

Table I. *Atomic coordinates*

Carbon atoms				Hydrogen atoms			
Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
<i>A</i>	-0.356	0.618	0.104	( <i>C</i> )H <sub>1</sub>	-2.633	2.030	0.614
<i>B</i>	-1.052	0.769	1.169	( <i>C</i> )H <sub>2</sub>	-1.119	2.781	1.181
<i>C</i>	-1.765	2.048	1.305	( <i>D</i> )H <sub>1</sub>	-2.776	3.070	2.676
<i>D</i>	-2.165	2.276	2.710	( <i>D</i> )H <sub>2</sub>	-1.333	2.455	2.422
<i>E</i>	-2.891	1.008	3.060	( <i>E</i> )H <sub>1</sub>	-3.279	1.167	3.894
<i>F</i>	-1.893	-0.108	3.310	( <i>E</i> )H <sub>2</sub>	-3.644	0.773	2.285
<i>G</i>	-1.092	-0.265	2.132	( <i>F</i> )H <sub>1</sub>	-1.217	0.091	4.166
<i>H</i>	-0.323	-1.421	1.941	( <i>F</i> )H <sub>2</sub>	-2.398	-0.957	3.383
<i>I</i>	0.352	-1.634	0.908	( <i>H</i> )H	-0.311	-2.139	2.589
				( <i>I</i> )H	0.847	-2.480	0.816

3.68 Å between atom *A* of the molecule at 0, 0, 0 and the atom *C* of the molecule at  $\frac{1}{2}, \frac{1}{2}, 0$ .

We are indebted to Prof. J. D. Bernal and to Prof. J. W. Cook for supplying crystals and to the Royal Society and the British Empire Cancer Campaign for apparatus grants. One of us (W. G. F.) wishes to thank the University of St. Andrews and Queen's College for a Research Scholarship. We should also like to thank Mrs N. M. Stott for help in calculating the final list of structure factors.

### References

- BERGHUIS, J., HAANAPPEL, I. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.  
 BERNAL, J. D. (1933). *Chem. Ind.* 267.  
 BURNS, D. M. & IBALL, J. (1955). *Proc. Roy. Soc. A*, **227**, 200.  
 MATHIESON, A. M., ROBERTSON, J. M. & SINCLAIR, V. C. (1950). *Acta Cryst.* **4**, 516.  
 ROBERTSON, J. M. (1934). *Phil. Mag.* (7), **18**, 729.  
 ROBINSON, B. W. (1929). *J. Sci. Instrum.* **10**, 233.

*Acta Cryst.* (1958). **11**, 329

## The Crystal Structure of 10-Methyl 1.2 Benzanthracene

BY R. MASON

*Department of Chemical Crystallography, University College, London W.C. 1, England*

(Received 22 November 1957)

The molecular 'aggregation' in the crystal structure of 10-methyl 1.2 benzanthracene is discussed in relation to the electron distribution in the crystal and associated effects.

### Introduction

X-ray crystallographic analyses of the monomethyl substituted 1.2 benzanthracenes were initiated with the purpose of examining the adequacy of the quantum mechanical predictions of the electron distribution in these molecules (Pullman, 1946), but the complexity of the crystal structures has prevented such a detailed survey. Some features of the crystal structure of 10-methyl 1.2 benzanthracene are, however, of interest in connexion with the hypothesis that some of the polycyclic carcinogens may act in a state of aggregation (Mason, 1956) and in a study of the polymorphism of organic crystals.

### Experimental

10-Methyl 1.2 benzanthracene, the most active agent in the isomeric series, crystallizes in the monoclinic

system (fine needles from ethanol) with the following unit cell satisfying the large majority of X-ray reflexions:

$$a = 24.2 \pm 0.2, \quad b = 5.77 \pm 0.03, \quad c = 94.4 \pm 0.9 \text{ \AA}, \\ \beta = 90^\circ 0' \pm 15'.$$

The observed density,  $\rho(20^\circ \text{C.}) = 1.20 \text{ g.cm.}^{-3}$ , corresponds to 40 molecules in the unit cell, and the systematic absences ( $h0l$  when  $h = 2n+1$ ,  $0k0$  when  $k = 2n+1$ ) require the space group  $P2_1/a-C_{2h}^2$  to relate the ten independent sets of four molecules.

A more detailed examination of the  $\{h0l\}$  Weissenberg data suggests that the crystal structure is based on a rather ill-defined superlattice arrangement. The  $\{00l\}$  reflexions occur for  $l = 10n$  only, and the further accidental absences which are observed among the general reflexions can be largely explained in the following way (Fig. 1). The co-ordinates of any reference

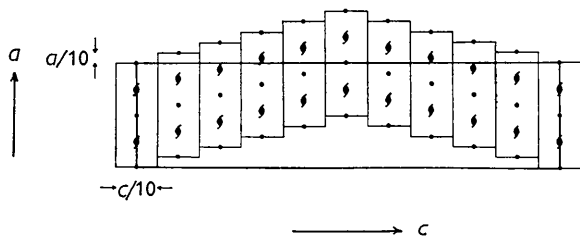


Fig. 1. The proposed superlattice arrangement projected on 010.

point in the molecule in such a scheme are

$$\pm \begin{cases} (x, z), & (x + \frac{1}{2}, z) \\ (x + 0.1, z + 0.1), & (x - 0.4, z + 0.1) \\ (x + 0.2, z + 0.2), & (x - 0.3, z + 0.2) \\ (x + 0.3, z + 0.3), & (x - 0.2, z + 0.3) \\ (x + 0.4, z + 0.4), & (x - 0.1, z + 0.4) \\ (x + 0.5, z + 0.5), & (x, z + 0.5) \\ (x + 0.4, z + 0.6), & (x - 0.1, z + 0.6) \\ (x + 0.3, z + 0.7), & (x - 0.2, z + 0.7) \\ (x + 0.2, z + 0.8), & (x - 0.3, z + 0.8) \\ (x + 0.1, z + 0.9), & (x - 0.4, z + 0.9) \end{cases}$$

This superlattice arrangement is similar to that proposed for other aromatic molecules, for example 2.4.6-trinitrotoluene (Ito, 1950), although it is not possible to discuss the X-ray data of 10-methyl 1.2 benzanthracene by suggesting that what appears externally as a single crystal is usually composed of a polysynthetic twin. Crystals which were grown from many solvents and under very different experimental conditions gave identical X-ray powder photographs so that any polymorphism which the compound may show has not been determined.

The high degree of ordering of the molecules, which is suggested by Fig. 1, is confirmed by the weighted reciprocal lattice which contains the Fourier transform of a single molecular unit only. This ordering is even more clearly pronounced in the  $a$  crystal projection since the  $\{0kl\}$  Weissenberg data reveal, in addition to the systematic space-group extinctions, the accidental absences  $\{0kl\}$  when  $l \neq 5n$ . Indeed, the majority of the 'strong' reflexions may be indexed on the basis of a cell with  $c = 9.44 \text{ \AA}$ . It is, however, clear from an examination of the  $\{hkl\}$  reflexions that this description of the crystal structure can be only approximate since a number of reflexions are observed which could only be indexed if  $c$  were  $283.2 \text{ \AA}$ —120 molecules per unit cell.

### Discussion

One interpretation of the 'aggregation' in 10-methyl 1.2 benzanthracene is to assume that the possibility of overlap of  $\pi$  orbitals between one molecule and its neighbours is increased; the banded electronic structure which would arise from such a delocalization effect will confer an extra stability on the crystal as

a result of the lowering of the total energy of the system. There is no direct structural evidence that the presence of several crystallographically non-equivalent molecules in the unit cell leads, of itself, to larger interaction effects between neighbouring molecules. It is of interest to note, however, that the crystal structure of 3.4:5.6 dibenzophenanthrene (McIntosh, Robertson & Vand, 1954), requiring two non-equivalent molecules in the asymmetric unit, demonstrates intermolecular contacts of  $3.2 \text{ \AA}$ , which represent an appreciable shortening of the usual van der Waals' distance for this type of compound. This shortening could certainly lead to increased  $\pi$ -orbital overlap since the overlap integral  $S(r=3.2 \text{ \AA}) \approx 0.034$ , whereas  $S(r=3.6 \text{ \AA}) \approx 0.016$  (Mulliken *et al.*, 1949). This must not be considered a conclusive argument, however, since the short intermolecular contacts may be more intimately connected with the intramolecular 'overcrowding' in this example.

If the concept that 'aggregation' of the molecules in the crystal leads to an increased delocalization of the  $\pi$  orbitals has any validity, we may expect the methyl benzanthracenes to show varying electrical conductivity properties. The semi-conducting properties of a number of organic molecules have been explained by assuming that the excited orbitals of the  $\pi$  electrons in the isolated molecule are combined to give non-localized orbitals extending throughout the crystal (Eley *et al.*, 1953). The effect of the aggregation discussed above would be to decrease the energy gap between the highest filled band and the lowest unfilled band in the crystal, so that the activation energy of 10-methyl 1.2 benzanthracene (aggregation factor  $N = 10$  (Mason, 1956)) will be less than that for 5-methyl 1.2 benzanthracene ( $N = 2$  or  $4$  depending on the choice of space group), which in turn will be less than the 8-methyl compound ( $N = 1$ ). The magnitude of the effect cannot, however, be predicted with the information available at present.

The associated effect of diamagnetic anisotropy should also reflect the increased delocalization of the electrons during 'aggregation', but it has not been found possible to grow crystals sufficiently large for crystal susceptibility measurements.

These investigations are supported by the British Empire Cancer Campaign.

### References

- ELEY, D. D., PARFITT, G. D., PERRY, M. J. & TAYSUM, D. H. (1953). *Trans. Faraday Soc.* **49**, 79.  
 ITO, T. (1950). *X-ray Studies in Polymorphism*. Tokyo: Maruzen.  
 MCINTOSH, A. O., ROBERTSON, J. M. & VAND, V. (1954). *J. Chem. Soc.* p. 1661.  
 MASON, R. (1956). *Naturwissenschaften*, **11**, 252.  
 MULLIKEN, R. S., RIEKE, C. A., ORLOFF, D. & ORLOFF, H. (1949). *J. Chem. Phys.* **17**, 1248.  
 PULLMAN, B. (1946). *Bull. Ass. franç. Cancer*, **33**, 120.