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Studies on Succinic Acids

IV.* Evidence for the Existence of Intramolecular Hydrogen Bonding in Certain Highly Alkylated Succinic Acids by Infra-Red Spectra

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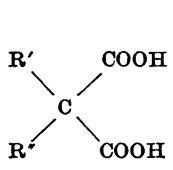
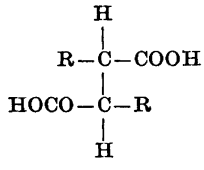
The infra-red spectra of *racem*-α,α'-di*iso*propyl-, *racem*-α,α'-di-(*tert.*-butyl)-, *racem*-α,α'-di*cyclo*hexyl-, and tetraethylsuccinic acid and their monopotassium salts have been found to be consistent with an intramolecularly hydrogen-bonded structure. All these acids have very large K_1/K_2-ratios. The infra-red spectra of *meso*-α,α'-di*iso*-propyl-, *meso*-α,α'-di-(*tert.*-butyl)-, and *meso*-α,α'-di*cyclo*hexylsuccinic acid and their monopotassium salts are compatible with a structure containing one carboxyl group and one carboxylate ion which are essentially independent of each other.

There is chemical and physico-chemical evidence for the existence of an intramolecular hydrogen bond in certain dibasic acids and their monoanions [1–4]. These include highly branched malonic acids (I), *racem*-α,α'-dialkylsuccinic acids (II) with bulky alkyl groups, tetraalkylsuccinic acids (III), β,β-dialkylglutaric acids (IV), *cis*-1,2-*cyclo*propanedicarboxylic acids (V), *cis*-1,2-dicarboxyethylenes (VI), and others.



I



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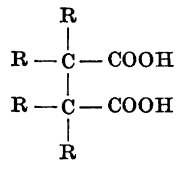

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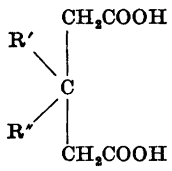

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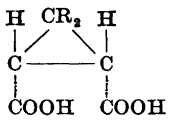

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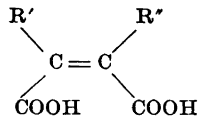

VI

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In all these cases the steric relationships probably play an important role. For example, it is well known that the accomodation of alkyl groups in a carbon chain capable of ring closure will increase the ease of formation and stability of the corresponding cyclic compound [5]. In an alkylated dibasic acid the formation of a cyclic structure can be accomplished by the formation of an intramolecular hydrogen bond, provided the arrangement of alkyl groups will be energetically favoured. In the other types of dibasic acids the carboxyl groups are rigidly held at distances which make hydrogen bonding possible. The most

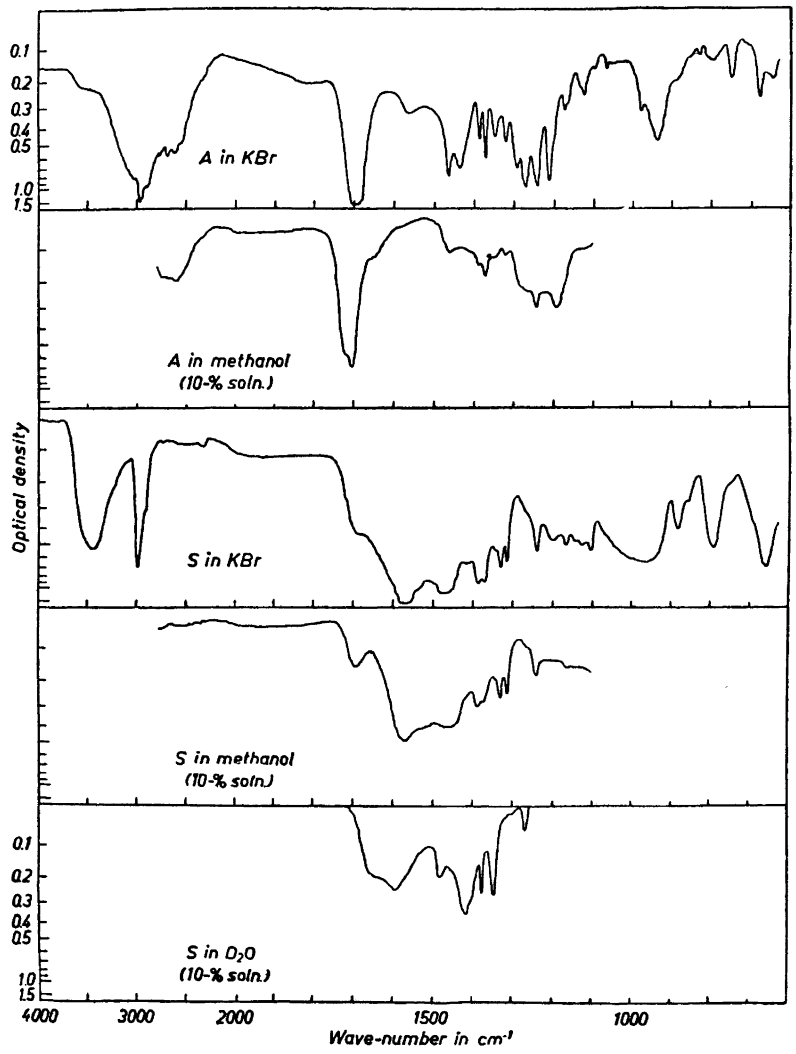


Fig. 1. Infra-red spectra of *racem*-α,α'-di*iso*propylsuccinic acid (A) and its monopotassium salt (S).

important arguments for the existence of an intramolecular hydrogen bond in dibasic acids of these kinds are:

1. They have anomalously high ratios between their first and second dissociation constants, which cannot be explained on the basis of electrostatic effects alone [1,3].

2. Measurements of the equilibrium constants of the reaction *meso*-acid ⇌ *racem*-acid for α,α'-dialkylsuccinic acids indicate that the *racemic* form is the

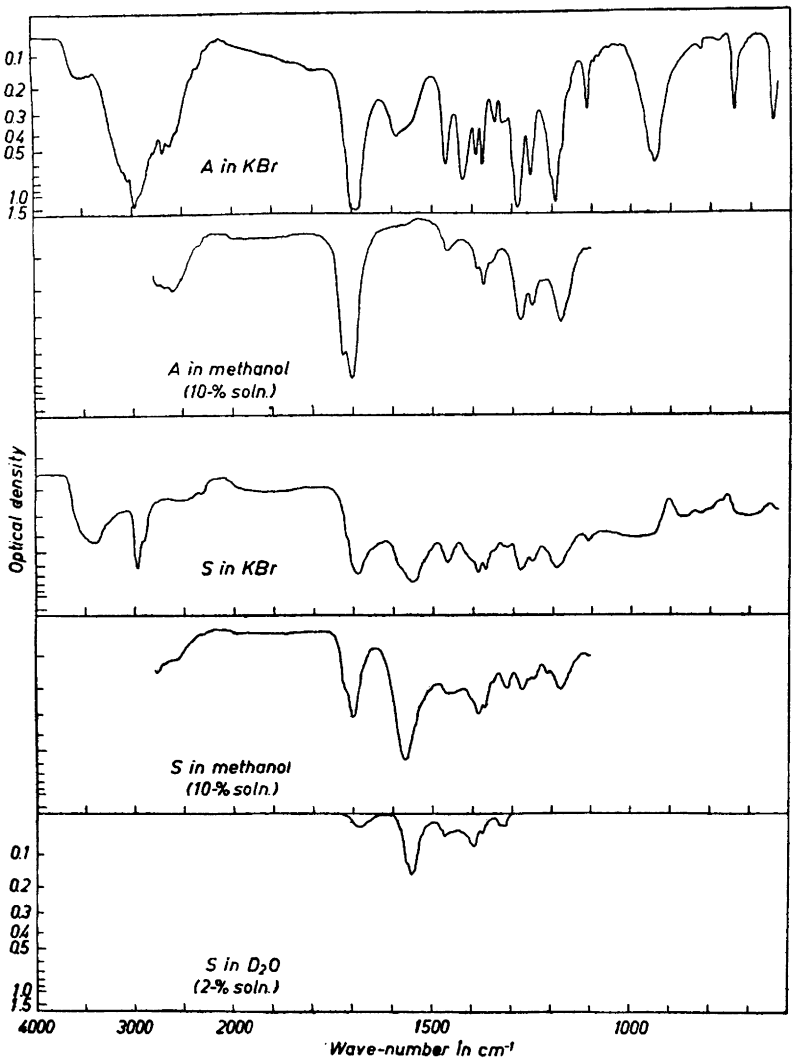


Fig. 2. Infra-red spectra of *meso*-a,a'-di*iso*propylsuccinic acid (A) and its monopotassium salt (S).

more stable isomer [2], *i. e.*, the stability order is the reverse of that predicted from conformational analytical considerations.

3. They are very easily anhydrized, some of them even in aqueous solution or in the solid state [4].

Shahat [6] has shown by X-ray analysis that in crystalline maleic acid there exists an unsymmetrical hydrogen bond. Cardwell *et al.*[7] have investigated maleic acid and its monopotassium salt in the solid state by means of infra-red

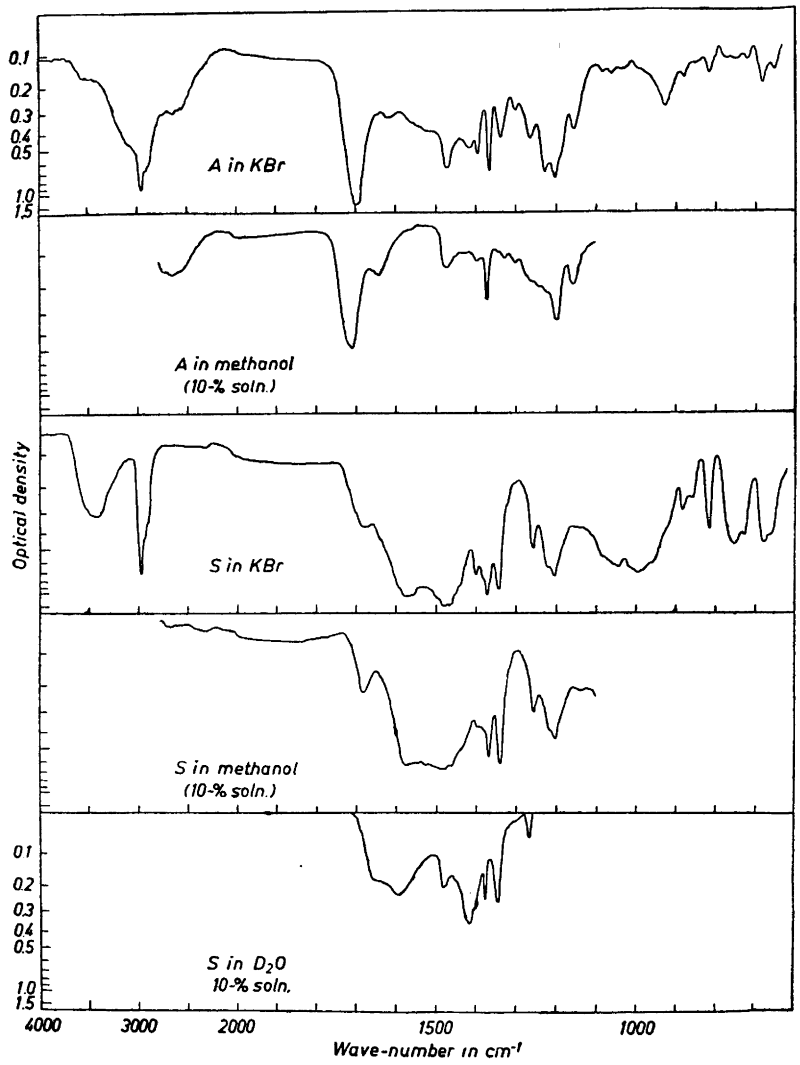


Fig. 3. Infra-red spectra of *racem*-α,α'-di-(*tert.*-butyl)-succinic acid (A) and its monopotassium salt (S).

spectra and found evidence for an intramolecular hydrogen bond in both acid and salt. In the latter case the absence of the carbonyl band indicated that the hydrogen bond might be symmetric.

The purpose of the present investigation was to study the infra-red spectra under various conditions for a series of alkylsubstituted succinic acids and their monopotassium salts. Four acids, *racem*-α,α'-di*iso*propyl-, *racem*-α,α'-di-(*tert.*-butyl)-, *racem*-α,α'-di*cyclo*hexyl-, and tetraethylsuccinic acid, which exhibit very high K_1/K_2-ratios (4×10^6—3.5×10^9 in 50 % aqueous ethanol) and three acids, the *meso* forms of the above acids, with low K_1/K_2-ratios (about 100) have been selected, and the infra-red spectra of the acids and their monopotassium salts have been examined in the solid state and in methanolic solution. Some of the salts were also studied in deuterium oxide solution. Methanol is the only solvent which meets the requirements of being transparent in the double bond stretching frequency region and of dissolving both

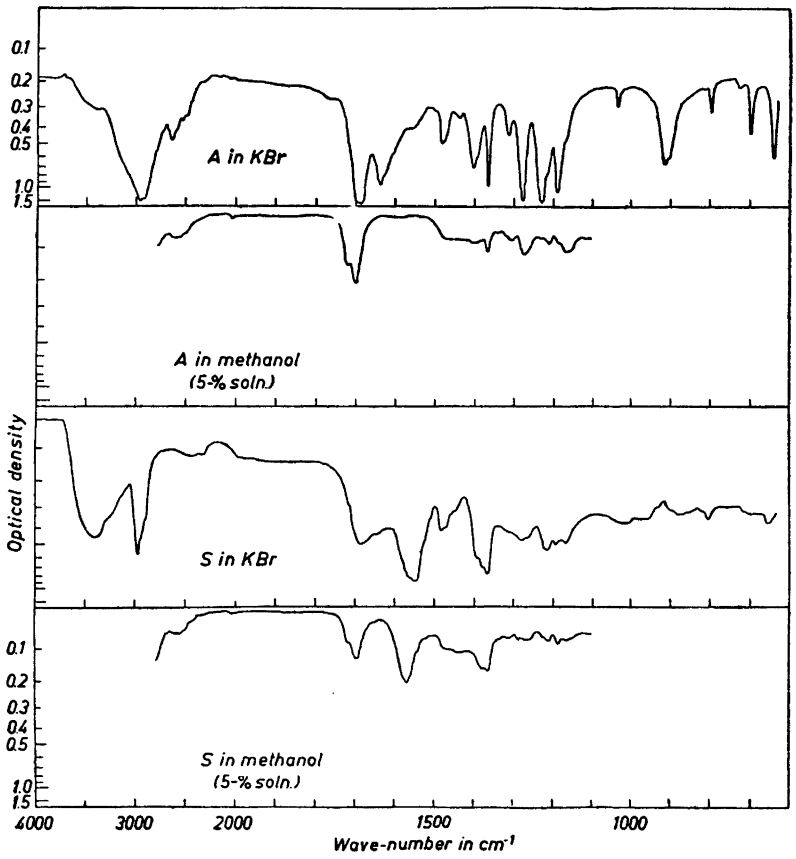


Fig. 1. Infra-red spectra of *meso*-α,α'-di-(*tert.*-butyl)-succinic acid (A) and its monopotassium salt (S).

acids and salts in sufficient concentrations. The discussion will be limited to a consideration of the carbonyl stretching frequency and the carboxylate asymmetric stretching frequency, as the other bands associated with these groups either are difficult to recognize or fall in a region where the solvent has a large absorption. The results are shown in Figs 1—7 and in Table 1, which gives the wave-numbers of the bands in the double bond region together with the approximate molar extinction coefficients in methanolic solution.

At a first glance it is seen that the spectra of the low-ratio acids and their salts are consistent with the structure VII for the acids and VIII for the monoanions.

Thus, in the solid state the carbonyl stretching frequency of the acids has a single peak at about 1 695 cm^{-1}, and no significant shift occurs in the spectra of the corresponding salts. In methanolic solution the situation is similar;

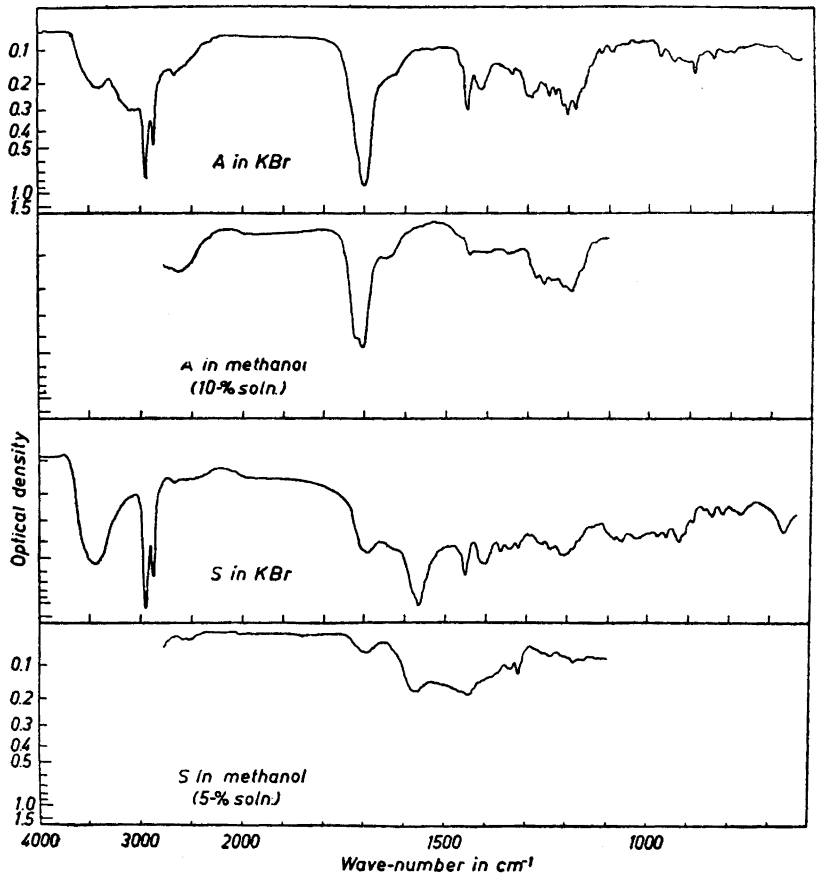
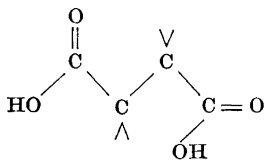
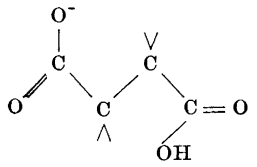


Fig. 5. Infra-red spectra of *racem-a,a'*-di*cyclo*hexylsuccinic acid (A) and its monopotassium salt (S).



VII



VIII

however, the carbonyl band has split into two peaks at about 1 720 and 1 700 cm^{-1}. These peaks are not shifted in the spectra of the salts in methanol, but the molar extinction coefficients are reduced to about half their values in the acids. The carboxylate asymmetric stretching frequency occurs in the solid state at 1 550—1 560 cm^{-1} and in methanol it is shifted to about 1 570 cm^{-1}. The only *meso* acid salt which has been studied in deuterium oxide solution

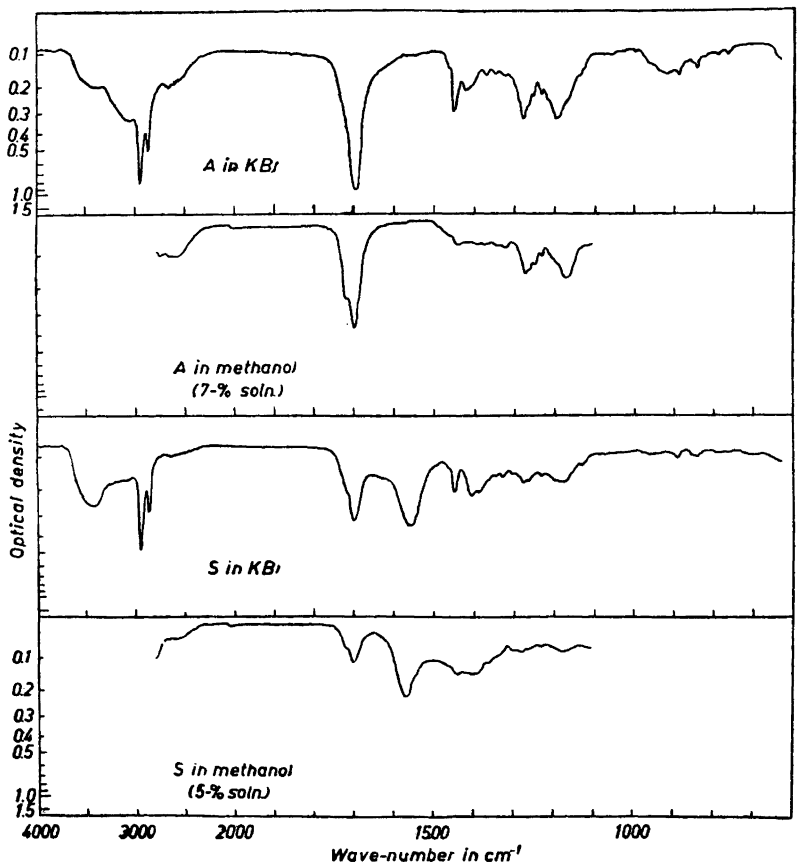


Fig. 6. Infra-red spectra of *meso*-α,α'-di*cyclo*hexylsuccinic acid (A) and its mono-potassium salt (S).

(the others are too slightly soluble) shows a single carbonyl peak at 1 680 cm^{-1} and the carboxylate band at 1 550 cm^{-1}, *i. e.*, both bands have shifted about 20 cm^{-1} towards lower wave-numbers as compared with the spectra in methanol. Summarizing, the double bond region of a low-ratio acid salt can be interpreted as a superposition of the carboxyl group and carboxylate ion spectra, and consequently the structure of the monoanions is best represented by VIII without interactions between the carboxyl groups.

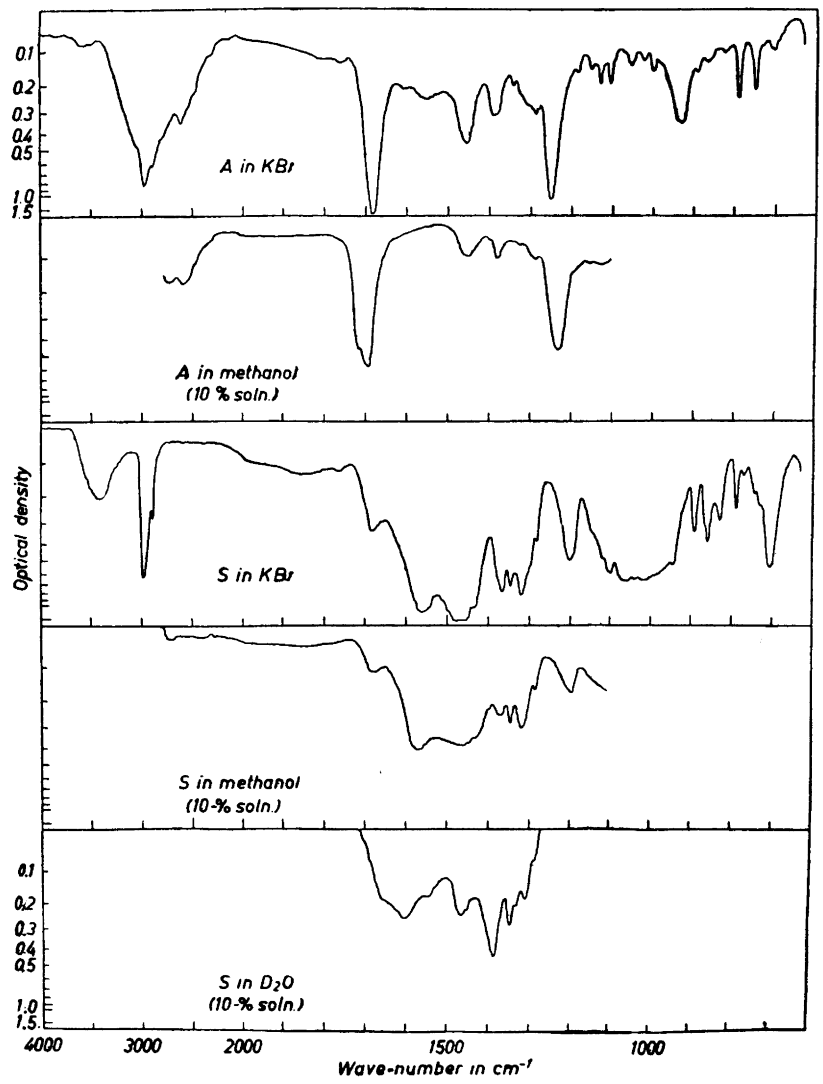


Fig. 7. Infra-red spectra of tetraethylsuccinic acid (A) and its monopotassium salt (S).

Table 1. Carbonyl frequencies of alkylsubstituted

Succinic acid	Carbonyl stretching frequency		
	In KBr, wave number in cm^{-1}	In methanol	
		wave number in cm^{-1}	Molar extinction coefficient ε
Racema-α,α'-di*iso*propyl-	1 695 vs	1 718 sh 1 704 1 650 sh	440 480 50
monopotassium salt	1 680 sh	1 690	110
Meso-α,α'-di*iso*propyl-	1 692 vs	1 723 1 701	350 510
monopotassium salt	1 687 sb	1 720 sh 1 700	150 250
Racem-α,α'-di-(*tert.*-butyl)-	1 695 vs 1 615 w	1 716 sh 1 708 1 640	390 110
monopotassium salt	1 675 mb	1 682	80
Meso-α,α'-di-(*tert.*-butyl)-	1 690 vs 1 635 s	1 720 1 700	330 500
monopotassium salt	1 687 sb	1 718 sh 1 695	170 270
Racem-α,α'-di*cyclo*hexyl-	1 700 s 1 625 sh	1 720 1 705 1 650	410 450 70
monopotassium salt	1 690 sb	1 695	110
Meso-α,α'-di*cyclo*hexyl-	1 695 s	1 717 1 697	330 540
monopotassium salt	1 697 m	1 717 1 698	130 240
Tetraethyl-	1 683 vs	1 716 1 691	360 550
monopotassium salt	1 682 m	1 678	70

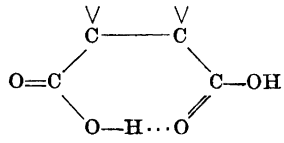
vs = very strong; s = strong; m = medium; w = weak; sh = shoulder; b = broad.

A similar interpretation is not possible for the spectra of the high-ratio acids and their salts. In methanolic solution all the *racem*-acids but not tetraethylsuccinic acid show a carbonyl band of low intensity at about 1 650 cm^{-1} (*racem*-α,α'-di-(*tert.*-butyl)-succinic acid has a weak band at 1 615 cm^{-1} also

succinic acids and their monopotassium salts.

In D_2O wave number in cm^{-1}	Carboxylate ion, asymm. stretching frequency				$\varepsilon_{C=O}$ (acid) / $\varepsilon_{C=O}$ (salt)
	In KBr, wave number in cm^{-1}	In methanol		In D_2O wave number in cm^{-1}	
		wave number in cm^{-1}	Molar extinction coefficient ε		
1 645 sh	1 570 vsb	1 568	400	1 590	4.4
1 680	1 550 sb	1 568	470	1 550	2.0
1 650 sh	1 570 vsb	1 575	290	1 590	5.0
	1 550 sb	1 568	450		1.9
	1 566 vs	1 573	360		4.1
	1 558 m	1 568	440		2.2
1 650 sh	1 560 vsb	1 568	340	1 605	7.9

in the solid state). This band must be due to a carbonyl group taking part in an intramolecular hydrogen bond (IX). A band at 1 630 cm^{-1} in solid maleic acid has been explained in the same way [7]. Accordingly, the peaks at 1 720 and 1 700 cm^{-1} are assigned to the other carbonyl group which may take



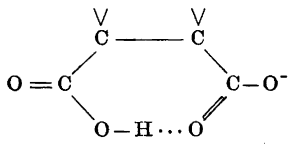
IX

part in an external hydrogen bond. The cause of the splitting around 1 700 cm^{-1} is probably coupling of the carbonyl frequencies[8-10], and not the existence of monomers and polymers in solution as the relative intensities of the two bands are independent of concentration.

The spectra of the *high*-ratio acid salts show the following main features. In both the solid state and in solution the salts have a large, almost continuous absorption in the region 1 600—1 400 cm^{-1}. In methanolic solution the carbonyl frequency has shifted by 10—25 cm^{-1} towards lower wave-numbers as compared with those of the acids, which is indicative of an intramolecular hydrogen bond [11]. The carbonyl band has been considerably reduced in intensity and its molar extinction coefficient is only a small fraction of that in the acid. In the hydrogen maleate ion the carbonyl band has completely disappeared [7], which points to the existence of a symmetric hydrogen bond in this ion with a structure intermediate between the extreme structures X a and X b.

X a X b

The fact that there actually is found a carbonyl peak in the spectra of the salts in question, though of appreciably reduced intensity, suggests that a structure for the monoanion with an unsymmetric intramolecular hydrogen bond (XI) is best compatible with the spectral data. In the deuterium oxide solution of a high-ratio acid salt the carbonyl peak has shifted towards lower wave-numbers and the carboxylate peak towards higher wave-numbers. This behaviour lends further support to an intramolecularly hydrogen-bonded structure.



XI

EXPERIMENTAL

The acids investigated in this paper were prepared and purified as described previously [4]. The monopotassium salts were prepared by dissolving accurately weighed amounts of acids and potassium carbonate (analytical grade reagent) in water or aqueous

ethanol by slight warming, filtering, and then evaporating *in vacuo* at room temperature. The last traces of solvent were removed by warming at 110° for 3 h. The purity was checked by analysis for carbon and hydrogen. It is by no means certain that a solid salt spectrum actually refers to the hydrogen potassium salt, but these spectra are given for comparison. The discussion above is based on the salt spectra in methanolic solution, where only the ion species HA^- is present.

The infra-red spectra were recorded by a Perkin Elmer model 21 spectrophotometer equipped with a sodium chloride prism. The solid samples of the acids and salts were examined in pressed potassium bromide plates. The wave-numbers given in Table 1 are accurate within ± 5 cm^{-1}.

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