CCCLX.—*Dimorphism in the Aliphatic Dicarboxylic Acid Series (Azelaic Acid).*

By William Augustus Caspari.

In a previous paper (J., 1928, 3235) some account was given of the way in which chain molecules are built up in the crystallisation of saturated dibasic acids having carboxyl groups at each end of the molecule. In the course of the investigation it was observed that the nine-carbon member of the series, azelaic acid, occurs in two crystalline modifications, of both of which well-shaped crystals were obtained without difficulty.

The α-modification is the one in which the seven dicarboxylic acids (including azelaic) previously dealt with crystallise. It is characterised by the occurrence of (110) as a face and as a cleavage plane. The new or β-modification of azelaic acid is, like the α-acid, monoclinic-prismatic and tabular upon (001), but does not show (110); on the other hand, (010) is invariably developed as a face and is a strong cleavage plane. When lying flat, α-crystals consequently tend to show a rhomboidal or a six-sided contour, whilst β-crystals have rectangular contours. Under the microscope the two can easily be distinguished by the formation of spearhead cleavage fragments in one case and right-angled ones in the other, when the crystals are gently crushed.

The β-modification usually separates when warm saturated solutions of the acid are cooled, whilst the α-modification is favoured when solutions evaporate slowly at ordinary temperatures. β-Crystals of reasonable size (2—3 mm. across and $\frac{1}{4}$—$\frac{1}{2}$ mm. thick) and perfection are best prepared by crystallisation from hot aqueous solutions containing several grams of acid. From the foregoing, it would appear that the β-, being favoured by hurried crystallisation, is the less stable modification of the two. Nevertheless, the difference in stability does not prevent the two from separating out side by side, as was commonly found to occur, for instance, when alcoholic solutions were allowed to crystallise at ordinary temperatures. Evidently the difference in lattice energy between the α- and the β-form is small, and this also follows from the fact that they cannot be distinguished by m. p. as determined by the ordinary method.

Crystals of β-azelaic acid are tabular upon (001) and show narrow faces of (100) and (010), all three being cleavage planes. Small developments of (120) were occasionally noted.

The crystal structure of the β-polymorph was examined by the usual *X*-ray methods. The monoclinic angle of the crystal, *i.e.*, the angle between (100) and (001), was measured goniometrically. The dimensions of the unit cell in Ångström units are as follows, those of the α-crystal as previously determined being quoted for comparison :

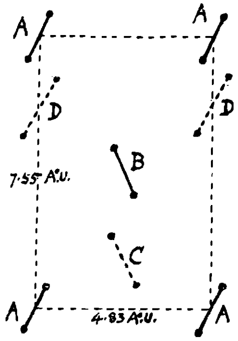
	a.	*b.*	*c.*	*β.*
β-Azelaic acid	5·61	9·58	27·20	136° 30′
α-Azelaic acid	9·72	4·83	27·14	129° 30′

From the volume, it may be calculated that the unit cell of each form contains the substance of four molecules.

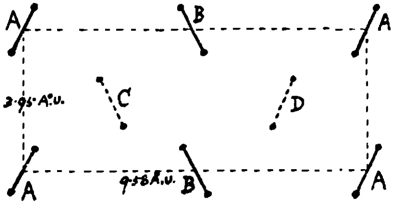
More than 50 crystal planes in all were identified as reflexion spots upon the rotation and oscillation photographs of the β-acids. The basal plane occurs only in its even orders (002), (006), and (008); this indicates a division of the unit cell across *c* into halves of approximately equal reflecting power. The cell has therefore the same two-storied structure as was found for the α-polymorph. No reflexions from (010) or its odd orders appear, but (020) is represented; hence parallel to (010) there are planes of rotation molecules lying between planes of A and B molecules. On the other hand, (100) gives the strongest reflexion of any plane, whilst (200) is absent, so that there can be no interleaving of the *a* cell-sides by planes of B molecules. Almost as strong is the reflexion from $(10\bar{1})$. The interleaving of the *b* cell-side is conspicuously shown by the *b*-axis rotation photographs, on which the second layer-line consists of more and much intenser reflexion spots than the first. On the *a*-axis photographs the first layer-line is the most intense.

No general halvings were noted either in the (*hkl*) or in the (*hol*) series, but (010), as mentioned above, is halved. The crystal is therefore to be assigned to space-group C_{2h}^{2}, for which four asymmetric molecules per cell are required. The space-group of the α-modification was previously found to be C_{2h}^5.

In its main features, the crystal structure of β-azelaic acid follows from the identity of its c axis with that of the α-acid. It is clear that the molecules, the backbone of which is a zigzag chain of nine carbon atoms, are laid along the c axis in much the same way whether the acid crystallises in the α- or the β-form. There remains the question of how the molecules of β-acid are planted out upon the base, the answer to which is given by the space-group and by the interleavings referred to above. The disposition of the molecules is best shown by a diagrammatic projection of the cell, not upon the base itself, but upon a cross-section normal to the c-axis, as in the accompanying figure. For comparison, the corresponding ground-plan of the α-acid cell is also given. Each stroke represents the projection of a molecule, the knobs at either end standing for centres of carbon atoms. The dotted strokes refer to molecules in the other half of the cell, above or below the plane of the paper; they do not necessarily lie in the exact centre of the half-cell. A being taken as primary molecules, the molecules B are derived from A by reflexion, C by rotation, and D by rotation and reflexion.



α-Azelaic acid.



β-Azelaic acid.

Polymorphism in the higher fatty compounds has long been suspected as a cause of abnormal behaviour in the neighbourhood of the m. p., more especially of triglycerides. In recent times X-ray evidence of polymorphism in higher hydrocarbons (Müller and Saville, J., 1925, **127**, 602) and fatty acids (Piper, Malkin, and Austin, J., 1926, 2310) has been brought forward, but single crystals of polymorphic forms were not isolated. In the dicarboxylic acid series, polymorphism does not hitherto appear to have been observed. From the present example it is clear that the elongated molecules of such a substance as azelaic acid can bundle themselves in at least two ways. In the more usual one the long chains are packed in nearly equilateral triangles of slightly less than 5 Å.U. side; in the other they are packed in oblongs of slightly less than 5 Å.U. by 4 Å.U. Similar alternative packings may be foreseen in other classes of straight-chain aliphatic compounds.

Numerous unsuccessful attempts were made to obtain β-modifications of suberic and sebacic acids, as representatives of the even-carbon members of the series. From solvents, from the melt, and by sublimation these acids were invariably found to crystallise in the α-form.

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DAVY FARADAY LABORATORY,
ROYAL INSTITUTION.

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