

Table 8. Fractional coordinate,  $z$ ,  $\alpha$  distances (Å) from Th in position 2(a) and from M in position 4(d) to neighbouring atoms

	M	=	Cr	Mn	Fe	Co	Ni	Cu
	Z	=	0.374	0.386	—	—	0.366	0.379
Th 2(a)	8 M 4(d)		3.328	3.304	3.179	3.160	3.139	3.208
	8 Si 4(e)		3.154	3.084	—	—	3.153	3.138
	2 Si 4(e)		3.956	4.050	—	—	3.496	3.738
M 4(d)	4 M 4(d)		2.859	2.843	2.855	2.839	2.882	2.902
	4 Si 4(e)		2.410	2.465	—	—	2.320	2.415

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## The Crystal Structure of 2,7-Diacetoxy-*trans*-15,16-dimethyl-15,16-dihydropyrene

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The crystal is monoclinic  $P2_1/a$ . At room temperature  $a = 20.07$ ,  $b = 7.56$ ,  $c = 5.88$  Å,  $\beta = 96.52^\circ$ ,  $Z = 2$ , formula  $C_{22}O_4H_{20}$ .

The structure was determined from a three-dimensional Patterson synthesis, and refined by least-squares procedures. Two sets of intensity data were used independently. One was collected at room temperature with the use of a scintillation counter; the other was recorded on Weissenberg photographs at  $-130^\circ\text{C}$ , and estimated visually.

The 14 peripheral atoms of the pyrene nucleus are approximately coplanar, and appear to form an aromatic system.

#### Introduction

The molecule under examination ( $C_{22}O_4H_{20}$ , Fig. 1) is a novel aromatic system in which the methyl groups reside within the cavity of the  $14\pi$ -electron system (Boekelheide & Phillips, 1963). The crystal structure analysis was undertaken in order to provide informa-

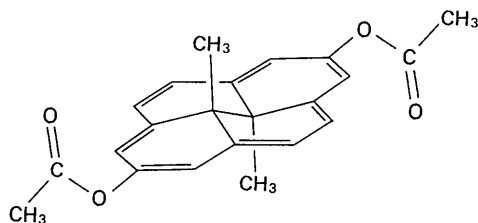


Fig. 1

tion to aid in the investigation of the physical and chemical properties of such systems.

#### Experimental

The elongated aspect of the molecule suggested that there would be significant anisotropy of thermal motion in the crystal and that it would be prudent to reduce this source of error by collecting intensity data at a reasonably low temperature. At the time of analysis, scintillation-counter techniques of data collection were available in this laboratory for use at room temperature only. Work at a lower temperature required the use of the less accurate photographic methods. The choice between the alternatives was so difficult that finally two sets of data were collected, one at  $-130^\circ\text{C}$ , using photographic methods, and one at room temperature, using the scintillation counter.

*Crystal data*

(Values in parentheses refer to the lower temperature)

Monoclinic

 $a = 20.07 \pm 0.03$  ( $19.93 \pm 0.06$ ),  $b = 7.56 \pm 0.01$  ( $7.52 \pm 0.02$ ),  $c = 5.88 \pm 0.01$  ( $5.81 \pm 0.02$ ) Å;  $\beta = 96.52 \pm 0.04$  ( $96.5 \pm 0.1$ )°
 $V = 886.4$  ( $865.2$ )

Formula weight 348.38

 $D_m$  (measured density) =  $1.31 \pm 0.01$  g.cm<sup>-3</sup> $D_x$  (calculated density) =  $1.305 \pm 0.005$  ( $1.34 \pm 0.01$ ) g.cm<sup>-3</sup> $Z = 2$  $\mu = 8.5$  cm<sup>-1</sup> (Cu  $K\alpha$ )Space group  $P2_1/a$  (from precession photographs.)Systematic absences  $h0l$  for  $h$  odd;  $0k0$  for  $k$  odd).

Molecular symmetry: centre.

The material crystallizes from acetone solution in prisms  $\{110\}$ , modified by pinacoids  $\{100\}$ . The crystals are deep green in colour; they were easily cut to give specimens suitable for intensity measurement.

The cell constants and relative intensities at room temperature were measured with the General Electric XRD5 spectrogoniometer and goniostat, using a scintillation counter. The specimen was approximately equidimensional, with no dimension exceeding 0.25 mm. Copper  $K\alpha$  radiation was used, and reasonable monochromatization was achieved by means of a  $K\beta$  filter and a reverter (pulse-height analyser). The moving-crystal moving-counter method of Furnas was used (1957). Goniostat settings were precomputed. Absorption corrections were deemed to be unnecessary. Of the 1964 accessible reflexions (those for which  $2\theta \leq 164^\circ$ ) significant counts were recorded for 1509.

At the lower temperature the cell constants were determined from zero-level precession photographs and the relative intensities from Weissenberg photographs. The specimen was maintained in a stream of cold gaseous nitrogen. For precession techniques this stream was surrounded by an envelope of warm dry air, while for Weissenberg techniques the layer-line screen was heated. Copper  $K\alpha$  radiation was used for all photographs. The working temperature was measured by substituting a thermocouple for the specimens. Two specimens were used, mounted with  $b$  and  $c$  respectively parallel to the rotation axis. The equi-inclination setting was used for upper levels, and all levels for which  $\mu \leq 45^\circ$  were recorded for each specimen. Correlation of relative intensities on different levels was accomplished by means of a double-slit technique. An integrating Weissenberg goniometer was used, and errors due to distortion of spots on upper-level photographs were reduced by means of some integration in the horizontal direction. Intensities were measured by comparison with a standard wedge. Absorption corrections were considered to be unnecessary. The two sets of photographic data so obtained were compared, and where appropriate, the values

were averaged. Finally, it was recognized that visual estimates of intensity commonly include a systematic error which is a function of the Bragg angle. Such errors are usually concealed by adjustment, during refinement, of the overall isotropic temperature factor. Ordinarily no harm results, but in the present case it was considered desirable to reduce this systematic error as far as possible, in order to facilitate comparison of the thermal motion at the two temperatures. A zone of reflexions was therefore recorded on a Weissenberg photograph, at room temperature. The relative intensities estimated from this photograph were then compared with the more objective values recorded on the scintillation counter. A curve of error against Bragg angle was devised, and was used to correct the low-temperature intensity data. Of the 1842 reflexions accessible on the Weissenberg photographs, intensities were estimated for 1495.

**Structure determination**

The molecule was known to occupy a centre of symmetry, and the orientation of a plausible model was readily deduced from a three-dimensional Patterson synthesis. Refinement of the room-temperature structure was begun with three-dimensional Fourier and differential syntheses, and the hydrogen atoms were found from a difference synthesis. It was completed by means of least-squares procedures, with the program of Mair (1963). This program uses the block-diagonal approximation with a  $3 \times 3$  matrix for the position parameters and a  $6 \times 6$  matrix (or  $1 \times 1$  if thermal motion is assumed to be isotropic) for the thermal parameters of each atom. The scale factor of observed structure amplitudes and the overall isotropic temperature factor are refined in a  $2 \times 2$  matrix (Cruickshank, 1961). Schomaker's correction (Hodgson & Rollett, 1963) is applied to the shifts of the thermal parameters. The weighting scheme used was  $1/w = 1 + \{(F_o - 5F_T)/8F_T\}^2$  where  $F_T$  is the nominal minimum value of  $F_o$ , in this case 1.4.

The thermal motion was assumed to be anisotropic for carbon and oxygen atoms, and isotropic for hydrogen atoms. The scattering factor curves of Freeman were used throughout (1959). No convergence acceleration factors were applied. After five cycles the indicated coordinate shifts were reasonably small (maximum  $1.1\sigma$ , average  $0.3\sigma$ ) and refinement was considered to be complete. A further, superfluous, cycle was completed, to discover whether the indicated shifts became appreciably smaller. They did not, and are not included in the positions given in Table 1.

The low-temperature structure was refined entirely by least-squares procedures, starting with the final positions of the room-temperature structure.  $F_T$  was given the value 2.0 in the weighting scheme. Refinement was considered to be complete after six cycles, as the coordinate shifts were then reasonably small (maximum  $1.0\sigma$ , average  $0.3\sigma$ ).

Table 1. *Final parameters of carbon and oxygen atoms*

$$\pm(x, y, z; \frac{1}{2}+x, \frac{1}{2}-y, z)$$

$$\text{T.F.} = \exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl) \}$$

Values in italics refer to structure at  $-130^\circ\text{C}$ .

Atom	$x$ $\times 10^4$	$y$ $\times 10^4$	$z$ $\times 10^4$	$\beta_{11}$ $\times 10^5$	$\beta_{22}$ $\times 10^5$	$\beta_{33}$ $\times 10^5$	$\beta_{12}$ $\times 10^5$	$\beta_{13}$ $\times 10^5$	$\beta_{23}$ $\times 10^5$	$B_1$ $\text{\AA}^2$	$B_2$ $\text{\AA}^2$	$B_3$ $\text{\AA}^2$
C(1)	1314 <i>1318</i>	1480 <i>1578</i>	-1461 <i>-1446</i>	196 <i>47</i>	1686 <i>765</i>	2766 <i>1131</i>	-154 <i>-72</i>	209 <i>19</i>	-497 <i>-441</i>	2.82 <i>0.69</i>	3.40 <i>1.27</i>	4.50 <i>2.04</i>
C(2)	1035 <i>1019</i>	3082 <i>3179</i>	-2221 <i>-2203</i>	246 <i>91</i>	1515 <i>569</i>	2184 <i>685</i>	-381 <i>-193</i>	137 <i>5</i>	-189 <i>-325</i>	2.48 <i>0.67</i>	3.00 <i>1.02</i>	4.88 <i>2.00</i>
C(3)	0366 <i>0341</i>	3516 <i>3583</i>	-2180 <i>-2189</i>	255 <i>103</i>	1239 <i>343</i>	2262 <i>935</i>	-128 <i>-6</i>	-61 <i>-30</i>	-157 <i>-185</i>	2.68 <i>0.73</i>	3.23 <i>1.33</i>	4.18 <i>1.64</i>
C(4)	-0064 <i>-0087</i>	2356 <i>2379</i>	-1234 <i>-1248</i>	224 <i>86</i>	1110 <i>402</i>	2069 <i>627</i>	-52 <i>-67</i>	36 <i>-124</i>	-427 <i>-377</i>	2.28 <i>0.46</i>	3.15 <i>1.23</i>	3.56 <i>1.53</i>
C(5)	-0752 <i>-0783</i>	2643 <i>2623</i>	-1247 <i>-1267</i>	226 <i>81</i>	1265 <i>335</i>	3200 <i>1128</i>	94 <i>88</i>	-32 <i>-55</i>	-130 <i>-234</i>	2.78 <i>0.62</i>	3.67 <i>1.24</i>	4.52 <i>1.73</i>
C(6)	-1163 <i>-1188</i>	1428 <i>1374</i>	-0300 <i>-0324</i>	194 <i>44</i>	1464 <i>693</i>	3574 <i>1333</i>	83 <i>18</i>	126 <i>-5</i>	-184 <i>-254</i>	2.89 <i>0.68</i>	3.49 <i>1.44</i>	4.96 <i>1.94</i>
C(7)	0239 <i>0236</i>	0789 <i>0819</i>	0128 <i>0136</i>	188 <i>71</i>	1117 <i>409</i>	2033 <i>930</i>	-72 <i>-15</i>	72 <i>12</i>	-361 <i>-2</i>	2.32 <i>0.91</i>	2.83 <i>1.14</i>	3.21 <i>1.25</i>
C(8)	0930 <i>0938</i>	0246 <i>0302</i>	-0456 <i>-0435</i>	183 <i>54</i>	1416 <i>565</i>	2440 <i>960</i>	-74 <i>-30</i>	65 <i>-33</i>	-574 <i>-423</i>	2.76 <i>0.74</i>	2.91 <i>1.04</i>	3.85 <i>1.66</i>
C(9)	0355 <i>0344</i>	1446 <i>1460</i>	2664 <i>2710</i>	267 <i>77</i>	1386 <i>444</i>	2135 <i>1121</i>	-170 <i>-45</i>	10 <i>-49</i>	-661 <i>-31</i>	2.47 <i>0.95</i>	3.47 <i>1.20</i>	4.46 <i>1.62</i>
C(10)	1960 <i>1953</i>	5046 <i>5171</i>	-2212 <i>-2173</i>	219 <i>57</i>	1562 <i>474</i>	3584 <i>1711</i>	-175 <i>-27</i>	336 <i>183</i>	-58 <i>-81</i>	2.83 <i>0.78</i>	3.86 <i>1.08</i>	5.17 <i>2.52</i>
C(11)	2308 <i>2293</i>	6223 <i>6394</i>	-3717 <i>-3737</i>	376 <i>145</i>	2715 <i>877</i>	4880 <i>2022</i>	-779 <i>-360</i>	738 <i>281</i>	804 <i>107</i>	2.77 <i>0.88</i>	7.26 <i>2.82</i>	8.57 <i>3.46</i>
O(12)	1417 <i>1395</i>	4269 <i>4410</i>	-3389 <i>-3386</i>	309 <i>99</i>	2067 <i>616</i>	2816 <i>1353</i>	-623 <i>-201</i>	162 <i>33</i>	576 <i>293</i>	2.52 <i>0.79</i>	4.26 <i>1.79</i>	6.72 <i>2.18</i>
O(13)	2115 <i>2122</i>	4804 <i>4891</i>	-0221 <i>-0175</i>	269 <i>66</i>	2249 <i>697</i>	3932 <i>1821</i>	-445 <i>-132</i>	-149 <i>-53</i>	366 <i>184</i>	3.30 <i>0.82</i>	5.16 <i>1.71</i>	6.52 <i>2.57</i>

Table 2. *Final parameters of hydrogen atoms*Values in italics refer to structure at  $-130^\circ\text{C}$ 

Atom	$x$ $\times 10^4$	$y$ $\times 10^4$	$z$ $\times 10^4$	$B$ $\text{\AA}^2$
H(1)	1769 <i>1775</i>	1241 <i>1192</i>	-1714 <i>-1559</i>	1.96 <i>0</i>
H(3)	0206 <i>0116</i>	4668 <i>4851</i>	-2927 <i>-3046</i>	1.81 <i>0</i>
H(5)	-0970 <i>-1016</i>	3743 <i>4022</i>	-2125 <i>-1965</i>	1.84 <i>0</i>
H(6)	-1683 <i>-1709</i>	1754 <i>1417</i>	-0208 <i>-0359</i>	1.42 <i>0</i>
H(9a)	-0092 <i>-0078</i>	1829 <i>1833</i>	3194 <i>3093</i>	2.03 <i>0</i>
H(9b)	0572 <i>0569</i>	0453 <i>0677</i>	3711 <i>3715</i>	1.95 <i>0</i>
H(9c)	0672 <i>0646</i>	2524 <i>2446</i>	2705 <i>3099</i>	1.91 <i>0</i>
H(11a)	2022 <i>2019</i>	7177 <i>7292</i>	-4241 <i>-4198</i>	8.95 <i>3.83</i>
H(11b)	2738 <i>2641</i>	6452 <i>6915</i>	-3081 <i>-2949</i>	8.03 <i>2.45</i>
H(11c)	2324 <i>2304</i>	5767 <i>5880</i>	-5090 <i>-5387</i>	7.21 <i>1.07</i>

Final parameters for both structures are given in Tables 1 and 2. In these tables it will be observed that the isotropic temperature factors given for nearly all the hydrogen atoms are much smaller than the average values for their bonded carbon atoms. (The exceptions, H(11a, 11b, 11c) belong to a methyl group which may well be in a state of hindered rotation). For the low-temperature structure the refinement procedure actually predicts *negative* temperature factors for many hydrogen atoms; such values were assumed to be zero for structure-factor calculations. It is not suggested that there is anything anomalous about the thermal motion of the hydrogen atoms. It may be questioned, however, whether the accepted scattering-factor curve is appropriate for structures of this sort. The same phenomenon has been observed by Sundaralingam & Jensen (1963).

#### Assessment of results

The agreement between observed and calculated structure amplitudes is reasonable, and there can be no doubt of the essential correctness of the proposed structures. It seems unnecessary to publish the very extensive tables of  $F_o$  and  $F_c$ , but copies may be obtained by applying to the National Science Library,

Table 3. Agreement summary

$$\Delta F = |F_o| - |F_c|$$

$$F_T = \text{estimated minimum observable structure amplitude for reflexion concerned.}$$

Category	20 °C		-130 °C	
	Observed	Unobserved	Observed	Unobserved
1. ( $ \Delta F  \leq \frac{1}{2} F_T$ or $ \Delta F  \leq 0.1 F_o$ )	1466	253	} 1459	} 333
2. ( $\frac{1}{2} F_T <  \Delta F  \leq F_T$ or $0.1 F_o <  \Delta F  \leq 0.2 F_o$ )	39	168		
3. ( $F_T <  \Delta F  \leq 3/2 F_T$ or $0.2 F_o <  \Delta F  \leq 0.3 F_o$ )	4	33		
4. ( $3/2 F_T <  \Delta F  \leq 2 F_T$ or $0.3 F_o <  \Delta F  \leq 0.4 F_o$ )		1		
R ( $\sum   F_o  -  F_c   / \sum  F_o $ ) (Observed reflexions only)	0.044		0.099	

Table 4(a). Bond lengths and their estimated standard deviations

Bond	Length at 20 °C Å	Length at -130 °C Å	"Preferred" value Å
C(1)C(2)	1.386 (2)	1.392 (6)	} 1.386 (2)
C(2)C(3)	1.385 (2)	1.386 (6)	
C(1)C(8)	1.384 (2)	1.393 (5)	} 1.389 (2)
C(3)C(4)	1.390 (2)	1.397 (5)	
C(4)C(5)	1.397 (2)	1.398 (5)	} 1.401 (2)
C(6)C(8')	1.403 (2)	1.408 (5)	
C(5)C(6)	1.392 (2)	1.391 (6)	1.392 (2)
C(4)C(7)	1.518 (2)	1.523 (5)	} 1.521 (2)
C(7)C(8)	1.522 (2)	1.524 (5)	
C(7)C(7')	1.527 (3)	1.547 (7)	1.533 (3)*
C(7)C(9)	1.564 (2)	1.563 (6)	1.564 (2)
C(2)O(12)	1.408 (2)	1.417 (5)	1.417 (5)**
C(10)O(12)	1.356 (2)	1.372 (5)	1.372 (5)**
C(10)C(11)	1.484 (3)	1.507 (6)	1.507 (6)**
C(10)O(13)	1.191 (2)	1.190 (5)	1.190 (5)**

Table 4(b). Bond angles and their estimated standard deviations

Angle	Value at 20 °C	Value at -130 °C	"Preferred" value
C(8)C(1)C(2)	120.15 (15)	119.69 (34)	} 120.11 (15)
C(2)C(3)C(4)	120.31 (15)	119.94 (37)	
C(3)C(4)C(7)	118.27 (14)	117.75 (34)	} 118.34 (14)
C(7)C(8)C(1)	118.71 (14)	118.20 (34)	
C(3)C(4)C(5)	123.91 (15)	124.14 (36)	} 124.03 (15)
C(1)C(8)C(6')	124.14 (15)	123.97 (36)	
C(4)C(5)C(6)	121.70 (16)	121.86 (36)	} 121.86 (16)
C(5)C(6)C(8')	122.03 (16)	121.82 (36)	
C(5)C(4)C(7)	117.42 (13)	117.71 (32)	} 117.25 (13)*
C(7)C(8)C(6')	116.81 (13)	117.48 (32)	
C(4)C(7)C(7')	110.35 (16)	110.10 (36)	} 110.17 (16)
C(8)C(7)C(7')	110.21 (16)	109.71 (36)	
C(4)C(7)C(9)	105.25 (13)	105.78 (31)	} 105.21 (13)
C(8)C(7)C(9)	105.07 (13)	104.87 (31)	
C(1)C(2)C(3)	123.93 (15)	124.79 (36)	124.18 (15)
C(4)C(7)C(8)	114.32 (12)	115.17 (30)	114.56 (12)*
C(9)C(7)C(7')	111.46 (16)	111.10 (36)	111.36 (16)
C(1)C(2)O(12)	119.44 (14)	119.17 (34)	119.17 (34)**
C(3)C(2)O(12)	116.12 (14)	115.42 (34)	115.42 (34)**
C(2)O(12)C(10)	118.51 (14)	117.76 (32)	117.76 (32)**
O(12)C(10)O(13)	122.71 (16)	123.42 (36)	123.42 (36)**
O(12)C(10)C(11)	111.12 (17)	109.79 (37)	109.79 (37)**
O(13)C(10)C(11)	126.18 (18)	126.82 (39)	126.82 (39)**

\* Averaged quantities differ significantly.

\*\* Room-temperature value not considered.

National Research Council, Ottawa, Canada, giving adequate reference to this paper. A summary of the agreement is given in Table 3.

A final three-dimensional difference synthesis for the room-temperature structure reveals electron-density anomalies of as much as  $0.2 \text{ e. \AA}^{-3}$ . These occur chiefly in the neighbourhood of hydrogen atoms, and probably result from the unrealistic assumption that the thermal motion of these atoms is isotropic.

For the room-temperature structure the standard deviations of the coordinates of carbon and oxygen atoms, estimated from the least-squares results, range from  $0.0014$  to  $0.0025 \text{ \AA}$ . For the low-temperature structure the e.s.d.'s range from  $0.0034$  to  $0.0051 \text{ \AA}$ .

### Description of the structure

In addition to the thermal vibration tensors expressed in the conventional form, Table 1 includes the radii of the vibration ellipsoids along their principal axes. From these values it can be seen that the thermal motion is severely anisotropic, particularly for the atoms (10 to 13) of the acetoxy group. Consideration of the relative orientations of the ellipsoids does not reveal any single mode of vibration, but much of it appears to be consistent with a rigid-body libration of the molecule about its centre. The r.m.s. amplitude of such a libration would be about  $2\frac{1}{2}^\circ$ , a magnitude which could hardly result in appreciable bond-length errors. However, it would be unwise to assume that the molecule is a rigid body. The acetoxy group can probably behave non-rigidly, and the magnitude of the thermal motion for the atoms of this group is a warning that there may be significant but indeterminate errors in the apparent bond lengths. (Similar considerations might apply to the bond of the internal methyl group [C(7)–C(9)] but the thermal motion of the methyl carbon is hardly great enough to warrant concern). At the lower temperature the thermal motion is still markedly anisotropic, and of similar character to that observed at room temperature. However, its magnitude, and the magnitude of resulting bond length errors, have been very much reduced.

Bond lengths and angles are compared in Table 4. With some exceptions, the quantities determined at the two temperatures agree very well. However, two of the bonds in the acetoxy group appear to be significantly shortened at the higher temperature. This result is not unexpected, and it is probably better to accept for this group the more reliable, but nominally less accurate values of bond length and angle determined at the lower temperature. Surprisingly, the central bond C(7)–C(7') also appears to be shorter at the higher temperature. The difference is significant at the 1% level, and can hardly result from errors due to thermal motion. Adjacent bonds are not affected, but the angle C(4)C(7)C(8) is significantly greater at the lower temperature, an effect which is consistent with the need to accommodate

a lengthened central bond. Although no reason for such behaviour can be advanced, the possibility must be considered that this bond is temperature dependent.

Except for the acetoxy group, the molecule has an approximate plane of symmetry passing through C(2), C(7), and C(9) (Fig. 2). Differences between chemically equivalent (that is, mirror-related) bond lengths are not significant at either temperature. At the higher temperature the difference between one pair of chemically equivalent angles [C(5)C(4)C(7) and C(7)C(8)C(6')] is significant at the 0.1% level.

In general the 'preferred' values given in Table 4 are the appropriately weighted means of the values obtained at the two temperatures. The estimated standard deviation quoted is that of the most accurate determination. For the acetoxy group, the low-temperature values are preferred. Chemically equivalent values have been averaged, also. For the central bond, and for certain of the angles, the quantities averaged differ significantly, and the preferred values must in such cases be regarded as somewhat idealized and hypothetical.

The lengths of the peripheral bonds of the pyrene nucleus are all quite close to the aromatic value of  $1.395 \text{ \AA}$ . Moreover, the peripheral atoms are approximately coplanar; the distances of these atoms (in the structure at room temperature) from their mean plane  $2.2385x + 3.0107y + 5.2445z = 0$  are given in Fig. 2(b). These distances indicate a significant, but nevertheless fairly small departure from planarity. The lengths of the bonds and the approximate coplana-

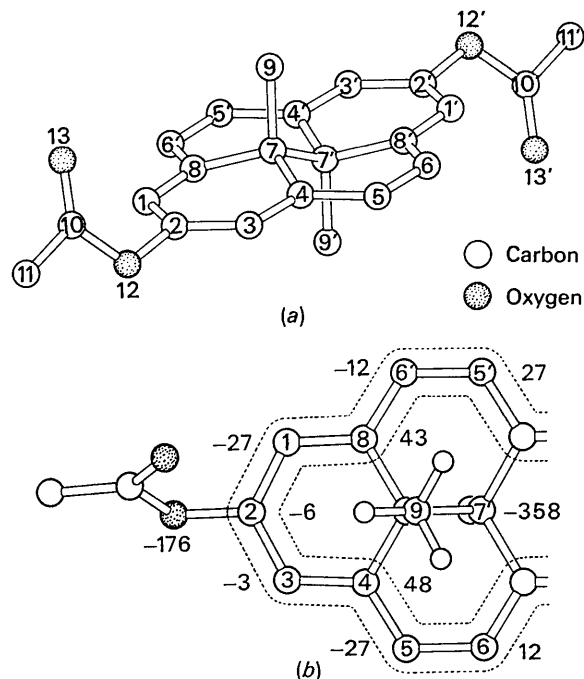


Fig. 2. (a) The molecule, viewed along *b*. (b) Part of the molecule, viewed along the normal to the mean plane of the peripheral atoms of the pyrene nucleus. The distances of some of the atoms from this plane, in  $\text{\AA} \times 1000$ , are indicated.

city of the atoms confirm the aromatic character of the 14-ring.

The hydrogen atoms have not been located with sufficient accuracy to merit discussion of bond lengths. The orientation of the internal methyl group is shown in Fig. 2(b). This is obviously a reasonable way for the group to accommodate itself to the 14- $\pi$ -electron cloud (also speculatively outlined). Nevertheless the length of the bond C(7) C(9) (1.563 Å, e.s.d. 0.002 Å) indicates some crowding.

Intermolecular distances are reasonable. For the room-temperature structure the closest approach is 3.39 Å, a value which becomes 3.36 Å for the low-temperature structure.

The specimen material was supplied by Professor V. Boekelheide. Computations were carried out on IBM 650 and 1620 computers, under the supervision of Dr

F. R. Ahmed, using his programs and those of Dr G. A. Mair, Dr E. J. Gabe, and Mrs M. E. Pippy. Their assistance, and the continued encouragement of Dr W. H. Barnes, are gratefully acknowledged.

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## Structure de la Bromo-2-naphthoquinone-1,4

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2-Bromo-1,4-naphthoquinone, C<sub>10</sub>O<sub>2</sub>H<sub>6</sub>, crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c* with cell dimensions:

$$a = 13.88 \pm 0.02, b = 3.98 \pm 0.02, c = 15.74 \pm 0.02 \text{ \AA}; \beta = 104^\circ \pm 30'$$

The structure was determined by the heavy atom method and geometrical considerations. Least-squares refinement has reduced the overall reliability index to 0.09.

### Introduction

La détermination de la structure de la bromo-2-naphthoquinone-1,4 fait partie d'une étude sur les dérivés de l' $\alpha$ -naphthoquinone dont certains sont des vitamines ou des antivitaminés K.

### Partie expérimentale

Les cristaux sont préparés par refroidissement lent d'une solution acétique sursaturée. La maille monoclinique est définie par les paramètres:

$$a = 13,88 \pm 0,02, b = 3,98 \pm 0,02, \\ c = 15,74 \pm 0,02 \text{ \AA}; \beta = 104^\circ \pm 30'$$

Groupe spatial *P*2<sub>1</sub>/*c*

Nombre de molécules par maille: 4

La densité calculée (1,87) est en accord avec la densité mesurée.

Le cristal tournant autour de la direction d'allongement [010], nous avons obtenu, au moyen du

rétigraphe de De Jong (radiation Cu  $K\alpha$ ), les quatre plans réciproques portant les taches *h*0*l*, *h*1*l*, *h*2*l*, *h*3*l* contenus dans la sphère de résolution.

Les intensités des 560 taches indépendantes ont été mesurées par comparaison visuelle avec une échelle d'intensité et corrigées par les facteurs de Lorentz et de polarisation (Gay, 1954). Aucune correction d'absorption n'a été effectuée; la section des monocristaux utilisés est de 0,2  $\times$  0,3 mm<sup>2</sup>.

Tous les calculs de séries de Fourier bidimensionnelles ont été effectués au moyen du photosommateur de von Eller (1955).

### Détermination de la structure

*Projection* (010)

Les coordonnées *x* et *z* de l'atome de brome ont été déterminées par la méthode des superpositions appliquée à la projection de la fonction de Patterson, les coordonnées des atomes légers par la méthode classique de l'atome lourd.