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The Crystal and Molecular Structure of Pyreno-(1′, 2′ : 1, 2)-pyrene. An Example of the Use of Linear Least-Squares for Structure Solution

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Pyreno-(1′,2′:1,2)-pyrene, $C_{30}H_{16}$, crystallizes in the monoclinic system. There are four molecules in a cell of dimensions $a=13{\cdot}17$, $b=7{\cdot}71$, $c=20{\cdot}32$ Å, $\beta=118{\cdot}5°$. The space group is $P2_1/c$. The structure was solved in the *b*-axis projection by molecular transform techniques. The *y* coordinates were subsequently derived by a linear least-squares procedure. The structure has been refined by block-diagonal least-squares methods to a conventional *R* value of 0·11 over 2284 intensity data, measured on a linear diffractometer. As a result of intramolecular overcrowding the molecule is propeller shaped, the minimum non-bonding C···C and H···H distances involving overcrowded atoms being 2·96 and 2·03 Å respectively. The observed bond lengths are in agreement with those predicted by simple VB and MO arguments.

In hydrocarbons of the 3,4-benzphenanthrene type a planar carbon skeleton would result in a non-bonded hydrogen–hydrogen contact of approximately 0·5 Å. Ferguson & Robertson (1963) and Trotter (1964) have reviewed the structural studies of such molecules. From these studies it is clear that the intramolecular overcrowding is mainly relieved by out of plane distortions spread over the entire carbon skeleton of the molecule; no study, however, is sufficiently accurate for any conclusions to be made regarding the effect of the overcrowding on bond distances and angles.

On the basis of a comparison between the observed bond lengths and those calculated from various theoretical models, Burns & Iball (1960) have suggested that in chrysene, overcrowding is at least partly relieved by extension of two of the carbon–carbon bonds by 0·03–0·04 Å; this suggestion has been widely accepted (*e.g.* Cruickshank & Sparks, 1960; Coulson & Haigh, 1963). The overcrowded hydrogen atoms in chrysene are about 1·7 Å apart. Since 3,4-benzphenanthrene and its derivatives are much more severely overcrowded than chrysene, larger departures of the bond lengths from predicted values might be expected. To investigate this we have determined the structure of pyrenopyrene.

Experimental

Crystal data

Pyrenopyrene, $C_{30}H_{16}$, F.W. 376·5. Monoclinic, $a=13{\cdot}17$, $b=7{\cdot}71$, $c=20{\cdot}32$ Å; $\beta=118{\cdot}5°$; $V=1813$ Å^3;

$D_m=1\cdot38$ (by flotation), $D_x=1\cdot379$ g.cm^{-3}; $Z=4$; $F(000)=784$, space group $P2_1/c$. Linear absorption coefficient (Mo $K\alpha$, $\lambda=0\cdot7107$ Å) $\mu=0\cdot8$ cm^{-1}.

A sample, consisting of red needle-shaped crystals, was kindly supplied by Professor E. Clar (Clar, Guye-Vuilleme & Stephan, 1964). The unit-cell parameters are means of the values obtained from rotation and Weissenberg photographs taken about the b axis with Cu $K\alpha$ radiation ($\lambda=1\cdot5418$ Å) and from linear diffractometer settings.

Intensity measurements were made with a crystal mounted about its b axis on a linear diffractometer (Arndt & Willis, 1966). Molybdenum radiation was used in conjunction with balanced ZrO_2–SrO filters and a pulse height analyser. The intensities of 3532 independent reflexions were measured. After correction for background, the measured intensities of 2284 reflexions were greater than zero, and only these reflexions were used in the final calculations. Lorentz and polarization factors appropriate to equi-inclination Weissenberg geometry were applied to the intensities. No corrections were made for absorption.

Structure analysis

The structure was solved in projection down the b axis by molecular transform methods; the position of the molecular centroid relative to the unit cell origin was determined by the graphical method of Taylor (1954). The model thus obtained was refined to an R value of 0·17 over 280 $h0l$ reflexions by minimum residual (Bhuiya & Stanley, 1964) and least-squares methods ($R=\sum|\Delta|/\sum|F_o|$, where $\Delta=|F_o|-|F_c|$, and F_o and F_c are respectively the observed and calculated structure factors).

After a number of trial and error approaches had failed, approximate y coordinates were obtained using the linear least-squares method of Kutschabsky & Höhne (1965). If the space group is $P2_1/c$, and there are N atoms in the asymmetric unit, the observational equations for reflexions with $h+l=2n$ are of the form

$$F_o=\mathbf{A}\,.\,\mathbf{p}$$

where **A** and **p** are N-fold vectors. Typical elements of **A** and **p** are:

$$A_i=4f_i\cos 2\pi(hx_i+lz_i)$$

and

$$p_i=\cos 2\pi ky_i\,.$$

Similar equations involving $q_i=\sin 2\pi ky_i$ are obtained for reflexions with $h+l=2n+1$.

Initially, the reflexions used were 100 $h1l$ spectra, for which the approximation $F_o=0$ could be made, and the strong reflexions 10,1,4 and 7,1,$\overline{15}$, which were arbitrarily assigned positive phases. The p_i and q_i obtained were normalized so that

$$p_i^2+q_i^2=1\ (i=1,N)$$

and then solved for the coordinates y_i. Since the coordinates in projection may refer either to an origin at (0,0,0) or (0,0,$\frac{1}{4}$) in the three-dimensional unit cell, the calculations were made for both possible origins. The correct choice was immediately apparent, since it gave a much lower value of $\sum\Delta^2$, and more constant values of $p_i^2+q_i^2$ before normalization. With approximate phases now available, the y_i were refined by extending the calculations, first over all the measured $h1l$ intensities, and then over all the measured $h2l$ intensities. Two solutions for each y_i are obtained in the latter case; that closer to the starting set was taken. The model so obtained gave an R value of 0·22 over the 2284 observed data.

The structure was then refined by the method of block-diagonal least-squares. The function minimized was $\sum w\Delta^2$. Adjustment of the positional and isotropic thermal parameters of the carbon atoms resulted in an R value of 0·19. Allowance for the anisotropic motions of the carbon atoms reduced R to 0·14. Peaks in the positions expected for all sixteen hydrogen atoms were then observed in a low angle difference synthesis. The hydrogen atoms were therefore included in the calculations and their positions and isotropic vibrational parameters were refined.

This refinement converged with values of R and R_w, where $R_w=(\sum w\Delta^2/\sum wF_o^2)^{1/2}$, of 0·11 and 0·13 respectively. In the later stages of refinement the weighting scheme used was $w=(24/F_o)^2$ if $F_o>24$, otherwise $w=1\cdot0$. An analysis of the agreement between F_o and F_c is presented in Table 1. Copies of the final F_o and F_c values may be obtained from the first author. Thoughout the analysis Stewart, Davidson & Simpson's (1965) hydrogen scattering factor and the valence carbon scattering factor from *International Tables for X-ray Crystallography* (1962) were used. In the final difference synthesis the function values ranged from 0·4 to $-0\cdot4$ e.Å^{-3}; the minimum height of a carbon atom in the final electron density synthesis was 4·5 e.Å^{-3}. Structure factors calculated over all 3533 reflexions gave an R value of 0·15; for all excluded reflexions $|F_c|$ was smaller than 10 electrons.

The final positional and vibrational parameters of the atoms are given in Table 2. An overall view of the molecule is shown in Fig. 1.

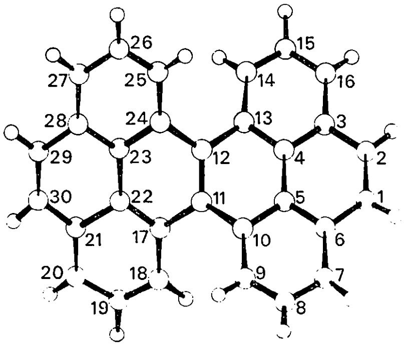


Fig. 1. A perspective view of the molecule, showing the numbering of the carbon atoms. Hydrogen atoms have the same numbers as the carbon atoms to which they are bonded.

Discussion

The molecular packing is illustrated in Fig. 2. The crystal structure is built from pyrenopyrene molecules separated by normal van der Waals distances (Table 3).

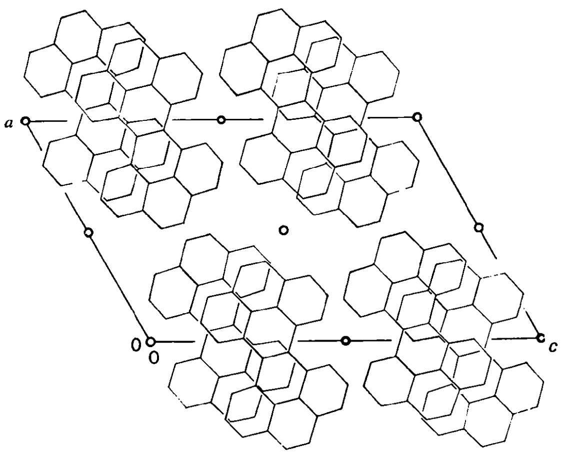
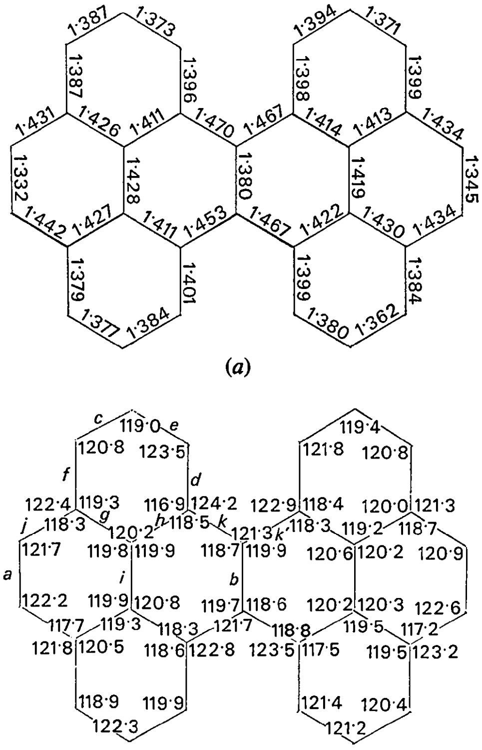


Fig. 2. The crystal structure viewed down the *b* axis. Hydrogen atoms are omitted for clarity.



(*a*)

(*b*)

Fig. 3. (*a*) Carbon–carbon bonded distances. Standard deviations range from 0·006 to 0·009 Å. (*b*) Interbond angles involving carbon atoms. Standard deviations range from 0·4 to 0·5°. Bond symbols used in Tables 4 and 5 are also shown.

Table 1. *Analysis of agreement between observed and calculated structure factors*

Range of $\lvert F_o\rvert$	$\sum\lvert F_o\rvert$	$\sum\lvert F_c\rvert$	$\sum\lvert\Delta\rvert$	N	R	$\sum\lvert\Delta\rvert/N$
0–5	2789	2261	927	712	0·332	1·30
5–10	5752	5455	869	832	0·151	1·04
10–15	4271	4269	278	349	0·065	0·80
15–20	2631	2598	134	152	0·051	0·88
20–25	1896	1872	102	85	0·054	1·20
25–30	1511	1527	87	55	0·057	1·58
30–40	1413	1406	64	42	0·045	1·52
40–50	975	983	41	22	0·042	1·85
50–100	2137	2156	107	32	0·050	3·33
100–200	318	321	4	3	0·013	1·41
ALL	23693	22848	2613	2284	0·110	1·14

Table 2

Fractional coordinates of the carbon atoms with corresponding standard deviations

	x	y	z
C(1)	−0·4864 (5)	0·7722 (9)	0·1948 (3)
C(2)	−0·4567 (5)	0·8313 (9)	0·2639 (3)
C(3)	−0·3381 (4)	0·8365 (8)	0·3208 (3)
C(4)	−0·2522 (4)	0·7830 (8)	0·3022 (3)
C(5)	−0·2836 (4)	0·7291 (8)	0·2282 (3)
C(6)	−0·4026 (4)	0·7155 (9)	0·1733 (3)
C(7)	−0·4318 (5)	0·6549 (9)	0·1024 (3)
C(8)	−0·3481 (5)	0·6031 (10)	0·0855 (3)
C(9)	−0·2325 (5)	0·6191 (9)	0·1367 (3)
C(10)	−0·1968 (4)	0·6907 (8)	0·2077 (3)
C(11)	−0·0751 (4)	0·7129 (8)	0·2637 (3)
C(12)	−0·0475 (4)	0·7259 (7)	0·3381 (3)
C(13)	−0·1352 (4)	0·7825 (8)	0·3585 (3)
C(14)	−0·1074 (5)	0·8542 (9)	0·4283 (3)
C(15)	−0·1922 (5)	0·9138 (9)	0·4451 (3)
C(16)	−0·3063 (5)	0·9007 (9)	0·3924 (3)
C(17)	0·0161 (4)	0·7193 (7)	0·2428 (3)
C(18)	−0·0043 (4)	0·7627 (8)	0·1706 (3)
C(19)	0·0870 (5)	0·7712 (9)	0·1550 (3)
C(20)	0·1987 (5)	0·7328 (9)	0·2076 (3)
C(21)	0·2219 (5)	0·6951 (8)	0·2798 (3)
C(22)	0·1312 (4)	0·6944 (8)	0·2993 (3)
C(23)	0·1571 (4)	0·6624 (7)	0·3750 (3)
C(24)	0·0692 (4)	0·6757 (7)	0·3956 (2)
C(25)	0·0968 (4)	0·6224 (8)	0·4679 (3)
C(26)	0·2046 (4)	0·5656 (9)	0·5194 (3)
C(27)	0·2928 (4)	0·5666 (9)	0·5004 (3)
C(28)	0·2711 (4)	0·6127 (8)	0·4289 (3)
C(29)	0·3597 (5)	0·6144 (10)	0·4072 (3)
C(30)	0·3370 (5)	0·6546 (9)	0·3377 (3)

Fractional coordinates and isotropic vibrational parameters of hydrogen atoms

	x	y	z	U_{iso}
H(1)	−0·563 (5)	0·773 (9)	0·155 (3)	0·076 (20)
H(2)	−0·517 (4)	0·889 (8)	0·276 (3)	0·063 (17)
H(7)	−0·514 (6)	0·663 (10)	0·057 (4)	0·099 (24)
H(8)	−0·364 (4)	0·552 (7)	0·043 (3)	0·044 (14)
H(9)	−0·177 (5)	0·583 (8)	0·123 (3)	0·070 (18)
H(14)	−0·032 (4)	0·870 (8)	0·461 (3)	0·055 (16)
H(15)	−0·166 (4)	0·976 (8)	0·498 (3)	0·060 (17)
H(16)	−0·359 (5)	0·945 (9)	0·404 (3)	0·071 (19)
H(18)	−0·081 (4)	0·794 (7)	0·128 (3)	0·045 (14)
H(19)	0·078 (4)	0·807 (8)	0·107 (3)	0·054 (15)
H(20)	0·261 (5)	0·717 (8)	0·194 (3)	0·067 (18)
H(25)	0·038 (4)	0·624 (7)	0·480 (3)	0·044 (14)
H(26)	0·225 (5)	0·499 (9)	0·571 (3)	0·084 (21)
H(27)	0·366 (4)	0·528 (8)	0·539 (3)	0·061 (17)
H(29)	0·433 (5)	0·570 (9)	0·446 (3)	0·074 (19)
H(30)	0·386 (5)	0·644 (8)	0·316 (3)	0·068 (18)

Table 2 (*cont.*)

Anisotropic vibrational parameters of the carbon atoms ($\times 10^4$)

The anisotropic temperature factor is of the form $\exp\left(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}a^*_i a^*_j h_i h_j\right)$

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	329 (27)	781 (53)	571 (34)	77 (62)	249 (49)	−111 (54)
C(2)	365 (28)	809 (55)	653 (37	−24 (65)	546 (54)	−24 (56)
C(3)	379 (27)	684 (48)	472 (29)	65 (54)	477 (47)	−33 (51)
C(4)	361 (26)	589 (40)	347 (24)	20 (45)	407 (41)	−23 (46)
C(5)	367 (26)	612 (43)	372 (25)	−7 (46)	404 (42)	−123 (46)
C(6)	389 (28)	655 (44)	395 (27)	0 (51)	208 (45)	−96 (51)
C(7)	490 (32)	692 (52)	476 (31)	−121 (57)	299 (51)	−283 (58)
C(8)	661 (38)	839 (54)	359 (28)	−226 (57)	384 (53)	−325 (68)
C(9)	558 (32)	607 (44)	332 (25)	−166 (48)	385 (47)	−126 (55)
C(10)	427 (27)	544 (39)	308 (23)	61 (44)	374 (41)	−3 (48)
C(11)	417 (27)	467 (37)	347 (24)	−43 (42)	429 (42)	−20 (45)
C(12)	333 (24)	541 (38)	327 (23)	14 (42)	430 (39)	−47 (42)
C(13)	377 (26)	550 (39)	339 (24)	−113 (45)	405 (41)	−119 (46)
C(14)	432 (28)	721 (47)	388 (27)	−32 (52)	445 (45)	−15 (53)
C(15)	553 (33)	878 (53)	411 (28)	−178 (57)	650 (51)	90 (62)
C(16)	521 (33)	805 (52)	565 (34)	53 (62)	756 (57)	210 (61)
C(17)	435 (27)	449 (35)	322 (22)	−22 (41)	510 (40)	88 (44)
C(18)	485 (30)	510 (42)	350 (25)	29 (44)	461 (45)	89 (48)
C(19)	749 (40)	732 (51)	473 (31)	44 (57)	922 (60)	71 (65)
C(20)	621 (36)	651 (50)	615 (35)	85 (60)	906 (61)	146 (60)
C(21)	497 (30)	576 (42)	528 (31)	82 (53)	694 (52)	78 (54)
C(22)	444 (28)	526 (39)	441 (27)	55 (48)	605 (46)	18 (48)
C(23)	370 (26)	520 (42)	335 (24)	52 (44)	333 (41)	56 (45)
C(24)	332 (23)	509 (38)	257 (21)	−140 (39)	310 (36)	−119 (42)
C(25)	446 (28)	578 (41)	400 (26)	7 (48)	513 (45)	32 (49)
C(26)	452 (29)	804 (50)	275 (23)	138 (51)	259 (43)	122 (56)
C(27)	378 (27)	844 (53)	365 (27)	65 (55)	155 (43)	144 (56)
C(28)	371 (26)	601 (43)	448 (29)	−56 (50)	343 (44)	17 (49)
C(29)	361 (27)	883 (53)	563 (34)	108 (63)	497 (50)	160 (58)
C(30)	501 (32)	730 (52)	566 (34)	19 (60)	710 (56)	50 (58)

Table 3

(*a*) Selected intramolecular non-bonded distances (Å)

C(9)····C(18)	2·96	C(14)···C(25)	3·00
C(9)····H(18)	2·48	C(14)···H(25)	2·45
C(18)···H(9)	2·44	C(25)···H(14)	2·51
H(9)····H(18)	2·03	H(14)···H(25)	2·07
C(10)···C(17)	2·55	C(13)···C(24)	2·56

(*b*) Selected intermolecular non-bonded distances (Å)

H(29)···H(29)$^{\mathrm{i}}$	2·33	C(23)···H(18)$^{\mathrm{v}}$	3·00
H(25)···H(19)$^{\mathrm{ii}}$	2·43	C(24)···H(18)$^{\mathrm{v}}$	3·00
H(14)···H(14)$^{\mathrm{iii}}$	2·44	C(25)···H(19)$^{\mathrm{ii}}$	3·00
H(25)···H(25)$^{\mathrm{iv}}$	2·46	C(24)···C(18)$^{\mathrm{v}}$	3·40
C(14)···H(14)$^{\mathrm{iii}}$	3·00	C(30)···C(5)$^{\mathrm{v}}$	3·49

Superscripts refer to the following transformations:

i	$1-x$,	$1-y$,	$1-z$	iv	$-x$,	$1-y$,	$1-z$
ii	x,	$\frac{3}{2}-y$,	$\frac{1}{2}+z$	v	$-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
iii	$-x$,	$2-y$,	$1-z$				

The most obvious effect of the intramolecular overcrowding is the adoption by the molecule of a non-planar propeller shape, with approximate 222 (D_2) symmetry (Fig. 1). As a result, the C(9)···C(18) and C(14···C(25) non-bonded distances are 2·96 and 3·00 Å, and the H(9)···H(18) and H(14)···H(25) distances are 2·03 and 2·07 Å. If the molecule were planar these C···C and H···H distances would be about 2·4 and 0·5 Å respectively. The overcrowding is thus much relieved, but the atoms involved are still closer than the sum of their van der Waals radii. These results confirm those of earlier workers, discussed by Ferguson & Robertson (1963) and Trotter (1964), both as to the magnitude of the distortion and to its type; in principle, buckling of the molecule so as to leave it with $\overline{1}$ (C_i) symmetry would also relieve the overcrowding, but no example of a centrosymmetrical distortion is known.

The 222 (D_2) symmetry is exact so far as the bond lengths are concerned [Fig. 3(*a*)]. Mean values of chemically equivalent bond lengths are given in Table 4, together with their standard deviations, calculated from the inverse least-squares matrix. The standard deviations of mean bond lengths so calculated are, in general, larger than those based on the range of the individual bond lengths. Table 4 also contains the bond distances predicted by simple VB and MO theory. The VB bond orders were calculated from the 35 Kekulé structures which can be written for the molecule; the MO bond orders were obtained from a simple Hückel calculation. The bond order bond length relationships suggested by Cruickshank & Sparks (1960) were used; in the MO calculations the bond length was taken to be linear with bond order, m, between 1·46 Å ($m=0·4$) and 1·34 Å ($m=0·85$). Both theories account about equally well for the observed bond lengths, the maximum differences between observed and calculated lengths being 0·022 and 0·021 Å for MO and VB theory respectively. The root mean square differences between the observed and calculated values are 0·014 Å for MO and 0·012 for VB theory. Interestingly, the observed value for bond *b*, for which the theoretical predictions differ by 0·029 Å, is almost the mean of the predicted values. A correction for librational effects (Cruickshank, 1956) resulted in a general increase in the mean bond lengths of 0·002 Å and did not improve the performance of the two theories. There is no suggestion, from the data in Table 4, that overcrowding has been relieved by significant changes in bond lengths. Bond *k* is the most likely to be affected in this way, and while it is the only bond length both theories underestimate by more than 0·01 Å the discrepancies are small enough to be ascribed to defects in the theoretical models and random experimental errors.

Table 4. *Mean observed and calculated bond lengths* (Å)

		VB		MO	
	Observed	Calculated	*Δ*	Calculated	*Δ*
a	1·339 (7)	1·356	−0·017	1·360	−0·021
b	1·380 (6)	1·369	0·011	1·398	−0·018
c	1·374 (4)	1·395	−0·021	1·386	−0·012
d	1·399 (4)	1·395	0·004	1·404	−0·005
e	1·383 (4)	1·399	−0·016	1·390	−0·007
f	1·387 (4)	1·399	−0·012	1·409	−0·022
g	1·424 (4)	1·420	0·004	1·426	−0·002
h	1·415 (3)	1·420	−0·005	1·425	−0·010
i	1·424 (5)	1·424	0·000	1·427	−0·003
j	1·435 (4)	1·447	−0·012	1·432	0·003
k	1·464 (3)	1·452	0·012	1·444	0·020

Clar, Guye-Vuilleme & Stephan (1964) showed that the Friedel–Crafts acylation of pyrenopyrene occurs at C(7). Of the three types of ring found in the molecule that containing C(7) is the most benzenoid, the range of individual bond lengths being smallest, and the mean bond length of 1·397 Å being closest to that found in benzene. Clar *et al.* (1964) have also suggested that the central bond in 1:2,7:8-dibenzchrysene is a fixed double bond, since it can be oxidized to give a diketone. The comparable bond in pyrenopyrene (bond *b*) is not particularly short; it is, however, in the region of greatest bond angle and out of plane distortion (*vide infra*).

The mean C–H bond length, 0·97 Å, with a standard deviation, estimated from the range of the sixteen individual measurements, of 0·015 Å, is significantly shorter than the value obtained spectroscopically for the C–H bond distance. Such an effect is to be expected (Stewart, Davidson & Simpson, 1965) and the values in Tables 3 and 6 involving hydrogen atoms should therefore be considered in error by about 0·1 Å.

The 222 (D_2) symmetry is also exact for the bond angles [Fig. 3(*b*)]. Values averaged over chemically equivalent bond angles are given in Table 5. Although the deviations from 120° are small, they appear to be significant for angles *dk*, *dh*, *hk*, and *kk'*, the largest deviation, of 3·4 (3)°, occurring with angle *dk*. These distortions are all in the sense which would relieve the overcrowding. The angles involving bond *j* also differ significantly from 120°; this seems to be a consequence of the shortness of bond *a*.

Table 5. *Mean interbond angles* (°)

aj	121·9 (4)	*ce*	120·5 (8)	*kb*	119·2 (4)
jf	122·2 (4)	*ed*	121·7 (8)	*kk'*	121·5 (3)
jg	118·0 (4)	*dh*	117·9 (4)	*hg*	119·6 (3)
fg	119·8 (3)	*dk*	123·4 (3)	*hi*	120·4 (3)
fc	120·2 (5)	*hk*	118·5 (3)	*gi*	120·1 (3)

(Standard deviations were estimated both from the least-squares matrix and from the range of individual values, and the greater of these was taken.)

The deviations of the atoms from the mean plane through the carbon atoms (Table 6) are only roughly in accord with 222 (D_2) symmetry, possibly because of the different crystal environments of the two overcrowded regions. The steric strain is relieved by a buckling of the entire molecule so that no single ring remains planar. The distortions are greatest at the central bond (*b*), the dihedral angle between the planes C(10), C(11), C(12), C(17) and C(11), C(12), C(13), C(24) being 24°.

Table 6. *Deviations from mean plane* (Å × 10^2) *defined by carbon atoms*

C(1)	−17	C(2)	21	C(29)	−18	C(30)	21
C(6)	−41	C(3)	37	C(28)	−40	C(21)	41
C(7)	−79	C(16)	78	C(27)	−84	C(20)	79
C(8)	−100	C(15)	100	C(26)	−105	C(19)	97
C(9)	−76	C(14)	74	C(25)	−72	C(18)	70
C(10)	−27	C(13)	27	C(24)	−24	C(17)	28
C(5)	−18	C(4)	15	C(23)	−13	C(22)	20
C(11)	2	C(12)	3				
H(1)	−23	H(2)	52	H(29)	−45	H(30)	27
H(7)	−80	H(16)	100	H(27)	−107	H(20)	81
H(8)	−133	H(15)	143	H(26)	−162	H(19)	131
H(9)	−90	H(14)	94	H(25)	−85	H(18)	88

Our results thus establish that in pyrenopyrene intramolecular overcrowding is relieved mainly by loss of planarity of the carbon skeleton of the molecule, and to a lesser extent, by deformation of interbond angles; unlike chrysene, changes in bond lengths as a result of the overcrowding are insignificant. Given the relative magnitudes for the force constants appropriate to these various distortions (see *e.g.* Coulson & Haigh, 1963; Coulson & Golebiewski, 1960) such a conclusion is to be expected.

The calculations were performed on the University of Glasgow KDF9 and the University of Sussex ICL 1905 computers, using D. W. J. Cruickshank and J. G. Smith's least-squares program, J. G. Sime's Fourier and data processing programs, and K. W. Muir and W. MacDonald's molecular geometry program.

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The Crystal and Molecular Structure of 9-Fluorenone

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The crystal structure of 9-fluorenone, $C_{13}H_8O$, a molecule with interesting spectroscopic and photochemical properties, has been determined from counter-recorded, single-crystal X-ray diffraction data. The crystals are orthorhombic; space group *Pcab*, with $a=16{\cdot}068$ (4), $b=18{\cdot}650$ (6), $c=12{\cdot}550$ (4) Å and $Z=16$. The structure was solved by direct methods and refined by least squares. Hydrogen atoms were located and refined. The final value of the agreement index is 0·056. The molecules are planar to 0·025 Å. The C–C bonds of the benzo rings average 1·383 (1) Å, but can be divided into two sets of alternate bonds which average 1·378 (1) and 1·388 (1) Å. The angles of the benzo rings can be divided into three distinct sets which average 118·0 (2), 120·4 (2), and 121·7 (2)°, the low average being at the C(1) and C(4) positions. The C–C bonds between the benzo rings are consistent with single bonds between sp^2 carbon atoms.

Introduction

The spectroscopic properties and photochemistry of 9-fluorenone have attracted increased attention in recent years (Kuboyama, 1964; Yoshihara & Kearns, 1966; Kuroda & Kunii, 1967; Liptay, Weisenberger, Tiemann, Eberlein & Konopka, 1968; Davis, Carapellucci, Szoc & Gresser, 1969; Singer, 1969; Caldwell, 1969; Marchetti, 1971). The first X-ray investigation of 9-fluorenone was by Iball (1936), in which he established the space group and lattice constants and suggested a possible molecular packing arrangement. Griffiths & Hine (1970) have reported the crystal structure of a bromine derivative, 2-bromo-9-fluorenone. The present structure determination of 9-fluorenone was undertaken to determine more accurate bond lengths and to describe the molecular packing.

Crystal data

9-Fluorenone $C_{13}H_8O$ M.W. 180·21
Yellow, long prismatic (*c*) crystals
Orthorhombic (Mo $K\alpha_1=0{\cdot}70926$ Å)
$a=16{\cdot}068\pm0{\cdot}004$, $b=18{\cdot}650\pm0{\cdot}006$,
$c=12{\cdot}550\pm0{\cdot}004$ Å
Volume of unit cell, $3760{\cdot}8\pm2{\cdot}0$ Å^3
Density, calculated ($Z=16$), 1·273 g.cm^{-3}
measured (flotation), 1·24 g.cm^{-3}
Linear absorption coefficient, $\mu=0{\cdot}86$ cm^{-1} (Mo $K\alpha$)
Total number of electrons per unit cell, $F(000)=1504$
Absent spectra: $0kl$ for l odd, $h0l$ for h odd, $hk0$ for k odd
Space group, *Pcab* (D_{2h}^{15})
General positions: $\pm(x,y,z;\ \tfrac{1}{2}+x,\tfrac{1}{2}-y,z;\ x,\tfrac{1}{2}+y,\tfrac{1}{2}-z;\ \tfrac{1}{2}+x,-y,\tfrac{1}{2}-z)$

Experimental

Single crystals grown from methanol were supplied by S. J. Marino of these laboratories. Space-group extinctions and preliminary lattice dimensions were obtained from precession photographs. A small crystal, 0·28 × 0·35 × 0·47 mm, was mounted on a thin glass rod with G. E. varnish cement and covered with a glass capillary to prevent sublimation. This crystal was used for intensity data collection on an automatic Picker 4-circle goniostat. To minimize the effect of multiple reflections (Zachariasen, 1965), the *c* axis was oriented 4° from the φ axis. Twenty reflections, at moderately high Bragg