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THE CRYSTAL STRUCTURE OF ETHYLENE.

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X-ray powder patterns of solid ethylene were obtained by Mooy [1] and Washer.[2] They could not be interpreted by the methods available for powder photographs, which are only applicable to the more symmetrical crystal systems—cubic, hexagonal and tetragonal; in both investigations it was therefore concluded that the crystal symmetry must be orthorhombic or lower.

Single-crystal X-ray patterns were obtained by Keesom and Taconis [3]; they concluded that the unit cell is orthorhombic, and suggested positions of the carbon atoms. The structure suggested (Fig. 1) is, however, inherently improbable, for two reasons. Firstly, interatomic distances are very different from those found in other substances: (*a*) The C=C distance is given as 1·55 A., whereas in ethylene gas [4] and in other substances containing double-bonded carbon atoms, the distance is 1·33 A.* (*b*) The nearest distance between carbon atoms in different molecules is, in Keesom and Taconis' structure, 2·59 A., whereas in other hydrocarbon crystals it is 3·5-4·2 A. Secondly, in the suggested arrangement, the two molecules in the unit cell are crystallographically non-equivalent; the physical meaning

Fig. 1.—Carbon positions suggested by Keesom and Taconis.

of this formal non-equivalence is that the surroundings of one of these molecules are different from those of the other. Such an arrangement is unlikely; in fact, if molecules were placed in such positions, and could retain their orientations, the forces between them would make the *b* and *c* axes equal; the symmetry would then be tetragonal and the molecules would become crystallographically equivalent. Furthermore, the structure is not only inherently unlikely, but does not account satisfactorily for the observed relative intensities of the X-ray reflections. In particular, the 021 reflection, which is required by the suggested structure to be moderately strong, is actually absent from the photographs.

For these reasons, the X-ray data of Keesom and Taconis have been reconsidered.

Unit Cell.—There seems no reason to doubt the correctness of the proposed unit cell since it was deduced from single-crystal moving-film photographs. The cell is rectangular (and therefore presumably orthorhombic in symmetry) and the edge-lengths at − 175° C. are $a = 4·87$ A.,

[1] Mooy, *Thesis*, Leiden. Mentioned in (3).

[2] Washer, *Chem. Abs.*, 1937, **31**, 922 (*Proc. Indiana Acad. Sci.*, 1935, **45**, 222).

[3] Keesom and Taconis, *Physica*, 1935, **2**, 463.

[4] Thompson, *Trans. Faraday Soc.*, 1939, **35**, 697.

* In a recent paper,[5] the slightly higher value of 1·35 A. is given; in relation to the present problem, this difference is inappreciable.

[5] Gallaway and Barker, *J. Chem. Physics*, 1942, **10**, 88.

$b = 6\cdot46$ A., $c = 4\cdot14$ A. (Keesom and Taconis' axes have been inter-changed, for a reason which will appear later.) The density at this tem-perature has not been measured, but by interpolation is expected to be about 0·70. Accepting this and the unit cell dimensions, the number of ethylene molecules per unit cell is found to be 2. (The calculated density for a two-molecule cell of the above dimensions is 0·717 at $-175°$ C.)

The Arrangement of the Molecules.—The amount of information available for deducing the symmetry of the atomic arrangement is small (see Table I). For this reason, the normal procedure of first deducing the

TABLE I

Spacing.	Indices.	Intensity * for Keesom & Taconis' Arrangement.	Observed Int.	Int.* for Present Arrangement.
3·87	110	100	s	100
3·49	011	129	vs	115
3·23	020	16	s	25
3·15	101	63	s	53
2·82	111	1·2	vw	6·3
2·70	120	3·5	m	11·2
2·53	021	9	—	0
2·43	200	1·0	—.	0·8
2·30	210, 121	15	s	22

* Expressed on the basis : intensity for 110 reflection = 100·0 units.

space group from the types of absent reflections, and then using the relative intensities of recorded reflections to settle the atomic parameters, will not be followed. Instead, all intensity information will be considered at once.

There are two molecules in the unit cell. If we take the centre of one molecule as the origin of the unit cell, the other molecule would be expected to lie at the centre of the cell, though it might conceivably lie at other positions, such as the centre of one of the cell faces. The absence of 100, 010 and 001 reflections, and the fact that 011, 101 and 110 are all strong, show without any doubt that it is in the centre of the cell. The orientation of the centre molecule is, however, not the same as that of the corner molecule, as is shown by the presence of a weak 111 reflection : in other words, the lattice is a primitive one.

If (as is probable) the two molecules in the cell are related to each other by symmetry operations, these symmetry operations can only be glide planes or screw axes. They cannot be rotation axes or reflection planes, because the second molecule does not lie on a face or edge of the cell, but at the centre. Any glide planes can only be diagonal glide planes (n) for the same reason. The presence of the 120 reflection (in which $h + k$ is odd) shows that there is no diagonal glide plane normal to the c axis ; but there are no $h0l$ reflections having $h + l$ odd, or $0kl$ reflections having $k + l$ odd ; hence there appear to be diagonal glide planes normal to the b and a axes. If so, the space group is either Pnn (C_{2v}^{10}) or $Pnnm$ (D_{2h}^{12}). The first of these is non-centrosymmetrical, and it is difficult to see how centrosymmetrical molecules (as ethylene molecules are) could form a non-centrosymmetrical arrangement. Hence, the space group $Pnnm$ is more probable. In any case, as far as carbon atoms only are concerned, the arrangement in Pnn is the same as that in $Pnnm$.

The only possible arrangement of four carbon atoms in either of these space groups is that shown in Fig. 2 ; they are at fourfold positions (g) (for $Pnnm$) of International Tables : xyo ; $\bar{x}\bar{y}o$; $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2}$; $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2}$. In remains to determine x and y. Assuming that the carbon-carbon distance is 1·33 A. (as in ethylene gas molecules [4]), calculations of
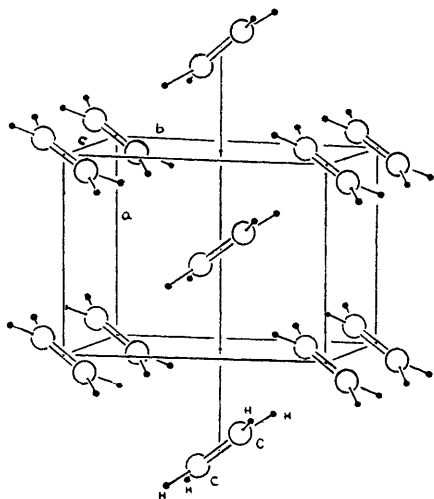
the intensities of the powder photograph reflections for various orientations of the molecule have been made.   Satisfactory agreement between observed and calculated intensities (see Table I) is obtained for $x = 0.11a$ and $y = 0.06b$.   (Intensity $= F^2[\theta]p$, where p is the number of equivalent crystal planes, $[\theta] = \dfrac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$ ($\theta =$ Bragg angle of reflection),

$$F = 4f \cos\ 2\pi\Big(hx + \frac{h + k + l}{4}\Big)\cos 2\pi\Big(ky - \frac{h + k + l}{4}\Big)\cos\ 2\pi lz,$$

f being the diffracting power of the carbon atoms.*

The positions of hydrogen atoms cannot usually be found from X-ray diffraction data, because their diffracting power is so small ; certainly there is no hope of finding their positions from such scanty data as exists for ethylene.   But the most likely positions, in view of the normal effective radii of hydrogen and carbon atoms (1.2 and 1.7 A. respectively) are those shown in Fig. 2.   These are, of course, only average positions ; there is probably considerable thermal movement, and in fact each molecule may rotate as a whole round the C=C bond ; but the hydrogen atoms are likely to spend most of their time in the positions shown. (Thermal movements cause the structure to assume—momentarily—lower symmetries, among them the *Pnn* arrangement mentioned previously.)

In the structure proposed here, the distances between atoms in neighbouring molecules agree with those found in other crystals.   The nearest distance between carbon atoms in neighbouring molecules is 3.8 A.   Assuming that the C—H distance in the ethylene molecule is 1.09 A. and the angle H—C—H is 118°,[4] the shortest distance between hydrogen atoms in neighbouring molecules is 2.4 A.   The shortest distance from a hydrogen atom to a carbon atom of a neighbouring molecule is 3.0 A.

FIG. 2.—Structure proposed in present work.

Summary.

Positions of carbon atoms which account for published X-ray data on ethylene crystals are suggested.   The details of this structure are :—

Unit cell—orthorhombic, with $a = 4.87$ A., $b = 6.46$ A., $c = 4.14$ A. Space group—*Pnnm* (D_{2h}^{12}).   Co-ordinates of carbon atoms—(1) xyo ; (2) $\bar{x}\bar{y}o$; (3) $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2}$; (4) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2}$, where $x = 0.11a$, and $y = 0.06b$.

The interatomic distances in this arrangement agree with those found in related substances.

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* Cox and Goodwin's figures [6] for f were used.
[6] Cox and Goodwin, *J. Chem. Soc.*, 1936, 769.