CCXXXII.—*The Dimorphism of Certain Higher Aliphatic Compounds.*

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IN a paper on the evaluation and interpretation of parachors (J., 1929, 2112), the present authors concluded from an examination of existing values that the CH_2-increment of 39 units adopted by Sugden (J., 1924, **125**, 1177) was too small, and should be replaced by one of 40 units. In continuation of this work, a number of cetyl and allied derivatives were prepared, and several of them were found to be capable of assuming more than one crystalline form. Pressure of other work prevented a thorough investigation being made, but, in view of the recent appearance of a paper dealing, *inter alia*, with the dimorphism of the ethyl esters of palmitic and stearic acids (Smith, this vol., p. 802), it is thought advisable to record our preliminary observations.

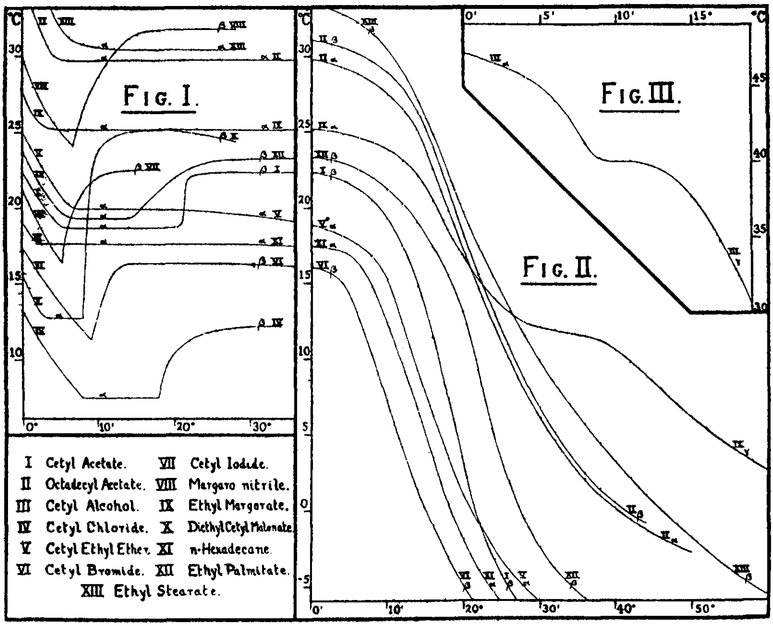
Enantiotropic dimorphism has been inferred from *X*-ray spacing data in the case of the higher members of many series of compounds, and has been directly observed with certain aliphatic acids by Garner and his co-workers (J., 1924, **125**, 881; 1926, 2491; 1929, 1849), but, at least so far as the simpler aliphatic compounds are concerned, the monotropic dimorphism noted by Smith and by the present authors appears to have escaped observation hitherto, apart from somewhat vague references in the early literature to change of crystalline form on standing.

In addition to the instances referred to by Smith, such monotropic dimorphism has been observed in the case of cetyl acetate (I), cetyl chloride (IV), and diethyl cetylmalonate (X), the rather large and transparent crystals first obtained on cooling the liquid being converted, by continued rubbing or seeding with crystals which had been cooled to below 0°, into a finer, more opaque, and higher-melting modification with considerable rise of temperature. The lower-melting or α-form in every case crystallised without supercooling (see Fig. 1).

With cetyl bromide (VI), cetyl iodide (VII), and margaronitrile (VIII), no α-modification could be obtained, the stable β-form crystallising from the supercooled liquid at a temperature apparently higher than the freezing point of the former (see Fig. 1). As, however, in the case of each compound, incidence of crystallisation in a number of freezing-point determinations occurred at approximately the same temperature, it is possible that the lower-melting forms were momentarily produced but spontaneously transformed into the β-varieties.

With octadecyl acetate (II), on the other hand, as with the isomeric ethyl stearate (XIII) (compare Smith, *loc. cit.*), great difficulty was experienced in effecting the change from α to β. The β-form appeared to be deposited from alcoholic solution, and the transformation to be favoured by rapid cooling, but the growth of β-crystals in the liquid ester at a temperature slightly above the melting point of the α-form was too slow for the freezing point of the β-variety to be determined in the ordinary way.

In the case of ethyl margarate (IX), and also of ethyl cetyl ether (V), only one modification was obtained, corresponding in transparent appearance and in crystallisation without supercooling to the α-form of the above. The margaric ester, however, when further cooled was found to change enantiotropically to a more opaque form, the transition temperature being 14·5° ± 3·0° (see Fig. 2). No such transformation was observed in the case of ethyl palmitate and stearate, or hexadecyl and octadecyl acetates when cooled to below 0°, but cetyl alcohol itself exhibited an analogous discontinuity in the vicinity of 40° (see Figs. 2 and 3). It is evident that these observations, if substantiated, have an important bearing on the problem of alternation of melting points in aliphatic series.



F.-p. curves. *Cooling curves.*

Finally, in view of the fact that two modifications of *n*-octadecane and eicosane have been inferred by Müller and Saville (J., 1925, **127**, 599) from *X*-ray spacing data, it is somewhat surprising that the cooling curve of *n*-hexadecane (XI), the parent of the cetyl series, showed no sign of an arrest from 17·6° (its f. p.) to − 10° (see Fig. 2).

EXPERIMENTAL.

(I) *Cetyl Acetate.*—Crude cetyl alcohol, obtained by hydrolysing spermaceti, was converted into the acetate, which was purified by repeated fractionation under reduced pressure (Krafft, *Ber.*, 1883, **16**, 1721). The large transparent α-crystals, f. p. 18·7° (no supercooling), first obtained on cooling, changed, when rubbed or further cooled, to a pearly white mass, with rise of temperature to 21—22° The f. p. of the latter, by seeding at 20°, was 22·3° (Krafft, *loc. cit.*, gives m. p. 22—23°; Youtz, *J. Amer. Chem. Soc.*, 1925, **47**, 2252, m. p. 22·7°). No discontinuity was observed in the cooling curve of the α-form down to 12°; at this temperature conversion to the β-form took place spontaneously, and no change in this form was noted down to − 10°.

(II) *Octadecyl Acetate.*—This was obtained as a by-product in the purification of the above, and recrystallised from alcohol. The transparent α-variety, f. p. 29·7° (no supercooling), when seeded with crystals which had been recrystallised from alcohol or cooled to below 0°, changed slowly to a pearly white mass, m. p. 31·3° (Krafft, *loc. cit.*, gives m. p. 31°). No discontinuity was observed in the cooling curve of either form down to 0°.

(III) *Cetyl Alcohol.*—By the hydrolysis of the acetate, cetyl alcohol, f. p. 49·1°, unchanged by recrystallisation from methyl alcohol or benzene–light petroleum, was obtained (Smith, *loc. cit.*, gives f. p. 49·27°). The cooling curve exhibited a well-defined arrest at about 40°, corresponding with a change in appearance from glassy to white and opaque.

(IV) *Cetyl Chloride.*—This compound was prepared from the alcohol with phosphorus pentachloride. The transparent α-variety, f. p. 7·4° (no supercooling), changed when seeded with crystals which had been cooled to 0°, to a fine white modification, f. p. 12·1° (seeded at 11°) [Norris and Taylor, *J. Amer. Chem. Soc.*, 1924, **46**, 753, and Clark and Streight, *Trans. Roy. Soc. Canada*, 1929, (3), **23**, Sect. 3, 77, give m. p. 13°].

(V) *Ethyl Cetyl Ether.*—From the chloride by the action of alcoholic potash, only the transparent variety, f. p. 19·9° (no supercooling), could be obtained, despite vigorous rubbing and seeding with crystals which had been cooled to − 10° (Becker, *Annalen*, 1857, **102**, 220, gives m. p. 20°). The cooling curve showed no arrest down to − 10°.

(VI) *Cetyl Bromide.*—The liquid prepared from the alcohol with phosphorus pentabromide was supercooled to 11—12°, and then crystallised, with rise of temperature, in a white opaque form, f. p. 16·3° (Fridau, *Annalen*, 1852, **83**, 15, gives m. p. 15°). Numerous attempts were made to obtain a lower-melting variety, by cooling slowly without stirring and so on, but in every instance crystallisation as above set in before the temperature fell below 11°. The cooling curve showed no discontinuity down to − 10°.

(VII) *Cetyl Iodide.*—Here, again, this substance (from the bromide by the action of sodium iodide in acetone) yielded only the higher-melting variety, f. p. 22·5° (with supercooling to 16—17°) (Krafft, *Ber.*, 1886, **19**, 2219, and Gascard, *Ann. Chim.*, 1921, **15**, 332, give m. p. 23°; Smith, this vol., p. 251, m. p. 23·3°).

(VIII) *Margaronitrile.*—As with the two previous compounds only the β-modification was obtained, f. p. 31·7° (with supercooling to 24—25°) (v. Braun and Sobecki, *Ber.*, 1911, **44**, 1464, give m. p. 29°). This nitrile was prepared from cetyl bromide by the action of potassium cyanide.

(IX) *Ethyl Margarate.*—The ester (from the nitrile by the imino-ether method) crystallised on cooling in large transparent plates, f. p. 25·2° (no supercooling), which could not be induced to assume a higher-melting β-form by continued rubbing, by seeding with ester which had been cooled to 0°, or by recrystallisation from alcohol (m. p. 25·8°). (Holde, *Ber.*, 1902, **35**, 4306, gives m. p. 24—25°; Bömer and Limprich, *Z. Unters. Nahr. Genussm.*, 1912, **23**, 641, m. p. 26·7°; Ruttan, *8th Intern. Cong. Appl. Chem.*, 1912, **25**, 431, m. p. 27·5°; and Le Sueur, J., 1904, **85**, 827, m. p. 28°.) On cooling, the solid changed enantiotropically to a more opaque γ-modification, the transition temperature being 11—12° from the cooling curve and 17—18° from the heating curve.

(X) *Diethyl Cetylmalonate.*—This was prepared from the bromide with sodiomalonic ester. The transparent α-variety, f. p. 12·7° (no supercooling), when seeded with ester which had been cooled to 0°, changed to a white powdery mass, f. p. 25·1° (Brigl, *Z. physiol. Chem.*, 1915, **95**, 161, gives m. p. 22°).

(XI) n-*Hexadecane.*—The liquid, prepared by the action of sodium on *n*-octyl bromide in ether, solidified on cooling to a wax-like mass, f. p. 17·6° (no supercooling) (Krafft, *loc. cit.*, and Landa, *Bull. Soc. chim.*, 1928, **43**, 1086, give m. p. 18°; Waterman, van 't Spijker, and van Westen, *Rec. trav. chim.*, 1929, **48**, 1103, m. p. 17·8°). The cooling curve of the solid showed no discontinuity down to − 10°.

(XII) *Ethyl Palmitate and* (XIII) *Stearate.*—These esters were obtained by esterification of commercial "purified" acids, and purified by fractionation under reduced pressure. Their dimorphism has been described in detail by Smith (*loc. cit.*). For the palmitate, the observed f. p.'s were: α-form 19·2° (no supercooling), β-form 23·2°, m. p. 24·1° (Smith gives m. p.'s 19·4 and 24·18°, respectively). With the stearate, the α-form had f. p. 30·4° (no supercooling), and the β-form, obtained by seeding with ester recrystallised from alcohol and keeping over-night, had m. p. 32·9° (Smith gives m. p.'s 30·9° and 33·4°, respectively). With both these esters the cooling curves of the β-forms were continuous down to − 10°. Those of the α-forms could not be realised owing to spontaneous transformation to the β-variety occurring, rapidly with rise of temperature in the case of the palmitate, but slowly with only retardation of the rate of cooling in the case of the stearate.

It is hoped to present the results of the parachor determinations on these and other compounds in a subsequent communication, but it may be mentioned here that they appear fully to substantiate our conclusion regarding the value of the CH_2-increment.

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[*Received, June 3rd,* 1931.]