms).

* The trace of S has been set to zero, e.s.d. of deleted S (3,3) is given.

period of three weeks. The structure factors were corrected for this variation and also for absorption. The absorption correction was carried out by using a modified version of Wells's (1960) program and treating the cylinder as a 16-sided prism. The linear absorption coefficient was determined by measuring the transmission of slabs of pyrene of thickness 1·40, 1·95, 3·00, 3·08, and 4·80 mm and was found to be $\mu = 1·55$ cm^{-1} with a standard deviation of 0·01 cm^{-1}.

Refinement

Refinement was carried out using Grønbæk Hazell's (1966) block-diagonal least-squares program G403. Starting values for the positional parameters of all atoms and the anisotropic temperature factor coefficient of carbon atoms were those of C & T. Arbitrary values were assigned to the temperature factor coefficients of the hydrogen atoms.

The scattering lengths for C and H were $0·665 \times 10^{-12}$ and $-0·372 \times 10^{-12}$ cm respectively, the values recommended by the Neutron Diffraction Commission (1969).

Refinement converged at an R value of 0·057. An isotropic extinction parameter, g, (Zachariasen, 1967) was introduced into the refinement in the manner proposed by Larson (1967):

$$F_c^* = F_c k (1 + g \frac{dA^*}{Ad\mu} \frac{1}{\sin 2\theta} F_c^2)^{-1/2}$$

where k is the scale factor, F_c^* the calculated structure factor, F_c the structure factor calculated neglecting extinction, A the transmission factor, and $dA^*/d\mu$ the change in absorption-correction factor with respect to the change in the linear absorption coefficient, μ. The quantity $dA^*/d\mu$ was calculated during the absorption correction. The final R index for the 1008 reflexions for which $F^2 > 2\sigma$ (F^2) was 0·034. 236 parameters were refined; the weighted R value was 0·032.

The weighting scheme used in the refinement was $w = 1/\sigma^2$ where

$$\sigma = \sqrt{\sigma_c(F^2)} + (1 + K)F^2 - |F| .$$

The parameter K was varied so that $\langle w|F_{obs} - F_{calc}| \rangle$ varied as little as possible with the magnitude of F_{obs}. The final value of K was 0·02, and the extinction factor was $2·12 \times 10^{-4}$.

The observed and calculated structure factors are listed in Table 1, the final atomic coordinates and thermal parameters in Tables 2 and 3.

Correction of parameters for thermal motion

The thermal motion of the carbon atoms was analysed, assuming that the molecule could be treated as

a rigid body, by the method of Schomaker & Trueblood (1968). Two calculations were performed, one in which the carbon framework was taken as the rigid body and a second in which all atoms were included. For the latter the contribution of each atom was weighted inversely as the absolute value of its scattering length. The values of **T**, **L**, and **S** together with their estimated standard deviations, and the r.m.s. value of Δu_{ij} where Δu_{ij} is the difference between u_{ij} observed and u_{ij} calculated, are given in Table 4.

The rigid-body model assumes a negligible amplitude for internal vibration modes and so underestimates the displacements of the hydrogen atoms (Pawley, 1971a, b). We have therefore corrected the bond distances for thermal vibration by using **L** calculated for the carbon framework alone, and have added an extra correction to the carbon–hydrogen bond distances assuming that the hydrogen atoms ride on the carbon framework.

The mean values of the differences between the observed thermal vibration parameters and the values calculated neglecting internal vibration modes, Δu_1, Δu_2, and Δu_3 where 1 is along the bond, 2 perpendicular to the bond and in the plane of the molecule, and 3 perpendicular to the molecule, are shown in Table 5, as are the values predicted by Pawley and the values he obtained from a constrained refinement in which mmm symmetry was assumed for the molecule. His refinements were carried out using our data.

Table 5. *The mean values (in Å^2) of the differences between the observed thermal vibration parameters for the hydrogen atoms and the values calculated neglecting internal vibration modes*

Δu_1 is along the bond, Δu_3 perpendicular to the molecule, and Δu_2 perpendicular to 1 and 3. The values are compared with those predicted by Pawley, and those he obtained from a constrained refinement using our data.

	Δu	$\sigma(\Delta u)$	Δu(Pawley)	Δu_{obs} (Pawley)
$\langle \Delta u_1 \rangle$	0·008	0·002	0·005	0·005
$\langle \Delta u_2 \rangle$	0·013	0·003	0·013	0·016
$\langle \Delta u_3 \rangle$	0·028	0·002	0·021	0·029
$\langle \Delta u_{iso} \rangle$	0·016	0·001	0·013	0·014

Discussion

The crystal structure is essentially the same as that previously described. The main difference is in the greater precision of the atomic coordinates and thermal parameters, both for the carbon atoms and for the hydrogen atoms. Since these parameters have been determined by neutron diffraction they are free from the systematic errors arising from the asphericity of the electron clouds. The bond lengths and angles are shown in Tables 6 and 7. Close approaches between molecules are given in Table 8.

Table 6. *Observed bond lengths, l, and bond lengths, l_{corr}, corrected for thermal vibration assuming rigid-body motion*

For C–H distances the extra correction for riding motion is included in the final column. The lower case letters refer to the notation in Fig. 1. Estimated standard deviations, $\sigma(l)$, are given in parentheses.

		l	$\sigma(l)$	l_{corr}	l_{corr} + riding
a	C(1)—C(2)	1·383	(3) Å	1·392 Å	
a	C(7)—C(8)	1·385	(3)	1·393	
a	C(8)—C(9)	1·388	(4)	1·396	
a	C(14)-C(1)	1·390	(3)	1·398	
b	C(2)—C(3)	1·402	(3)	1·409	
b	C(6)—C(7)	1·386	(3)	1·392	
b	C(9)—C(10)	1·407	(3)	1·414	
b	C(13)-C(14)	1·400	(3)	1·407	
c	C(3)—C(15)	1·420	(2)	1·429	
c	C(6)—C(16)	1·418	(3)	1·426	
c	C(10)-C(16)	1·416	(2)	1·425	
c	C(13)-C(15)	1·412	(3)	1·421	
d	C(3)—C(4)	1·424	(3)	1·433	
d	C(5)—C(6)	1·431	(3)	1·439	
d	C(10)-C(11)	1·427	(3)	1·435	
d	C(12)-C(13)	1·435	(3)	1·444	
e	C(15)-C(16)	1·423	(2)	1·430	
f	C(11)-C(12)	1·358	(3)	1·365	
f	C(4)—C(5)	1·362	(3)	1·369	
g	C(1)—H(1)	1·059	(6)	1·064	1·074 Å
g	C(8)—H(8)	1·079	(6)	1·084	1·100
h	C(2)—H(2)	1·084	(5)	1·090	1·109
h	C(7)—H(7)	1·070	(6)	1·077	1·099
h	C(9)—H(9)	1·079	(6)	1·085	1·113
h	C(14)-H(14)	1·076	(6)	1·083	1·098
i	C(11)-H(11)	1·092	(6)	1·099	1·126
i	C(12)-H(12)	1·072	(6)	1·078	1·091
i	C(4)—H(4)	1·068	(5)	1·074	1·097
i	C(5)—H(5)	1·070	(6)	1·076	1·098

Table 7. *Bond angles corrected for thermal vibration, with their estimated standard deviations*

The lower case letters refer to the notation in Fig. 1, *e.g.* ab means the angle between bonds a and b.

aa	C(14)-C(1)—C(2)	120·66 (20)°
aa	C(7)—C(8)—C(9)	120·71 (20)
ab	C(1)—C(2)—C(3)	120·66 (19)
ab	C(1)—C(14)-C(13)	120·46 (20)
ab	C(6)—C(7)—C(8)	120·79 (21)
ab	C(8)—C(9)—C(10)	120·36 (20)
bc	C(2)—C(3)—C(15)	118·94 (18)
bc	C(14)-C(13)-C(15)	119·22 (17)
bc	C(7)—C(6)—C(16)	119·35 (18)
bc	C(9)—C(10)—C(16)	118·76 (19)
bd	C(2)—C(3)—C(4)	121·94 (17)
bd	C(12)-C(13)—C(14)	121·97 (19)
bd	C(5)—C(6)—C(7)	121·82 (19)
bd	C(9)—C(10)—C(11)	122·52 (18)
cc	C(3)—C(15)—C(13)	120·05 (15)
cc	C(6)—C(16)-C(10)	120·04 (16)
cd	C(4)—C(3)—C(15)	119·13 (16)
cd	C(12)-C(13)—C(15)	118·82 (16)
cd	C(5)—C(6)—C(16)	118·84 (16)
cd	C(11)-C(10)—C(16)	118·73 (17)
df	C(3)—C(4)—C(5)	121·17 (19)
df	C(11)-C(12)-C(13)	120·69 (20)
df	C(4)—C(5)—C(6)	121·06 (20)
df	C(10)-C(11)—C(12)	121·66 (19)
ce	C(3)—C(15)—C(16)	119·70 (16)
ce	C(13)-C(15)—C(16)	120·26 (15)
ce	C(6)—C(16)-C(15)	120·11 (15)

Table 7 (cont.)

ce	C(10)–C(16)–C(15)	119·85 (17)
ag	C(2)—C(1)—H(1)	120·28 (40)
ag	C(14)-C(1)—H(1)	119·07 (40)
ag	C(7)—C(8)—H(8)	120·98 (42)
ag	C(9)—C(8)—H(8)	118·31 (41)
ah	C(1)—C(2)—H(2)	120·63 (36)
ah	C(1)—C(14)-H(14)	120·22 (36)
ah	C(8)—C(7)—H(7)	120·98 (35)
ah	C(8)—C(9)—H(9)	120·49 (41)
bh	C(3)—C(2)—H(2)	118·72 (36)
bh	C(13)-C(14)-H(14)	119·32 (37)
bh	C(6)—C(7)—H(7)	118·23 (36)
bh	C(10)-C(9)—H(9)	119·15 (42)
ci	C(3)—C(4)—H(4)	118·38 (36)
ci	C(13)-C(12)-H(12)	118·97 (34)
ci	C(6)—C(5)—H(5)	118·99 (33)
ci	C(10)-C(11)-H(11)	118·42 (38)
fi	C(5)—C(4)—H(4)	120·25 (38)
fi	C(4)—C(5)—H(5)	119·95 (35)
fi	C(12)-C(11)—H(11)	119·92 (40)
fi	C(11)-C(12)-H(12)	120·34 (35)

Table 8. *Close approaches between molecules, H$\cdots$H distances less than 2·85 Å, C$\cdots$H less than 3·1 Å, and C$\cdots$C less than 3·75 Å*

Distances are calculated from coordinates that have been corrected for rigid-body motion.

Symmetry code:

i	$\frac{1}{2}+x$,	$-\frac{1}{2}-y$,	$1+z$;	vi	$\frac{1}{2}-x$, $-\frac{1}{2}+y$,	$-z$
ii	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$1-z$;	vii	$-x$, $-y$,	$-1-z$
iii	$\frac{1}{2}+x$,	$-\frac{1}{2}-y$,	z;	viii	$\frac{1}{2}-x$, $-\frac{1}{2}+y$,	$1-z$
iv	$-x$,	$-y$,	$-z$;	ix	x, y,	$1+z$
v	x,	y,	$-1+z$;	x	$\frac{1}{2}-x$, $\frac{1}{2}+y$,	$-z$.

H(1)$\cdots$H(8^i)	2·551 (9) Å
H(1)$\cdots$H(12^{ii})	2·457 (8)
H(2)$\cdots$H(11^{iii})	2·675 (8)
H(2)$\cdots$H(14^{ii})	2·717 (8)
H(7)$\cdots$H(7^{iv})	2·067 (10)
H(7)$\cdots$H(14^v)	2·586 (9)
C(1)$\cdots$H(8^i)	2·921 (6)
C(2)$\cdots$H(11^{iii})	2·756 (6)
C(2)$\cdots$H(14^{ii})	3·098 (6)
C(3)$\cdots$H(11^{iii})	2·973 (6)
C(7)$\cdots$H(2^{vi})	3·075 (6)
C(7)$\cdots$H(7^{vii})	2·929 (6)
C(7)$\cdots$H(14^v)	2·994 (7)
C(10)$\cdots$H(4^{vi})	2·842 (5)
C(12)$\cdots$H(1^{viii})	3·052 (6)
C(13)$\cdots$H(4^{vi})	3·038 (6)
C(14)$\cdots$H(7^{ix})	2·963 (6)
C(14)$\cdots$H(8^i)	3·085 (6)
C(15)$\cdots$H(4^{vi})	2·714 (5)
C(16)$\cdots$H(4^{vi})	2·609 (5)
C(3)$\cdots$C(8^{iv})	3·720 (3)
C(3)$\cdots$C(9^{iv})	3·542 (3)
C(4)$\cdots$C(9^{iv})	3·727 (3)
C(4)$\cdots$C(15^x)	3·629 (3)
C(4)$\cdots$C(16^x)	3·646 (3)
C(5)$\cdots$C(10^{iv})	3·717 (3)
C(5)$\cdots$C(11^{iv})	3·554 (3)
C(6)$\cdots$C(10^{iv})	3·689 (3)
C(6)$\cdots$C(16^{iv})	3·713 (3)
C(7)$\cdots$C(13^{iv})	3·561 (3)
C(7)$\cdots$C(14^v)	3·655 (3)
C(7)$\cdots$C(15^{iv})	3·708 (3)
C(8)$\cdots$C(15^{iv})	3·669 (3)
C(16)$\cdots$C(16^{iv})	3·528 (3)

The molecule, which is depicted in Fig. 1, does not possess *mmm* symmetry in the crystal and deviates significantly from planarity. The standard deviations have been somewhat underestimated as the parameters were refined by the block-diagonal procedure, but even if the standard deviations were twice the estimated value the molecule would still deviate significantly from planarity [$\chi^2 = \sum(\Delta/\sigma)^2 = 48\cdot8$ for 13 degrees of freedom where $\sigma = 2 \times \sigma_{est}$]. Confirmation of the non-planarity comes from Allmann's work; the deviations from the least-squares best planes are given in Table 9. The deviations from planarity seem to be systematic, the molecule being folded about a line through atoms C(3) and C(10) (see Fig. 1).

Table 9. *Deviations from the best plane through the carbon framework*

ΔN refers to this work, ΔX the values obtained by Allmann (1970). Deviations are given in Å × 10⁻³.

	ΔN	Δx
C(1)	2	−1
C(2)	10	12
C(3)	3	8
C(4)	−2	−7
C(5)	−4	−3
C(5)	−4	0
C(7)	−6	−9
C(8)	−4	−6
C(9)	3	3
C(10)	2	7
C(11)	4	4
C(12)	1	−3
C(13)	−4	−4
C(14)	−20	−20
C(15)	8	9
C(16)	10	10

The lengths of chemically equivalent bonds do not differ at the 5% significance level. The mean values of equivalent bonds are given in Table 10 (the notation
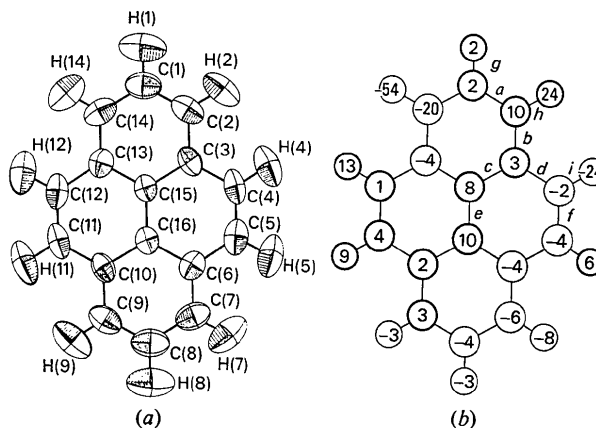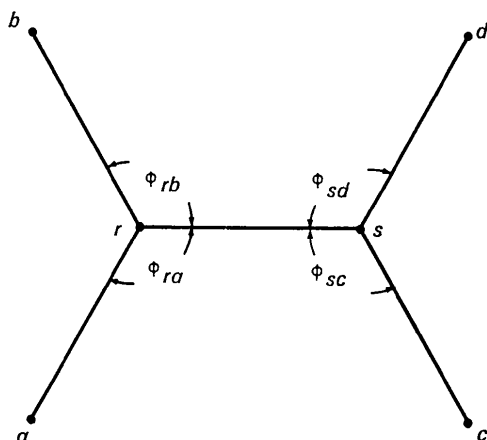

Fig. 1. The pyrene molecule viewed at right angles to the best plane showing (a) the numbering of the atoms and the thermal ellipsoids (at 50% probability) calculated using *ORTEP* (Johnson, 1965); (b) the notation of the bonds and the deviations (in Å × 10⁻³) from the best plane.

Fig. 2. The definition of the angles φ_{ij}.

is shown in Fig. 2) where they are compared with the values found by C & T and by Allmann. The bond lengths for 2,7-di-t-butylpyrene (Hazell & Lomborg, 1969, 1972), for the low temperature form of the pyrene–PMDA complex (Herbstein & Snyman, 1969), and for the pyrene–TCNE complex (Krebs Larsen, Little & Coppens, 1972) are also given as are the results of several theoretical calculations.

The most striking feature is the variation of the length of bond f, which was found by C & T to be 1·320 (14) Å which is considerably shorter than theoretical values and is even shorter than the value observed for the double bond in ethylene, 1·337 ± 0·003 Å (Allen & Plyler, 1958). The recent X-ray results give 1·342 (4) Å which, though longer than C & T's value,

is still short of the values obtained by neutron diffraction or from theoretical calculations. The discrepancies between the X-ray and neutron-diffraction determinations are due to the fact that with neutrons the positions of the nuclei are determined whereas with X-rays the centre of the charge cloud is determined.

The centres of the charge clouds will be displaced in the direction of the bond of highest bond order. A measure of this displacement is given by a function of the bond orders.

$$P_{rs} = 2p_{rs} + \cos \varphi_{ra}p_{ra} + \cos \varphi_{rb}p_{rb} + \cos \varphi_{sc}p_{sc}$$
$$+ \cos \varphi_{sd}p_{sd} \quad (1)$$

where p_{ij} is the bond order for the bond between atoms i and j; the meaning of the angles φ_{ij} can be seen in Fig. 2. Fig. 3 shows Δ(N–X) plotted against P_{rs} for pyrene; the X-ray results are those of Allmann and P_{rs} is calculated from the π-bond orders of Warren & Yandle (1968). The points are seen to lie close to the least-squares best straight line

$$\Delta(N-X) = A + BP_{rs} \quad (2)$$

where $A = 0·0013$ and $B = 0·0178$ (the correlation coefficient is 0·89 for 4 degrees of freedom i.e. $P < 1\%$). Equation 2 may be used for making empirical corrections to bond lengths determined by X-ray diffraction in this type of compound. The validity of this procedure is discussed in detail elsewhere (Hazell, 1972).

Table 10. Mean bond lengths (in Å) with their estimated standard deviations (in Å × 10^{-3}) for pyrene and related compounds

Theoretical distances are also given.

	Neutron	C & T	Allmann	Pyrene TCNE	2,7-Di-t-butyl-pyrene	Pyrene PMDA
a	1·395 (2)	1·380 (11)	1·379 (3)	1·390 (3)	1·394 (3)	1·403 (6)
b	1·406 (2)	1·420 (11)	1·405 (4)	1·402 (3)	1·390 (3)	1·394 (5)
c	1·425 (2)	1·417 (7)	1·424 (3)	1·422 (2)	1·417 (3)	1·430 (2)
d	1·438 (2)	1·442 (9)	1·434 (3)	1·440 (2)	1·437 (4)	1·445 (4)
e	1·430 (2)	1·417 (14)	1·429 (4)	1·426 (3)	1·418 (4)	1·426 (1)
f	1·367 (3)	1·320 (14)	1·341 (4)	1·351 (2)	1·346 (5)	1·352 (2)

	A	B	C	D	E	F	G	Mean theoretical
a	1·393	1·393	1·395	1·396	1·394	1·390	1·399	1·394
b	1·400	1·398	1·393	1·407	1·405	1·397	1·409	1·401
c	1·409	1·406	1·421	1·419	1·419	1·407	1·421	1·415
d	1·441	1·449	1·468	1·437	1·436	1·427	1·446	1·445
e	1·431	1·438	1·427	1·427	1·425	1·417	1·434	1·428
f	1·359	1·354	1·354	1·369	1·365	1·364	1·363	1·361

A Dewar & Gleicher, PPP (1965).
B Dewar & Gleicher, SPO (1965).
C Försterling, Huber & Kuhn (1967).
D Warren & Yandle (1968).
E Boyd & Singer (1966).
F Leroy & Jaspers (1967).
G Lo & Whitehead (1968).

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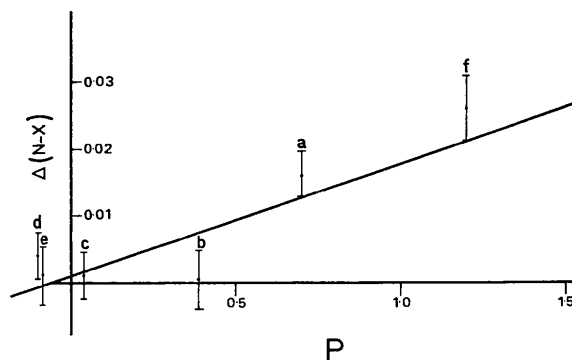NEUTRON DIFFRACTION COMMISSION (1969). *Acta Cryst.* A**25**, 391.

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Fig. 3. The difference (in Å) between the bond distances as determined by neutron and by X-ray diffraction, $\Delta(N-X)_j$ plotted *vs.* P_j. The vertical bars represent plus or minus the standard deviation of $\Delta(N-X)$ for bond *j*.

Etude par Diffraction X des Structures Cristallines du Furanne à la Pression Atmosphérique

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Single-crystal X-ray diffraction data of two polymorphic forms of furan have been collected at atmospheric pressure and low temperature by the precession technique. The disordered phase I (stable between 187 and 150°K) is orthorhombic, space-group *Cmca*, with four molecules in the unit cell; at 152°K, $a = 8.65$, $b = 6.70$, $c = 6.75$ Å; from X-ray diffraction, calorimetric, dielectric and n.m.r. data, it is concluded that the dynamics of the disorder are well interpreted by the Frenkel model and each molecule randomly occupies four coplanar positions related by the space-group symmetry; the molecular packing has been group-refined to an *R* index of 0.078. The ordered phase II, stable below 150°K, is tetragonal, space group $P4_12_12$ or $P4_32_12$, with four molecules in the unit cell; at 123°K, $a = 5.69$, $c = 11.92$ Å; the crystal and molecular structures have been solved and refined to an *R* index of 0.065.

I. Introduction

Le furanne (formule C_4H_4O) est un hétérocycle simple qui a fait l'objet d'un grand nombre d'investigations tant théoriques qu'expérimentales; ce composé fond à 187°K avec une entropie de fusion, relativement faible, de 4,8 u.e.; la courbe de chaleur spécifique à pression ambiante présente une transition isotherme à 150°K, l'entropie de transition étant de 3,26 u.e. (Guthrie *et al.*, 1952). Une étude radiocristallographique préliminaire (Fourme, 1969) des phases solides à pression ambiante est reprise ici de manière détaillée; nous