

Crystals Exhibiting Disorder – The Monoclinic Polymorph of 9-Chloro-10-methylantracene

BY RAYMOND D. G. JONES AND T. R. WELBERRY

Research School of Chemistry, Australian National University, PO Box 4, Canberra, ACT 2600, Australia

(Received 24 September 1980; accepted 29 December 1980)

Abstract. $C_{15}H_{11}Cl$, $M_r = 226.7$, monoclinic, $P2_1/c$, $a = 8.197$ (2), $b = 9.884$ (4), $c = 13.580$ (8) Å, $\beta = 95.33$ (3)°, $U = 1095$ Å³, $Z = 4$, $d_c = 1.37$ Mg m⁻³, $\mu(Cu K\alpha) = 2.653$ mm⁻¹. $R = 0.057$ for 1193 reflexions. The crystal structure shows disorder with respect to Cl and methyl, the occupancy factor for Cl at the 9 position being 0.686 (4). The structure is isomorphous with the bromo analogue.

Introduction. Jones & Welberry (1980) discussed disordered molecular crystals and reported on the structure of 9-bromo-10-methylantracene, BMA. Available evidence suggested the present compound, CMA, was isomorphous with BMA. We undertook the present study for comparison with BMA.

CMA was prepared by the method of Heller & Schmidt (1971). Yellow rhomb-shaped crystals were grown from petroleum ether (b.p. 333–353 K). Cell dimensions were determined from 2θ values of Cu $K\alpha_1$ reflexions recorded by the Weissenberg method. The camera had a radius of 57.3 mm, the film being loaded in the Straumanis mode. Intensities were photographically recorded by the equi-inclination Weissenberg method. Graphite-monochromated Cu $K\alpha$ radiation was used. Two crystals were used to record layers $h0l - h8l$ and $hk0 - hk2$. Films were scanned with an Optronics P1700 densitometer and intensities and indices subsequently determined.* Intensities were corrected for absorption, and Lorentz and polarization factors (Levy & Ellison, 1960), and the different layers placed on a common scale (Rae & Blake, 1966). These and subsequent calculations were carried out with *SHELX* (Sheldrick, 1976). There were 1193 unique observed reflexions. E.s.d.'s for the observations were determined according to Einstein & Jones (1971) with $A = 1.5$, $B = 6.0$ and $C = 14.9$.

The coordinates of BMA were used initially. Coordinates and anisotropic thermal parameters for Cl and C, the occupancy of chlorine at Cl and an

* Software for the Optronics P1700 and for subsequent intensity and index determinations was kindly made available by Dr M. Elder, Daresbury Laboratory, Science Research Council, Daresbury, Warrington, England.

Table 1. Final fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters

	x	y	z	B_{eq} (Å ²)†
Cl	2362 (1)	5704 (1)	8249 (1)	4.80
C(1)	2825 (4)	3742 (4)	9947 (3)	3.93
C(2)	3149 (5)	2890 (4)	10737 (3)	4.64
C(3)	1933 (6)	2014 (5)	11019 (3)	4.95
C(4)	412 (5)	2000 (4)	10519 (3)	4.19
C(5)	-3496 (4)	3805 (4)	7823 (3)	3.97
C(6)	-3804 (5)	4672 (4)	7050 (3)	4.54
C(7)	-2589 (5)	5552 (4)	6772 (3)	4.52
C(8)	-1072 (5)	5553 (4)	7264 (3)	4.07
C(9)	878 (4)	4637 (3)	8603 (3)	3.36
C(10)	-1558 (4)	2876 (3)	9179 (3)	3.33
C(11)	1254 (4)	3765 (3)	9410 (3)	3.23
C(12)	6 (4)	2873 (3)	9698 (3)	3.14
C(13)	-1912 (4)	3762 (3)	8375 (2)	3.10
C(14)	-685 (4)	4664 (3)	8075 (3)	3.30
C(15)	-2975 (3)	1843 (3)	9497 (2)	5.60

$$\dagger B_{eq} = \frac{2}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Table 2. A least-squares plane and deviations (Å) of atoms from it

The equation to the plane of best fit for the anthracene moiety is $0.3550X - 0.6984Y - 0.6214Z + 10.57 = 0$, where X , Y and Z (in Å) are along a , b and c *.

C(1)	0.004 (4)	C(9)	0.009 (4)
C(2)	-0.014 (4)	C(10)	0.006 (4)
C(3)	-0.012 (5)	C(11)	0.006 (4)
C(4)	-0.003 (4)	C(12)	0.004 (4)
C(5)	0.000 (4)	C(13)	0.003 (4)
C(6)	-0.004 (4)	C(14)	0.002 (4)
C(7)	-0.012 (4)	C(15)†	0.017 (1)
C(8)	-0.006 (4)	Cl†	0.024 (2)

† Atoms not included in the plane calculation.

extinction factor defined by Sheldrick (1976) were refined. H atoms were placed 0.95 Å from the bonded C. At convergence, R and wR were 0.057. A difference map was featureless. Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974) and Cromer & Liberman (1970), respectively.

Positional parameters are in Table 1.* Table 2 gives information on the least-squares plane through the anthracene moiety.

Discussion. The disorder observed shows that Cl and CH₃ have similar substitutional-disorder properties to Br and CH₃. The Cl occupancy at the 9,10-substituent positions is 0.686/0.314, cf. 0.643/0.357 for BMA. The X-ray diffuse scattering is similar to BMA (Welberry & Jones, 1980), except that the [011], [01 $\bar{1}$] streaking is more pronounced for CMA, suggesting larger amplitudes of molecular motion in those directions. The streaking is substantially diminished in intensity on cooling the crystal to ~160 K whereas the

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35800 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

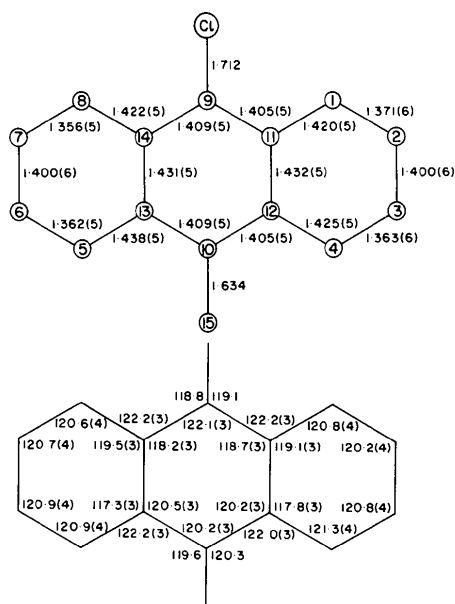


Fig. 1. Interatomic distances (Å) and angles (°). E.s.d.'s are shown in parentheses.

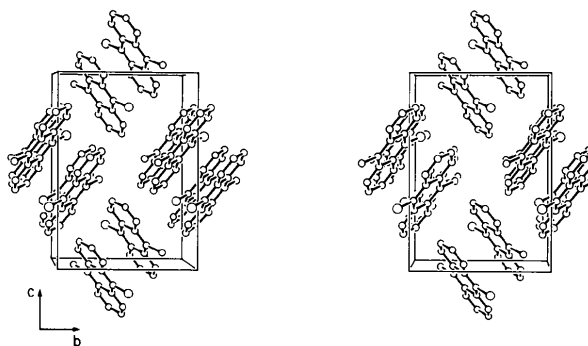


Fig. 2. Stereoscopic view of the structure down a*.

other diffuse-scattering features are not. The details of the relationship between crystal geometry, intermolecular forces and observed diffuse scattering for this and other disordered molecular crystals will be the subject of a future paper.

Fig. 1 shows interatomic distances and angles. No atomic resolution of Cl/C could be made at Cl and C(15) and so distances to these positions from C(9) and C(10) lie between C—C and C—Cl. The geometry of the anthracene moiety is virtually the same as in BMA. Fig. 2 shows that centrosymmetrically related pairs of molecules do not overlap completely. Only the central and end rings are in close contact.

References

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- EINSTEIN, F. W. B. & JONES, R. D. G. (1971). *J. Chem. Soc. A*, pp. 3359–3363.
- HELLER, E. & SCHMIDT, G. M. J. (1971). *Isr. J. Chem.* **9**, 449–462.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JONES, R. D. G. & WELBERRY, T. R. (1980). *Acta Cryst.* **B36**, 852–857.
- LEVY, H. A. & ELLISON, R. D. (1960). *Acta Cryst.* **13**, 270–271.
- RAE, A. D. & BLAKE, A. B. (1966). *Acta Cryst.* **20**, 586.
- SHELDRIK, G. M. (1976). *SHELX*. A program for crystal structure determination. Univ. of Cambridge, England.
- WELBERRY, T. R. & JONES, R. D. G. (1980). *J. Appl. Cryst.* **13**, 244–251.