Infrared Spectra and Crystallinity. Part II. αω-Dicarboxylic Acids.*

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Infrared spectra of the αω-dicarboxylic acids $CO_2H\cdot[CH_2]_n\cdot CO_2H$ with $n = 2$—8, 10, 14, and 16 have been measured from 3500 to 670 cm.$^{-1}$, with both crystalline and molten material. The spectra of crystalline material are consistent with an approximately planar *trans*-configuration of the $[CH_2]_n$ chain and association of the type (I) (p. 2434). On melting of the materials, however, the spectra change considerably, many bands blurring or disappearing. These changes are attributed to a break-up of the normal association and a loss of the planar configuration. It is considered that the molten acids adopt a continuous range of configurations rather than a number of discrete rotational isomers.

In Part I * it was reported that amorphous aliphatic polyesters gave unusually ill-defined spectra, but that they showed sharp bands in the crystalline state. In particular the absorption at about 720 cm.$^{-1}$ (the rocking mode of a $[CH_2]_n$ chain) virtually disappeared on melting.

As the spectral changes on melting are attributed to configurational changes of the acid portion of the polyesters, the dicarboxylic acids themselves have now been examined.

Previous infrared studies of aliphatic dicarboxylic acids have been made by Flett (*J.*, 1951, 962) and Hadži and Sheppard (*Proc. Roy. Soc.*, 1953, *A*, **216**, 247). Adipic acid has also been studied with polarised radiation by Mann and Thompson (*ibid.*, 1948, *A*, **192**, 489) and by Kuratani (*J. Chem. Soc. Japan*, 1951, **72**, 924) who also examined succinic acid. In all these studies the acids were examined only in the crystalline state. After the

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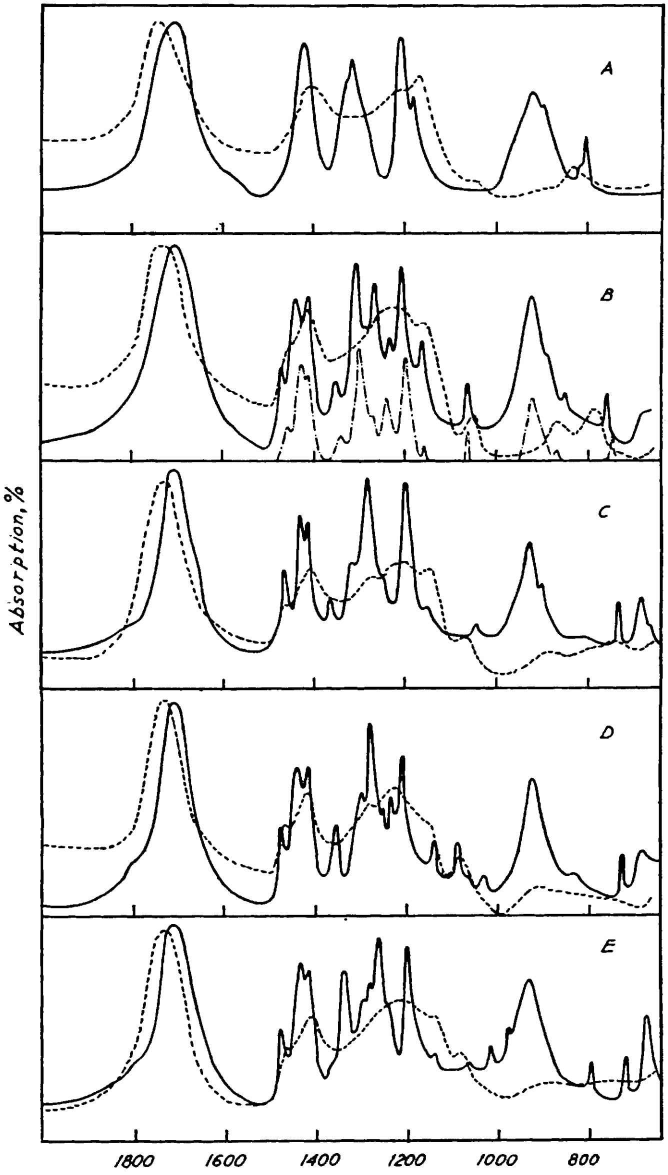
* Part I, preceding paper.

completion of this work, our attention was drawn to a paper on the spectra of dicarboxylic acids of $n = 3$—7 (Schonmann, *Helv. Phys. Acta*, **1943, 16,** 343) in which spectral differences were reported for crystalline and liquid glutaric acid only.

FIG. 1. *Infrared spectra of dicarboxylic acids* ($CO_2H\cdot[CH_2]_n\cdot CO_2H$), *crystalline* (——) *and molten* (– – –)



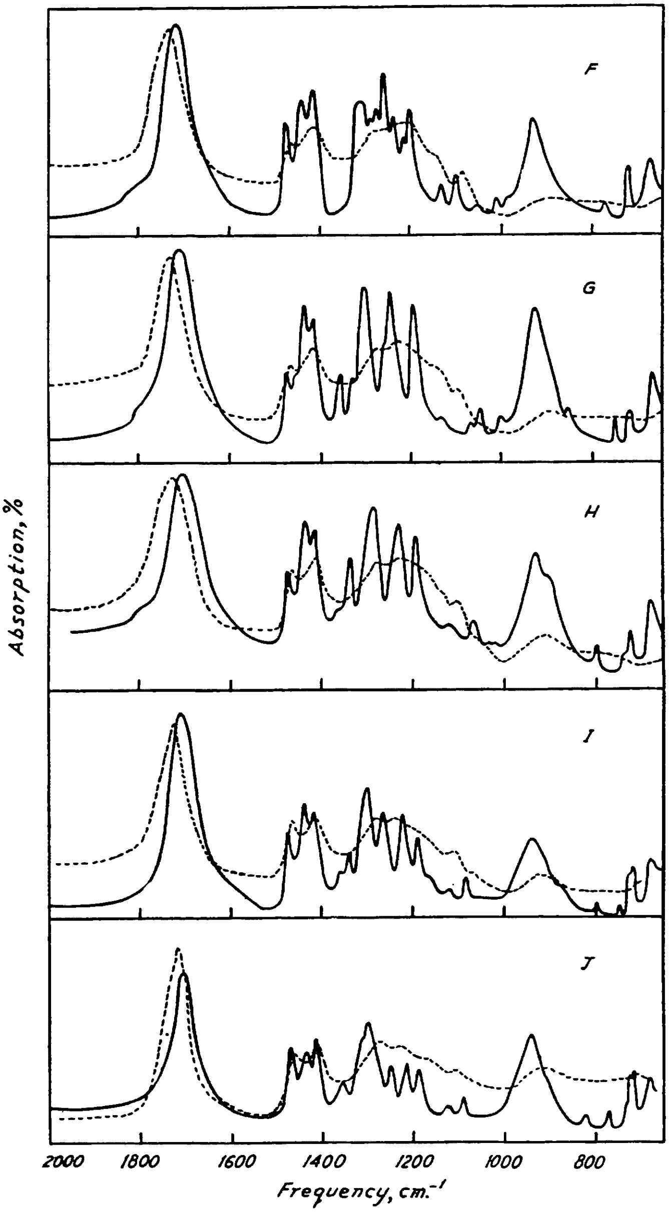
A, β-Succinic acid ($n = 2$).
B, β-Glutaric acid ($n = 3$) [chain-line (— • —) is of α-glutaric acid, displaced].
C, Adipic acid ($n = 4$).
D, Pimelic acid ($n = 5$).
E, Suberic acid ($n = 6$).

EXPERIMENTAL

The acids used were mostly good-quality commercial materials, whose m. p.s agreed satisfactorily with the literature. The acid with $n = 16$ was prepared by Dr. G. B. Barlow by a Kolbe synthesis.

Samples were originally prepared for spectroscopic measurement by squeezing when molten between rock-salt plates and allowing them to crystallise. The spectra of the molten materials were measured on the same cells at a temperature just above the m. p., a hot cell being used.

FIG. 2. *Infrared spectra of dicarboxylic acids* ($CO_2H{\cdot}[CH_2]_n{\cdot}CO_2H$), *crystalline* (——) *and molten* (- - -).



F, Azelaic acid (n = 7).
G, Sebacic acid (n = 8).
H, Dodecanedioic acid (n = 10).
I, Hexadecanedioic acid (n = 14).
J, Octadecanedioic acid (n = 16).

After recrystallisation, the spectra were re-measured to confirm that no decomposition had taken place. With succinic acid, some anhydride was formed. The acids (except n = 16) were re-measured in pressed discs of potassium chloride by means of a die of the type described by Ford and Wilkinson (*J. Sci. Instr.*, **1954**, **31**, 338).

The spectra of the crystalline acids measured as pressed discs differed appreciably from those measured between rock-salt plates, particularly in showing a stronger 1435-cm.$^{-1}$ band. This was shown to be due to orientation in the samples recrystallised between plates, by re-measuring these at an inclination of 45° to the beam. Except for $n = 16$, all the spectra shown in Figs. 1 and 2 are of pressed disc samples.

Glutaric acid was converted into a metastable α-form (shown by a chain line in Fig. 1) with a band at 754 cm.$^{-1}$ (cf. 762 cm.$^{-1}$ for the stable β-polymorph) when allowed to recrystallise from the melt between rock-salt plates or in pressed discs of sodium or potassium chloride. This metastable form reverted to the stable one on being ground at room temperature.

The pressed-disc technique ensures that the molten and crystalline samples are of the same thickness. Recrystallisation after melting of the samples is, however, usuallv slow and sometimes incomplete.

DISCUSSION.

On melting of the acids there is a general loss of definition and a broadening of all the bands, but a number of more specific changes are also observed. We will first consider those due to hydrogen-bonding.

X-Ray diffraction evidence (Morrison and Robertson, *J.*, 1949, 980, 987, 993, 1001) shows that the dicarboxylic acids are associated as infinite chains in the crystalline state; the hydrogen-bonding is of the dimeric type (I) and the infrared spectra of the crystalline acids are consistent with this type of association (Hadži and Sheppard, *loc. cit.*). There is a marked change in the OH stretching region on melting (as shown in Fig. 3 for adipic acid), the main ν(OH) absorption shifting from about 2700 to 3200 cm.$^{-1}$; a similar change has been reported for glutaric acid (Schonmann, *loc. cit.*). At the same time the strong band at 930 cm.$^{-1}$, which has been assigned to δ(OH) of a dimeric associated carboxyl group (Hadži and Sheppard, *loc. cit.*), practically disappears. These changes show the break-up of the normal dimeric association; the frequency of ν(OH) indicates a looser type of association such as (II). The frequency of the bonded carbonyl (*b*) would be similar

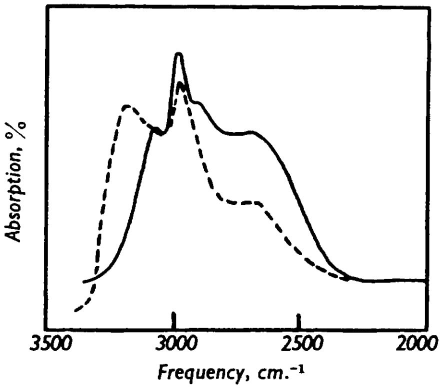
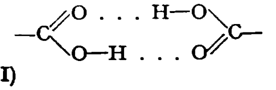
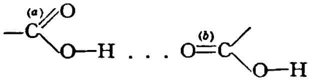


FIG. 3. *Adipic acid, crystalline* (——) *and molten* (– – –).


(I)



(II)

to that of adipic acid in *iso*propyl alcohol, *i.e.*, 1720 cm.$^{-1}$. The frequency for the unbonded carbonyl (*a*) would not be that for a monomeric acid but at a lower frequency owing to participation of the hydroxyl group in external hydrogen-bonding; *e.g.*, adipic acid in dioxan has an absorption at 1735 cm.$^{-1}$.

Carbonyl absorptions of acids in ether or dioxan are usually about 20 cm.$^{-1}$ lower than the monomeric bands in dilute solution in carbon tetrachloride (Davison, unpublished work); this shift is significantly greater that that due to normal solvent effects (Hartwell, Richards, and Thompson, *J.*, 1943, 1936). On melting, the carbonyl absorptions of the dicarboxylic acids shift from 1700 to about 1730 cm.$^{-1}$; they become broad with evidence of complexity and are consistent with the loose type of association (II).

In the 1450-cm.$^{-1}$ region, the crystalline acids (except succinic) show three distinct bands, at 1475, 1435, and 1415 cm.$^{-1}$, which we assign respectively to a normal $\delta(CH_2)$ bending, a carboxyl vibration (Hadži and Sheppard, *loc. cit.*), and a $\delta(CH_2)$ bending perturbed by an adjacent carbonyl group (Francis, *J. Chem. Phys.*, 1951, **19**, 942; Jones, Cole, and Nolin, *J. Amer. Chem. Soc.*, 1952, **74**, 5662). The assignment of the 1435-cm.$^{-1}$ band to a different mode from the other two is confirmed by its dependence on orientation. Its absence in the molten acids confirms its assignment to a dimer-associated carboxyl group.

Table of $\delta[CH_2]_n$ *rocking frequencies.*

n	Acid	(cm.$^{-1}$)	$H\cdot[CH_2]_n\cdot H$ (cm.$^{-1}$)	Polyesters of acid (cm.$^{-1}$)	*n*	Acid	(cm.$^{-1}$)	$H\cdot[CH_2]_n\cdot H$ (cm.$^{-1}$)	Polyesters of acid (cm.$^{-1}$)
2	Succinic (β)	804	822	800—810	7	Azelaic	726	723	—
3	Glutaric (α)	754	748	—	8	Sebacic	722	722	720—725
4	Adipic	733	732	733—740	10	Dodecanedioic	723	720	—
5	Pimelic	731	728	—	14	Hexadecanedioic	727, 721	722	—
6	Suberic	725	726	—	16	Octadecanedioic	727, 720	—	—

The crystalline bands at 1300—1350 cm.$^{-1}$ are assigned to $\delta(CH_2)$ wag or twist (Sheppard and Simpson, *Quart. Rev.*, 1953, **7**, 1, 19) and are also dependent upon configuration. We assign the " crystalline " bands given in the Table to the out-of-plane $[CH_2]_n$ deformations of a methylene chain (Vallance-Jones and Sutherland, *Nature*, 1947, **160**, 567; Sheppard and Sutherland, *ibid.*, **159**, 739; Sheppard and Simpson, *loc. cit.*; Axford and Rank, *J. Chem. Phys.*, 1950, **18**, 51). Sheppard and Simpson (*loc. cit.*) discuss this assignment in detail and state that it only occurs in substantially *trans*-configurations. Where other discrete rotational isomers occur (Brown, Sheppard, and Simpson, *Discuss. Faraday Soc.*, 1950, **9**, 261) the corresponding vibration moves to higher frequencies. Calculations (Person and Pimental, *J. Amer. Chem. Soc.*, 1953, **75**, 532) of the dependence of the frequency of this vibration upon the phase angle of the chain confirm that this assignment relates to the zig-zag *trans*-configuration of the $[CH_2]_n$ chain.

Good agreement is observed (see Table) between the frequencies of $\delta[CH_2]_n$ rocking for dicarboxylic acids and the corresponding *n*-paraffins. The virtual absence of this $\delta[CH_2]_n$ band in the molten dicarboxylic acids is therefore interpreted as meaning that no appreciable proportion of the molecules retain the *trans*-configuration. In some of the dicarboxylic acids, this might have been plausibly accounted for by cyclic association favouring other configurations, but as the same phenomenon is observed in their polyesters (Part I, *loc. cit.*) the explanation is not favoured. Instead, we put forward the hypothesis of a continuous and random configuration of the $[CH_2]_n$ chains. To distinguish this from the normal type of discrete rotational isomers we propose the term " non-discrete rotational isomerism " for this phenomenon.

During this investigation our attention was drawn to the work of Sinclair, McKay, and Jones (*J. Amer. Chem. Soc.*, 1952, **74**, 2570), who reported that the spectra of long-chain monocarboxylic acids show similar changes, being ill-defined in the amorphous state. Subsequently, Neuilly (*Compt. rend.*, 1954, **238**, 63) observed similar changes for somewhat shorter-chain acids. In the monocarboxylic acids, however, the effects are less marked in that neither the 720-cm.$^{-1}$ ($\delta[CH_2]_n$) nor the 930-cm.$^{-1}$ [$\delta(OH)$] band actually disappears in the liquid state, although they become somewhat less intense.

Sinclair *et al.* and Neuilly put forward the explanation of rotational isomerism, but regard the liquids as containing a large number of discrete isomers, although separate bands are not observable for these. Since the acids examined by Sinclair *et al.* were from C_{14} to C_{21}, the number of discrete isomers would be so large as to make it impracticable to decide whether the rotational isomerism is discrete or non-discrete. However, the shorter dicarboxylic acids considered in this paper show no evidence of discrete rotational isomers in the liquid state, although in the corresponding *n*-paraffins these are clearly shown (Axford and Rank, *J. Chem. Phys.*, 1949, **17**, 430). We regard this as clear evidence for non-discrete rotational isomerism in the dicarboxylic acids.

In non-associating liquids, the only force tending to overcome the barrier to free rotation about the C–C bonds (*ca.* 3 kcal./mole; Pauling, " Nature of the Chemical Bond," Oxford, **1948**, p. 90) is that arising from collisions involving van der Waals forces. This is normally only sufficient to rotate the molecule from one discrete rotational isomer to another. However, where strong intermolecular forces are involved [the energy of hydrogen-bonding in the acids is *ca.* 8 kcal./(CO_2H); Pauling, *op. cit.*, p. 307] the extra force is considered sufficient not only to rotate the bonds, but also to constrain them in any intermediate configuration. The molecules therefore adopt a continuous range of random configurations rather than a number of discrete rotational isomers.

The constraining effect of the terminal carboxyl groups should be somewhat less noticeable for longer-chain acids for which discrete rotational isomerism of the type proposed by Sinclair *et al.* (*loc. cit.*) may occur. Moreover, since $\delta[CH_2]_n$ rocking is asymptotic to 720 cm.$^{-1}$ in long-chain compounds, a considerable proportion of rotational isomers would contain *trans*-segments of $n \geqslant 6$ and thus show a 720-cm.$^{-1}$ band.

Polymorphism of Glutaric Acid.—It is well known (Kendall, *Analyt. Chem.*, 1953, **25**, 382) that polymorphic modifications show spectral differences. The polymorphs of glutaric acid show a shift of the $\delta[CH_2]_n$ band from 762 cm.$^{-1}$ for the β-form to 754 cm.$^{-1}$ for the metastable α-form (obtained from the melt). This implies (Person and Pimental, *loc. cit.*) that the β-form has the less planar configuration, and is in agreement with *X*-ray findings (Morrison and Robertson, *J.*, 1949, 1001), *i.e.*, that the $C_{(1)}$–$C_{(2)}$ bond is rotated 14°. No *X*-ray work on α-glutaric acid is known, but from the $\delta[CH_2]_n$ absorption we would expect that it would have a more planar configuration of the carbon chain.

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