

The Crystal Structure of Ethyl Stearate

BY A. McL. MATHIESON

Division of Chemical Physics, C.S.I.R.O. Chemical Research Laboratories, Melbourne, Australia

AND H. K. WELSH

Division of Applied Physics, C.S.I.R.O. National Standards Laboratory, Sydney, Australia

(Received 11 May 1964 and in revised form 11 August 1964)

Evidence is presented that the space group of ethyl stearate, on the basis of the cell, $a=5.59$, $b=7.40$, $c=57.1$ Å, $\beta=118^\circ$ is $1a$ and not Aa as reported by Aleby (1962). As a result, reinterpretation of his data has removed the anomalies in the conformation of the ester group which existed in the original analysis.

The specific shape of the ester group has an important influence on the dipole moment of the group and hence on the dielectric properties of long-chain esters (Welsh, 1959; Dryden & Welsh, 1964). As part of a programme aimed at correlating dielectric properties and structure, a crystal analysis of one such ester, ethyl behenate, has been initiated. This work has led us to a careful assessment of the evidence presented by Aleby (1962) for the dimensions and conformation of the ester group in ethyl stearate, a homologue of ethyl behenate. As reported by Aleby, the crystal structure of ethyl stearate contains two unusual features in the ester group $-\text{CO}-\text{O}-\text{C}-\text{C}$. The angles $\text{C}-\text{O}-\text{C}$ and $\text{O}-\text{C}-\text{C}$ are 138° and 140° respectively and the alcohol α -carbon is *trans* to the $\text{C}=\text{O}$ group [Fig. 1(a)]; both features are sufficiently unexpected and contradictory to the available evidence to warrant close inspection.

The shape of the ester group

The evidence (Wheland, 1955; Bender, 1960; Huisgen & Ott, 1959; Mathieson & Taylor, 1961; Fridrichsons & Mathieson, 1962) regarding the ester group indicates that it is planar, that the nominally single $\text{C}-\text{O}$ bond-lengths differ by ~ 0.1 Å, that the angles $\text{C}-\text{O}-\text{C}$ and

$\text{O}-\text{C}-\text{C}$ are in the range of 108 – 115° and that the ester moiety is *cis* to the $\text{C}=\text{O}$ group [Fig. 1(b)]. The opening-out of the bond angles and the adoption of a *trans* configuration (relative to $\text{C}=\text{O}$) both involve the expenditure of energy. Thus the energy of bending a $\text{C}-\text{C}-\text{C}$ bond angle through 30° can be estimated to be of the order of 17 kcal.mole $^{-1}$, using the data in Westheimer (1956) (see also Hendrickson, 1961), while the energy difference between *cis* and *trans* conformations in liquid ethyl formate has been determined as 2.5 kcal.mole $^{-1}$ by Tabuchi (1958). Prelog (1963) has presented evidence to show that, in large-ring systems, conformational adjustments take place preferentially by rotation around bonds to maintain normal bond angles. It would therefore be expected that any restraints on the ester group in ethyl stearate would have been relieved by torque around some of the single bonds.

Only when forming part of a small ring is the alcohol α -carbon found in the energetically less-favoured *trans* position to $\text{C}=\text{O}$ (Huisgen & Ott, 1959) while still satisfying the other dimensional and conformational restrictions (Mathieson & Taylor, 1961; Mathieson, 1963). All other evidence regarding molecules incorporating an unstrained ester group, including the structure of methyl stearate (Aleby & von Sydow, 1960), shows a *cis* conformation. The *trans* conformation in a linear molecule proposed for ethyl stearate is therefore unique.

The structure according to Aleby

The analysis is based on projections down the a and b axes. The projection down the a axis delineates separate molecules lying approximately parallel to the c axis. The ester group is clearly peri-planar. In the projection down the b axis however, an ambiguity can exist in the interpretation of the electron density distribution in the neighbourhood of the ester group. The atom $\text{O}(1)$ may be attached to $\text{C}(\text{O}1)$ or to atom $\text{C}(\text{O}1')$, related to $\text{C}(\text{O}1)$ by the a glide (Fig. 2). A decision is not possible from the projections alone. Without re-

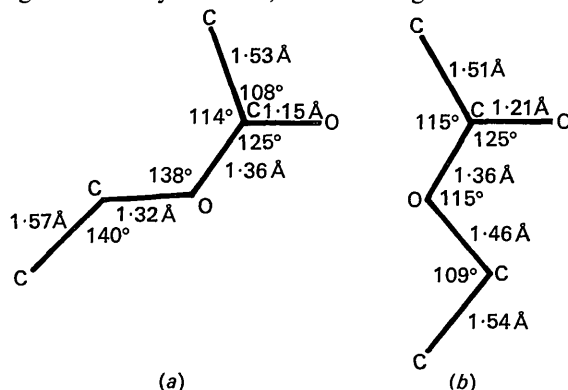


Fig. 1. Dimensions of the ester group (a) in ethyl stearate according to Aleby (1962), (b) average values and standard conformation derived from available structural evidence of esters.

course to full or partial three-dimensional data, additional evidence of a more general nature must be invoked. Aleby mentioned this dilemma but suggested that it could be resolved by reference to van der Waals contacts. On the basis of the packing of the terminal chain atoms, C(18), and the ethyl groups, $-C(O1)-C(O2)$, he concluded that, since the plane through the alcohol group is parallel to (010), the atom C(O1) must be on the same level as O(1); otherwise the approach distance $C(O2) \cdots C(18)$ would be ~ 2.5 Å. We have confirmed this with a ball-on-spike model of the interface packing. *This choice defines the conformation of the ester group.* Furthermore this choice is inevitable if the space group is *Aa* as reported.

The modified structure

Examination of the model made it clear that the conflict between the shape of the ester group and end-packing could be resolved if the space group was *Ia*, which is indistinguishable from *Aa* by reference solely to the projections down the *a* and *b* axes. The alter-

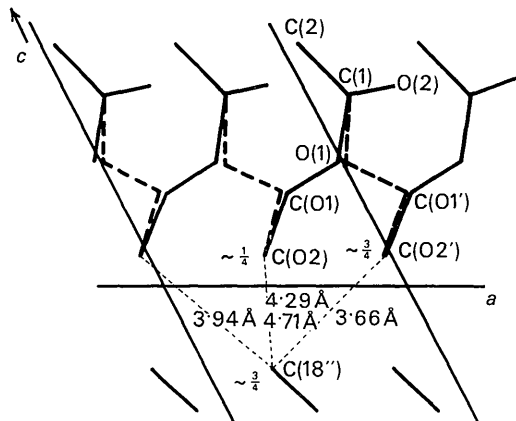


Fig. 2. The structure of ethyl stearate viewed down the *b* axis. The structure in full lines is that proposed by Aleby while the dashed lines indicate the alternative linkage of atoms. Small displacements of O(1) and C(O1) compatible with $g(x, z)$, Fig. 2 in Aleby (1962), are shown.

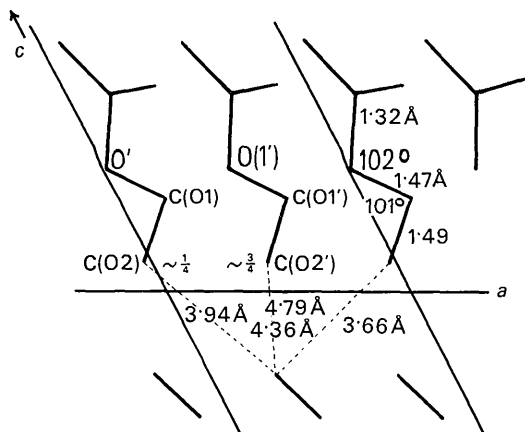


Fig. 3. The modified structure based on the space group *Ia*. Detail of the ester group.

native ester arrangement (Figs. 2 and 3) is now permitted. With the same *x, z* parameters as in Aleby's Table 1 and using $\frac{1}{2} + x$ for C(O1) and C(O2), the angles C-O-C and O-C-C are both 90° , while C(1)-O(1) and O(1)-C(O1) are 1.34 and 1.74 Å respectively. Small shifts of O(1) by 0.2 Å to $x = +0.02$ and of C(O1) by -0.1 Å to $x = +0.19$, adjustments compatible with $g(x, z)$, Fig. 2 in Aleby (1962), lead to the dimensions in Fig. 3. The bond lengths and angles are now more reasonable and the ester group has the *cis* configuration. More accurate values for the bond lengths and angles would require further refinement with the available data on the basis of the modified molecular model.

The space group

The internal evidence offered above indicates that with the cell defined so that the interaxial angle $\beta = 118^\circ$, the space group must be *Ia*. It was not at first possible to make a direct check on ethyl stearate crystals, but excellent crystals of a homologue, ethyl behenate, $C_2H_5-O-CO \cdot C_{21}H_{43}$, had been prepared. If these esters are isostructural with the molecular axes nearly parallel to (001), the addition of an even number of CH_2 groups will not greatly modify the packing.

The measured *a* and *b* dimensions of ethyl behenate are almost identical with those of ethyl stearate. To ascertain the space group allocation, a crystal was mounted on the *b* axis and zero- and first-layer equi-inclination Weissenberg films were exposed over the same angular (ω) range. The two films were superimposed and 00 l aligned with 01 l . The run of intensities for 20 l with small l parallels that reported for ethyl stearate, as is expected for similar structures, and was used to identify the 200 reflexion in conformity with the stearate allocation. The corresponding β angle is 118° . The distinction between *A*-face centring and body-centring of the unit cell thus specified was made by reference to the 11 l run. Here the existence of 110 and in general 11 l for $h+k+l=2n$ fixes the space group as *Ia* for ethyl behenate with a cell $a=5.54$, $b=7.43$, $c=67.0$ Å, $\beta=118^\circ$.

Subsequently a single-crystal specimen of ethyl stearate was obtained, making a direct comparison possible. Using the same procedure with zero- and first-layer equi-inclination Weissenberg and selecting a^* (with $\beta=118^\circ$) by reference to the run of 20 l intensities reported by Aleby, it was confirmed, in particular for the 11 l run, that $h+k+l=2n$ and the space group for ethyl stearate is indeed *Ia*.

Conclusion

The space group for ethyl stearate has been erroneously determined as *Aa* by Aleby. Evidence is presented for a homologue, ethyl behenate, and for ethyl stearate itself that the correct space group is *Ia*. With this latter space group, the structural data for ethyl stearate no longer present anomalies in the dimensions and con-