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Short Communications

Crystal Modifications of Bigeranyl Tetrahydrochloride

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Bigeranyl tetrahydrochloride, $C_{20}H_{38}Cl_4$, first described by Sörensen *et al.*[1], is a lower homologue of squalene hexahydrochloride, $C_{30}H_{56}Cl_6$, which has previously been investigated by Sörum and Dale [2], with the result that the two crystalline isomers could be identified as the two *meso*-forms out of the six possible diastereoisomers. From the point of view of a complete structure determination, bigeranyl tetrahydrochloride might be expected to be more favourable than the squalene derivatives, as its carbon chain is only two thirds of that of the latter.

For bigeranyl tetrahydrochloride two diastereoisomers should be possible; one *meso*-form, and one enantiomorphic pair. From the X-ray data given below it was concluded that the crystalline isomer is the *meso*-form. It was not possible to isolate the other isomer, either because it may not be formed at all by the addition of hydrogen chloride to bigeranyl, or, more likely, because it does not readily crystallize. However, it was found that the *meso*-form crystallized in two modifications: thin plates of approximately hexagonal form, melting at 95° C, and long needleshaped crystals, melting at 110° C. The lower melting form can be obtained by crystallization from cold acetone, the higher melting one by evaporation of a carbon disulfide solution at room temperature. The lower melting modification is labile and is spon-

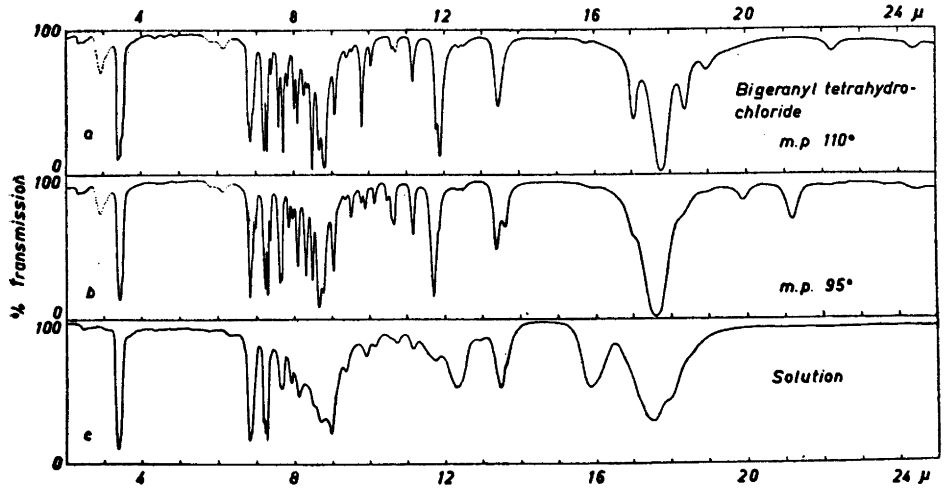

Fig. 1. Infrared absorption spectra from 2—15 μ (NaCl-prism) and from 15—25 μ (KBr-prism) of a) the higher melting and b) the lower melting crystal form of bigeranyl tetrahydrochloride as pressed KBr-disks, and of c) solutions in CCl_4 (2—8 μ, 15—25 μ) and in CS_2 (8—15 μ).

taneously converted in the solid phase to the higher melting and stable modification. This conversion may take several weeks at room temperature, but only minutes or hours at 80° C. After melting at 95° C the substance may solidify on further heating and melt again at 110° C. The degree of conversion may be established by X-ray diffraction, but more conveniently by infrared spectroscopy (Fig. 1).

Some preliminary crystal data for the two modifications of bigeranyl tetrahydrochloride have been collected for further determination of their structures, and shall be reported here. For the *lower melting form* the unit cell dimensions obtained from oscillation and Weissenberg photographs using Cu$K\alpha$ radiation, are: $a = 38.6 \pm 0.1$ Å; $b = 10.20 \pm 0.05$ Å; $c = 5.99 \pm 0.02$ Å, $\gamma = 93.0 \pm 0.3°$, $V = 2\,358$ Å^3, $Z = 4$ mol./u.c., $d_{calc} = 1.181$ g/cm^3, $d_{obs} \approx 1.18$ g/cm^3. Systematic absences are found for $00l$ when l odd; for $hk0$ when k is odd. The same systematic weaknesses of the reflections as for the isomers of squalene hexahydrochloride are also found, *i. e.*, $h00$ when h is odd; $0k0$ when k is odd; and $h0l$ when $h + l$ is odd. Space group $P2_1/b$.

A comparison of these data with those of the squalene hexahydrochloride isomers [2] will show that the a-axis length for bigeranyl tetrahydrochloride is about two thirds of that of squalene hexahydrochloride, the other data being very closely the same for both compounds. A one-dimensional projection of electron density on the a-axis has been calculated, and this synthesis also shows that the low melting modification of bigeranyl tetrahydrochloride closely resembles the squalene hexahydrochloride isomers, especially the higher melting one; hence, it must be the *meso*-form.

A single crystal of the *higher melting form* of approximate size $0.5 \times 1.0 \times 10$ mm has been prepared. This shows good cleavages parallel to (100) and (010), but inferior parallel to (001). The crystal data for this modification are: $a = 20.91 \pm 0.05$ Å; $b = 9.77 \pm 0.02$ Å; $c = 6.04 \pm 0.02$ Å; $\alpha = 87°\ 13' \pm 10'$; $\beta = 92°\ 52' \pm 10'$; $\gamma = 102°\ 55' \pm 10'$; $V = 1\,175$ Å^3; $Z = 2$ mol./u.c.; $d_{calc} = 1.186$ g/cm^3; $d_{obs} \approx 1.19$ g/cm^3.

By comparing the crystal data and the infrared spectra (Fig. 1) of the two crystalline isomers it may be seen that marked differences exist, indicating that we have to do with two different conformational isomers. The spontaneous solid phase conversion of one form into the other can therefore hardly be due to simple translations of the molecules in the crystal lattice, but must rather involve a rotation about some of the bonds in the chain. It is instructive to note the remarkable difference between the spectra of these two conformational isomers even in the C—Cl stretching frequency region, 17—18 μ, where one would expect a fairly constant "group frequency". The solution spectrum represents, of course, the equilibrium mixture of a very large number of conformational isomers and is accordingly more diffuse and less characteristic.

1. Sörensen, N. A., Gillebo, T., Holtermann, H. and Sörensen, J. S. *Acta Chem. Scand.* **5** (1951) 757.
2. Sörum, H. and Dale, J. *Acta Chem. Scand.* **9** (1955) 141.

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Transformation of 2-(β,β-Dicarbomethoxyethyl)-furan into *m*-Hydroxybenzoic Acid

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Furans with suitable substituents in the 2-position may be transformed into other systems with aromatic character by methoxylation to cyclic acetals of 1,4-dicarbonyl compounds, followed by intramolecular condensation in acid solution [1-6]. Further application of this principle has led to the transformation of 2-(β,β-dicarbomethoxyethyl)-furan (I) into *m*-hydroxybenzoic acid (III) as shown below.

Trans-2-furanacrylic acid was isolated as a by-product of the reaction (yield 2 %). This indicates that to a small extent an ethylenic linkage has been formed in the side-chain of I by oxidation during electrolysis.

I was prepared from furfuryl chloride as shown below *cf.* [7]. Dimethyl difurfuryl malonate (IV) was isolated as a by-product of this reaction.