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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

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The bond lengths in chrysene.

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The crystal structure of chrysene has been re-investigated with a view to obtaining the C–C bond lengths. Starting from the approximate atomic coordinates given by Iball (1934), further ($h0l$) and ($0kl$) Fourier syntheses have been computed with Iball's structure factors (which were obtained by using an integrating photometer on Weissenberg photographs) together with some additional structure factors obtained by visual estimates of the intensity on photographs taken recently. The complete three-dimensional data for Cu $K\alpha$ radiation is being collected and it is hoped to improve on the accuracy obtained so far from two-dimensional Fourier syntheses. However, as the three-dimensional work will take some time to complete, this note gives the present position.

The atomic coordinates have been refined in the following way:

(*a*) Two-dimensional Fourier syntheses were computed on the ($0kl$) and ($h0l$) zones, all the observed structure factors being used in each case. The electron-density peaks were determined by the semi-analytical method of Burns & Iball (1955) modified slightly to take advantage of the suggestions put forward by Megaw (1954). The modification consists of using eleven points surrounding the highest recorded electron density and, from three linear combinations of these points, constructing three curves which should intersect at the true peak position. Usually the curves enclose a small triangle and the centroid is taken as the true position. In addition, the logarithms of the densities are used instead of the electron densities themselves.

(*b*) With the coordinates obtained from (*a*) all the structure factors for the two zones were calculated, including those too small to be observed. Errors due to series termination and overlapping were corrected by (i) computing new Fourier syntheses but now including the calculated value of the missing reflexions in the Cu $K\alpha$ reciprocal-lattice sphere (hydrogen atoms were taken into account in calculating the structure factors); (ii) determining the true electron peak positions by the above method again; and then (iii) correcting for the effect of nearest neighbours, as was done in the case of fluorene (Burns & Iball, 1955). In the case of fluorene, however, the table of corrections was obtained by the use of an atomic profile given by $\varrho(r) = A \exp [-pr^2]$, which does not have the diffraction ripples which cause series-termination errors. In the present work a table of corrections has been constructed from the atomic profile obtained by calculating the integral

$$\varrho'(r) = \int_0^{s_0} 2\pi s f(s) \, . \, J_0(2\pi r s) \, ds \; ,$$

where $f(s)$ is the Cu $K\alpha$ scattering curve for carbon, terminated at $\sin\theta = 1$. (It is desirable when one is using

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this method to know the upper limit of integration precisely, and that is why the calculated structure factors of the unobserved reflexions within the Cu $K\alpha$ reciprocal-lattice sphere were included in the Fourier synthesis.) The profile obtained in this way does have diffraction ripples and is likely to give a truer value for the correction for series-termination errors.

The ($h0l$) zone F_o synthesis (Fig. 1(a)) was computed at intervals of $a/60$ (= 0·140 Å) and $c/240$ (= 0·105 Å).

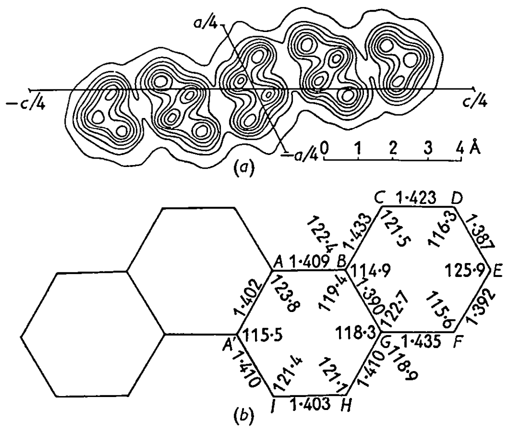

Fig. 1. (a) Chrysene ($C_{18}H_{10}$): electron-density map of projection on (010). (b) Bond lengths (Å) and angles (°).

Every atom gives a resolved peak in this projection, and the correct positions for the electron-density maxima can be determined with considerable accuracy.

The observed and calculated structure factors agree very well if McWeeny's (1951) scattering curve for carbon is used with a temperature factor (B) of 3·97 Å^2. The reliability indices $R\ (= \Sigma|F_o|-|F_c| \div \Sigma|F_o|)$, including only those planes actually observed, are, $R(0kl) = 13{\cdot}1\%$, $R(h0l) = 9{\cdot}3\%$.

Referring the coordinates to orthogonal axes x', y and z', where x' and y are parallel to a and b respectively, and z' is perpendicular to the plane (001), the mean plane of the molecule is given by the equation

$$0{\cdot}8559x'+0{\cdot}4789y+0{\cdot}1952z' = 0\ .$$

The crystals are monoclinic with

$$a = 8{\cdot}39,\ b = 6{\cdot}20,\ c = 25{\cdot}20\ \text{Å},\ \beta = 116{\cdot}2°;$$

space group, $I2/c$; 4 molecules per unit cell. The maximum, mean and r.m.s. values for the distances of the atoms from the mean plane are, respectively, 0·031, 0·012, 0·0145 Å.

The bond lengths and bond angles are shown in Fig. 1(b). The mean bond length is 1·408$_5$ Å and the maximum deviation from this mean is 0·026$_5$ Å, which is not statistically significant if we take the r.m.s. value of the deviation of the atoms from the mean plane as a measure of the accuracy of the atomic coordinates.

Pritchard & Sumner (1954) have recently calculated the bond lengths in chrysene using a self-consistent molecular-orbital approximation, and Table 1 gives a comparison of the experimental and the two theoretical values, M.O. and S.C.M.O., quoted from their paper.

Table 1. *Bond lengths in chrysene*

Bond	Expt. (Å)	M.O. (Å)	S.C.M.O. (Å)
A–B	1·409	1·426	1·438
B–C	1·433	1·404	1·423
C–D	1·423	1·381	1·363
D–E	1·387	1·398	1·423
E–F	1·392	1·380	1·363
F–G	1·435	1·407	1·424
G–H	1·410	1·417	1·439
H–I	1·403	1·372	1·355
A–A′	1·402	1·413	1·438
B–G	1·390	1·414	1·388

The agreement between experimental and theoretical values is not very good but it is perhaps significant that there is a wider range of values in the calculated bond lengths than in those found experimentally.

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Polarization correction for crystal-monochromatized X-radiation.

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In a previous publication bearing the above title (Azaroff, 1955), it was stated that the polarization correction for the equi-inclination method would have to be determined, individually, for each reflection. In a recent publication, Whittaker (1953) has derived a straightforward equation using reciprocal-lattice coordinates, μ, ν, and γ, for performing these calculations for an entire level at a time. A new calculation, however, should be made for each new crystal. The purpose of this note is to correct the omission of this reference from the original paper.

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