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THE CONFORMATION OF SUCCINIC ACID IN AQUEOUS SOLUTION STUDIED BY ^1H AND ^{13}C NMR

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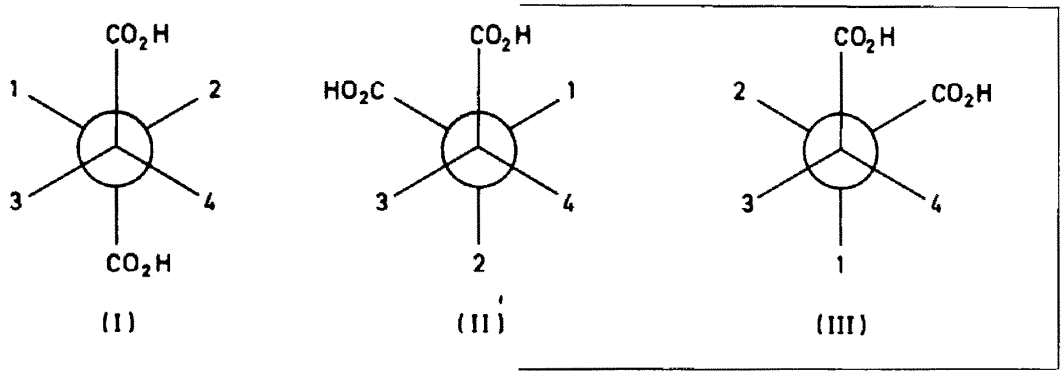
Abstract- The vicinal H–H coupling constants of succinic acid were obtained as a function of pH and related to its conformation. The *syn*-clinal arrangement of the two CO_2H groups appears as more stable than the *anti*-periplanar conformation, at variance with previous work but in agreement with recent data on similar molecules. The vicinal $^{13}CO_2H$–^1H coupling constant was also obtained and is found to support that conclusion. The analysis was extended to solvents of variable dielectric constant and no significant effect was found.

In their ^1H NMR work on succinic acid in aqueous solution, Zetta and Gatti[1] concluded for only a small energy difference between the anti-periplanar(I) and the two (enantiomeric) syn-clinal (II, III) conformations thus contributing to the removal of apparent discrepancies between Raman,[2] dipole moment[3] and ionization data.[4] By arbitrarily assuming I to be more stable than II or III, they found $\Delta E = E_{II} - E_I = 0.22$ kcal mol^{-1}. This result was obtained from a quantitative comparison[5] between the observed vicinal H–H coupling constants (analysis of ^{13}C–H satellites) and values attributed to the individual conformers.

A similar assumption was made when dealing with methylsuccinic acid. This has, however, been proved by Rétey *et al.*[6] to be incorrect by means of ^1H NMR of stereospecifically deuterated methylsuccinic acid. They found that the conformation where the two CO_2H groups are in a *syn*-clinal arrangement (the Me group and the β CO_2H group being *anti*-periplanar) is more stable than that where the two CO_2H groups are *anti*-periplanar. The same conclusion has been reached in a ^1H and ^{13}C NMR study of the conformation of meso-tartaric acid.[7]

Aiming at a clarification of the conformation of succinic acid, we now report a full pH-dependence study of the corresponding ^{13}C–H satellites, as well as an investigation in other solvents. Relevant ^{13}C–H coupling data has also been obtained and related to the conformation of the acid.



RESULTS AND DISCUSSION

The ^{13}C–H satellites of succinic acid at any pH are the AA′BB′ subspectra of AA′BB′X spectra, where X = ^{13}C. A typical spectrum showing all the 8 distinct lines is given in Fig. 1. The analysis of such subspectra yield the vicinal H–H coupling constants shown in Table 1.

The assignment of J_{14} and J_{24} was initially based on the reasonable assumptions that, at high pH, conformer (I) prevails, leading to $J_{14} > J_{24}$, and that both coupling constants should vary monotonically with pH. This renders $J_{14} < J_{24}$ for the lower pH values, at variance with the assignment made by Zetta and Gatti.[1] In turn, this leads to the conclusion that I is less stable than II or III for pH $\lesssim$ 5, *if*, as is usually done, the observed coupling constants are taken as weighted averages of the corresponding values attributed to the three staggered rotamers. This

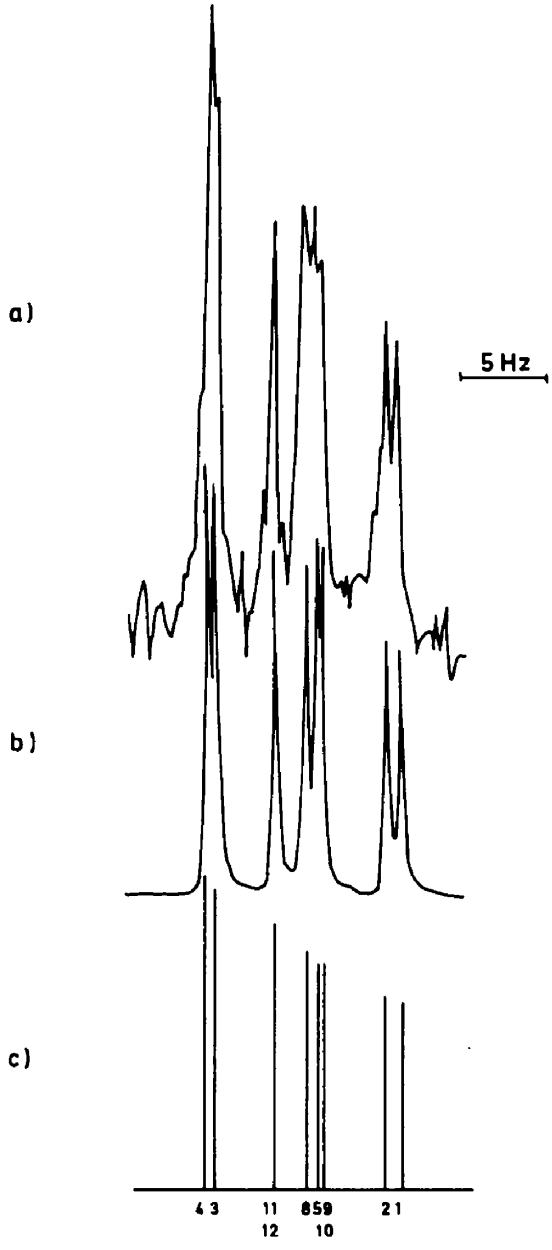


Fig. 1. Observed (a) and calculated (b, c) high field $^{13}C-H$ satellite of succinic acid (0.2 M in D_2O, pH* = 6.80, T = 343 K).

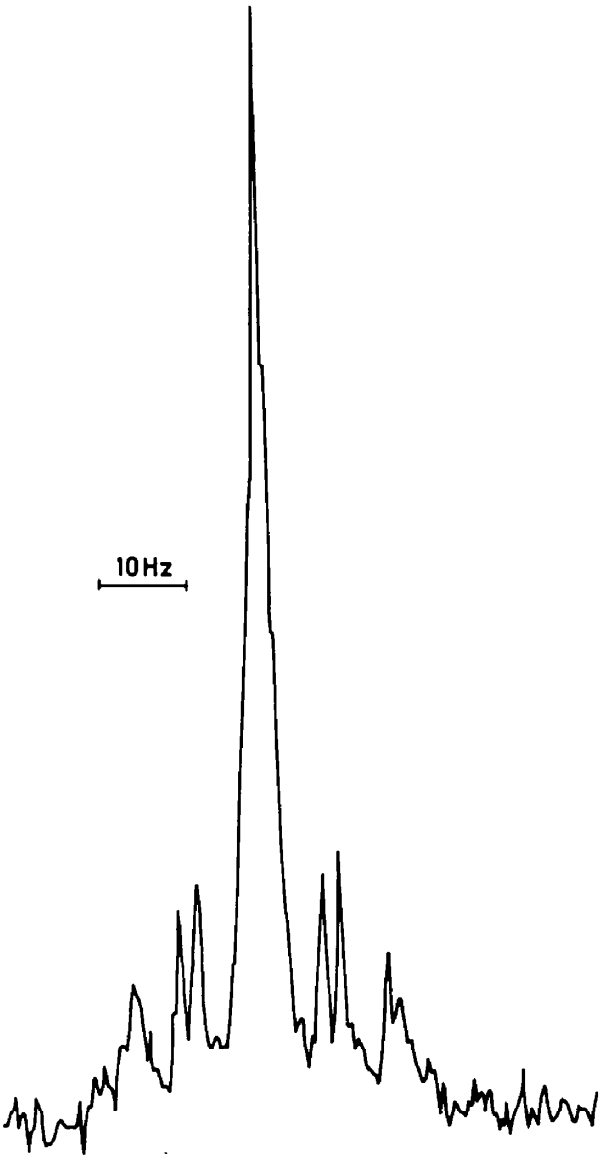


Fig. 2. ^{13}C signal of the CO_2H groups of succinic acid (3M in H_2O)

conclusion is supported by the value obtained for the vicinal $^{13}CO_2H-^1H$ coupling constant from the ^{13}C signal of the carboxyl groups (Fig. 2). This corresponds to the X part of a $A_2A'_2X$ spectrum and is a triplet (J = 7.2 Hz) of triplets (J = 5.6 Hz). By assigning the bigger splitting to the geminal coupling on comparison with similar compounds[8], we get 5.6 Hz for the vicinal coupling constant. From the value known for propionic acid[8]—5.5 Hz—, where the three staggered rotamers are isoenergetic, and due to the effect of the second electronegative CO_2H group, a smaller value should occur for succinic acid if the three conformations remained equally populated;[9,10] an

Table 1. Vicinal H-H coupling constants (Hz) of succinic acid (0.2 M in D_2O, T = 293 K)

pH*	0.20	2.29	4.01	4.81	4.93	5.15	5.89	6.80	9.30	12.14
$^3J_{14}$	5.3	5.5	5.9	6.7	7.0	8.0	9.3	10.0	10.2	9.9
$^3J_{24}$	7.4	7.5	7.5	7.5	7.5	6.8	6.4	6.3	6.1	6.2

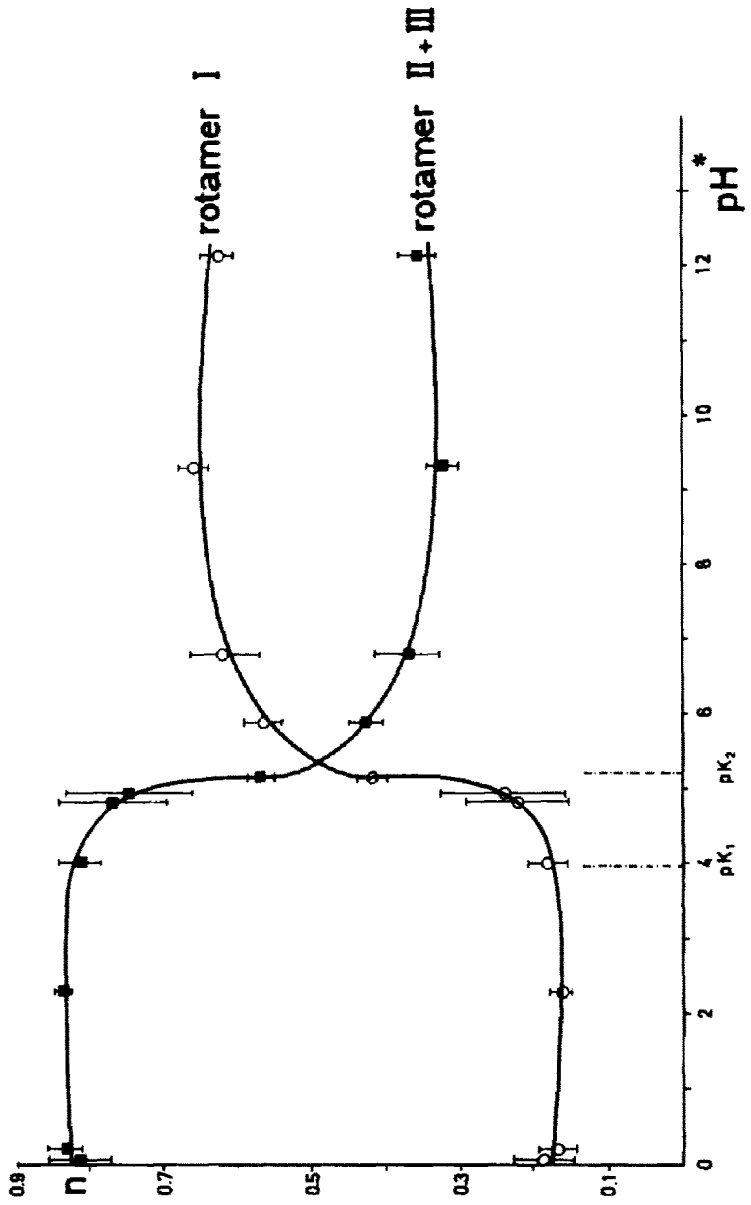


Fig. 3. Effective populations of the three staggered conformers of succinic acid as a function of pH (the bars correspond to the differences between the values obtained from J_{14} and J_{24}).

Table 2. Vicinal H H coupling constants (Hz) of succinic acid in solvents of variable dielectric constant ε (0.2 M solutions, T = 293 K)

	Dioxane (d_8)	Acetone (d_6)	Dioxane (d_8)+D_2O (50%+50%, T=343 K)	D_2O
	ε=2	ε=21	ε=32	ε=80
$^3J_{14}$	5.7	6.0	5.9	5.5
$^3J_{24}$	7.5	7.7	7.6	7.5

even smaller coupling constant would be expected if I was the most populated form, because such rotamer contributes only *gauche* coupling constants for the observed average value. To explain the observed coupling value of 5.6 Hz it is thus necessary to assume that II and III, which contribute one *gauche* and one *trans* coupling constant, are more populated than I.

Approximate effective populations of the three staggered conformers calculated in the usual manner from reasonable $^3J_{HH}$ values attributed to them and from the observed average values are shown in Fig. 3 as a function of pH. The J-values attributed to the various conformers were

$$J_{14}^{(I)} = 13.0 \quad J_{14}^{(II)} = 4.0 \quad J_{14}^{(III)} = 4.0$$
$$J_{24}^{(I)} = 5.1 \quad J_{24}^{(II)} = 2.9 \quad J_{24}^{(III)} = 13.0 \quad \text{Hz}$$

and were obtained from the values estimated by Abraham *et al*[5] for the *trans* and *gauche* coupling constants in ethane (14.2 and 4.5 Hz, respectively) together with orientational dependent CO_2H effects;[11] the joint effect of the two carboxyl groups was assumed to be *ca* 3/4 of the sum of the effects each CO_2H group would have individually (in propionic acid).[11]

By taking the populations for pH* = 2 and the observed $^{13}CO_2H$–^1H coupling constant, the following approximate values for J_{CO_2H-H} (*trans*) and J_{CO_2H-H} (*gauche*) are obtained

$$J_{CH}^{t} \simeq 9.6 \text{ Hz}$$

$$J_{CH}^{g} \simeq 2.7$$

which are reasonable values.[8] It has been assumed that $J_{CH}^{t} + 2J_{CH}^{g} \simeq 15$ Hz, less than the corresponding value in propionic acid (16.5 Hz) due to the presence of an electronegative second CO_2H group; the orientational dependence of the effect of this group has been ignored. We note that should the values of J_{14} and J_{24} be reversed for the acid, the populations calculated from both coupling constants would be respectively, $n_I \simeq 38\%$, $n_{II} = n_{III} \simeq 31\%$ and $n_I \simeq 86\%$, $n_{II} = n_{III} \simeq 7\%$. Apart from the big difference between these results, they would lead to $J_{CH}^{t} \simeq -11$, $J_{CH}^{g} \simeq 13$ Hz and $J_{CH}^{t} \simeq 3$, $J_{CH}^{g} \simeq 6$ Hz, respectively, which are unacceptable.[8]

The estimated populations for pH* $\simeq$ 2 correspond to a calculated ΔE value

$$\Delta E = E_I - E_{II} = 0.6 \text{ kcal mol}^{-1}$$

whereas for the dissodium salt we get

$$\Delta E = E_{II} - E_I = 0.8 \text{ kcal mol}^{-1}.$$

A possible contribution for the unexpected (if we accept the ionization data as indicating no important intramolecular H-bonding[4]) stability of *syn*-clinal arrangements of two CO_2H groups could come from the fact that such polar conformations become extra-stabilized in a solvent of high dielectric constant. In order to test this hypothesis we have obtained the vicinal H–H coupling constants in other solvents (Table 2). They are found to be almost independent of solvent. Therefore other explanation must be sought for the stability of the *syn*-clinal arrangement of two carboxyl groups.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Jeol PS-100 spectrometer in the Fourier transform mode. The pH was adjusted with NaOD and DCl; the pH* values quoted are the direct pH meter readings. Gated irradiation of protons was used to observe NOE in the ^{13}C spectra without decoupling.

The C^{13} H satellite spectra were analysed using the computer program LAOCOON 1968.

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