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Intramolecular Hydrogen Bonds. XIII.[1] The Preferable Conformation of α-Hydroxy-carboxylic and *o*-Hydroxybenzoic Acids

Nobuo Mori, Yuzuru Asano, Toshiko Irie and Yojiro Tsuzuki

Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo

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The infrared hydroxyl and carbonyl stretching absorption spectra of salicylic, mandelic, and α-hydroxyisobutyric acids have been measured in dilute carbon tetrachloride solutions. The spectral data indicate that the first two acids exist exclusively in an internally-bonded conformation, one where the phenolic and the alcoholic hydroxyl groups form a hydrogen bond with the carbonyl oxygen atom of the *cis*-carboxyl structure, while the last acid takes, apart from such a conformation, another internally-bonded conformation, one where the hydroxyl group of the *trans*-carboxyl structure interacts with the alcoholic oxygen atom.

It is well known that the carboxyl group in a carboxylic acid takes the *cis*-structure exclusively, a structure in which the carbonyl and the hydroxyl group are *cis* in respect of the C–O bond, but not the *trans*-structure where both groups are *trans.*

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[1] Part XII: N. Mori, Y. Asano and Y. Tsuzuki, This Bulletin, **41**, 1871 (1968).

An indirect estimation of the stabilization energy indicates the former to be more stable by *ca.* 3 kcal/mol than the latter.[2] When a strong proton-acceptor atom, such as an oxygen or a nitrogen atom, is present close to the carboxyl group, the *trans*-structure can exist to a considerable extent as a result of the hydrogen bond formation between that atom and the carboxyl-OH group; the enthalpy of this hydrogen bond formation is, in general, at most 1.5 kcal/mol with α-alkoxyalkanoic acids[3] and at most 3.3 kcal/mol with *o*-alkoxybenzoic acids.[4] These values are comparable to those of ordinary intramolecular OH-to-O hydrogen bonds forming similar 5- or 6-membered rings (*e. g.*, 2.2 and 2.1 kcal/mol with β-methoxyethanol and γ-methoxypropanol respectively[5]). A simple comparison of these energies seems to suggest that, in α-hydroxy-carboxylic and *o*-hydroxybenzoic acids, the carboxyl group may take the *trans*-structure to a significant extent, working through hydrogen bonding with the α- or *o*-hydroxyl-oxygen atom. In order to verify this suggestion,we have attempted the infrared investigation of the intramolecular hydrogen bonding in salicylic, mandelic, and α-hydroxyisobutyric acids in dilute carbon tetrachloride solutions. The last two acids examined as α-hydroxy acids are not indispensable, but they are accessible in the pure, crystalline form.

Experimental

Samples. All the acids were known crystalline compounds; they were prepared and purified by the methods described in the literature, and some known derivatives of them were prepared. Their melting and boiling points were equal to, or very close to, the reported values. The carbon tetrachloride was fractionated over phosphorus pentoxide.

Infrared Measurements. The hydroxyl- and the carbonyl-stretching region were measured at 25°C using a grating, double-beam spectrophotometer, Model DS-403G, of the Japan Spectroscopic Co., Ltd. Since the solubility of each acid in the solvent is very low, in most cases saturated solutions were employed. The concentrations of the derivatived used were 0.002 and 0.001 mol/*l* for the OH and the CO measurements respectively. The cells used were 5.0 and 1.0 cm in optical path length for the OH and the CO measurements respectively. The observed frequencies were calibrated against those of a standard polystyrene film.

Results and Discussion

The OH and the CO spectra of representative acids are shown in Figs. 1—3, while the spectral data of all the compounds are summarized in Tables 1 and 2.

Salicylic Acids (1—6).[*1] In the monomeric OH region, each of the acids shows only two bonded OH bands, with maxima around 3530 and 3200 cm^{-1}; the higher frequency band is sharp and almost symmetric, while the lower frequency band is broad and is obscured by the C–H and the dimeric carboxyl-OH bands.

These acids can take the three internally-bonded forms, I, II, and III, shown in Fig. 4. In this figure, the numerical values added to Form I are the observed frequencies of the respective groups, while those in parentheses added to the other

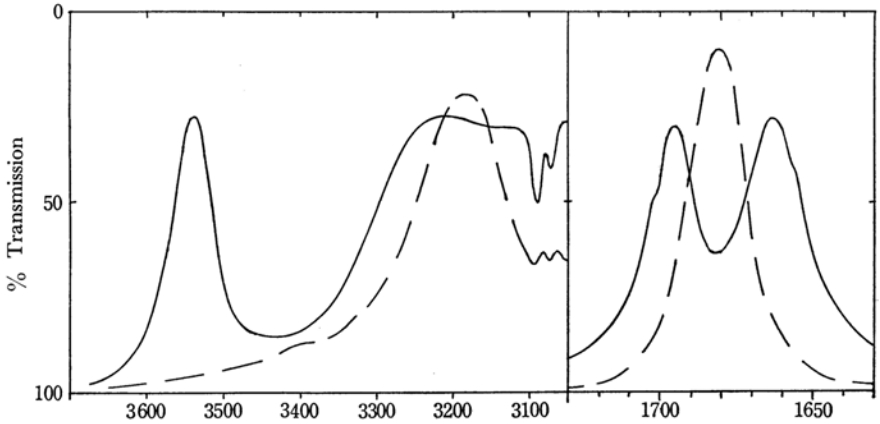

Fig. 1. The IR OH and C=O spectra: salicylic acid (1) ——, methyl salicylate (9) — —.

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[2] M. Ōki and M. Hirota, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86,** 115 (1965).

[3] M. Ōki and M. Hirota, This Bulletin, **36,** 290 (1963).

[4] M. Davies, "Hydrogen Bonding," ed. by D. Hadzi, Pergamon Press, London (1959), p. 393; M. Ōki and M. Hirota, This Bulletin, **37,** 209 (1964); M. Ōki, M. Hirota and S. Hirofuji, *Spectrochim. Acta,* **22,** 1537 (1966).

[5] L. P. Kuhn and R. A. Wires, *J. Am. Chem. Soc.,* **86,** 2161 (1964).

[*1] Brooks and his co-workers[6] have previously reported and discussed the spectral data of some salicylic acids in dilute carbon tetrachloride solutions. However, there have been no discussions of the possibility of the presence of the *trans*-carboxyl structure.

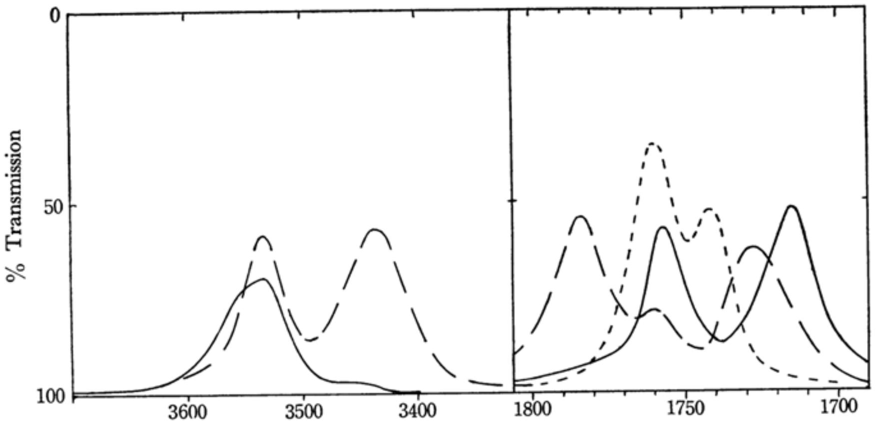


Fig. 2. The IR OH and C=O spectra: mandelic acid (13) ——, α-methoxyphenyl acetic acid (20) — —, methyl α-methoxyphenylacetate (22) - - - - -.

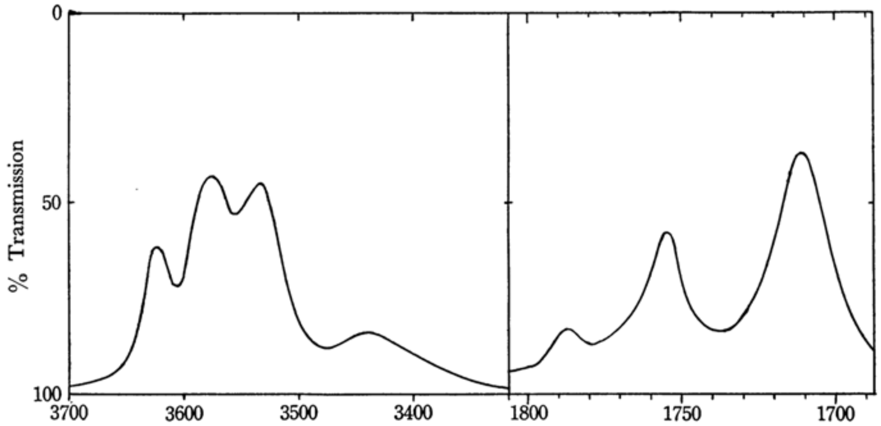
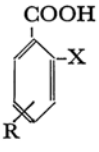
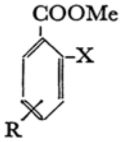


Fig. 3. The IR OH and C=O spectra of α-hydroxyisobutyric acid (23).

TABLE 1. SPECTRAL DATA OF SALICYLIC ACIDS AND SOME DERIVATIVES THEREOF



No.	X	R	Monomeric ν_{OH}			Monomeric $\nu_{C=O}$		Dimeric $\nu_{C=O}$
			Free *cis*-COOH	Bonded *trans*-COOH	Bonded phenolic OH[*1]	Bonded *cis*-COOH	*trans*-COOH	
1	OH	H	3538	—	3205	1695	—	1662
2	OH	4-Me	3540	—	3205	1695	—	1660
3	OH	4-Cl	3531	—	3175	1698	—	1664
4	OH	4-Br	3532	—	3170	1698	—	1665
5	OH	5-Me	3538	—	3215	1696	—	1662
6	OH	5-MeO	3536	—	3227	1698	—	1667
7[7]	H	H	3540	—		1744[*2]	—	1697
8[7]	MeO	H	3530	3365		1751[*2]	1760	1702

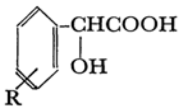


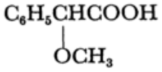
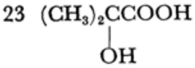
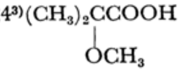
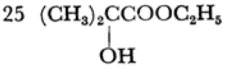
No.	X	R	Bonded phenolic OH	Bonded *cis*-COOMe
9	OH	H	3185	1680
10	OH	4-Cl	3160	1681
11	OH	5-MeO	3222	1684
12[6]	OH	6-OH	3205 3470	1686

*1 Inexact because of overlapping with the C—H and the dimeric COOH absorption band.

*2 Free carbonyl.

TABLE 2. SPECTRAL DATA OF MANDELIC AND α-HYDROXYISOBUTYRIC ACIDS AND OF SOME DERIVATIVES THEREOF



		Monomeric ν_{OH}					Monomeric $\nu_{C=O}$		
No.	R	Free alcoholic OH	Bonded alcoholic OH	Bonded *cis*-COOH	*trans*-COOH	C=O overtone*1	Bonded *cis*-COOH	*trans*-COOH	Dimeric $\nu_{C=O}$
13	H	—	3564*2	3534	—	3445	1756	—	1714
14*4	*p*-NO_2	—		3534					
15	*p*-Br	—	3565*2	3532	—	3445	1758	—	1713
16	*p*-Cl	—	3570*2	3536	—	3445	1759	—	1714
17	*p*-CH_3	—	3566*2	3536	—	3440	1755	—	1709
18	*p*-CH_3O	—	3566*2	3536	—	3445	1756	—	1710
19	*m*-Cl	—	3566*2	3533	—	3445	1759	—	1715
20	 $C_6H_5\underset{\substack{\vert \\ OCH_3}}{C}HCOOH$			3533	3435*5		1760	1784	1728
21	 $C_6H_5\underset{\substack{\vert \\ OH}}{C}HCOOCH_3$	—	3613, 3610[9] 3551, 3536[9]			3455	1737		
22	 $C_6H_5\underset{\substack{\vert \\ OCH_3}}{C}HCOOCH_3$					3500	1759*3 1741		
23	 $(CH_3)_2\underset{\substack{\vert \\ OH}}{C}COOH$	3623	3575	3537	3436*5		1755	1788	1712
24[3]	 $(CH_3)_2\underset{\substack{\vert \\ OCH_3}}{C}COOH$			3528.1	3408.8		1762.2	1789.0	
25	 $(CH_3)_2\underset{\substack{\vert \\ OH}}{C}COOC_2H_5$	—	3606[10] 3544			3460	1732		

*1 The relative intensity to the OH band is about 0.015.

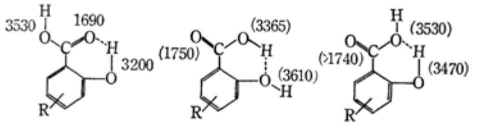
*2 The approximate frequency of the center of the broadened part on the higher frequency side of the monomeric *cis*-COOH band.

*3 These two bands are associated with two rotational isomers (*cis* and gauche form) around the C_1–O bond of the COOMe group.[1]

*4 Very slightly soluble.

*5 This band probably contains the C=O overtone band.

forms are the frequencies which would be expected on the basis of the reported spectral data of the reference compounds, including *o*-methoxybenzoic acid (8), methyl salicylates (9—11), and methyl *o,o′*-dihydroxybenzoate (12).



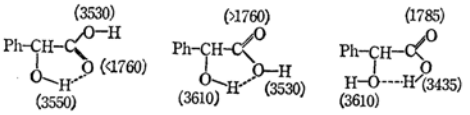
Form I Form II Form III

Fig. 4. Internally-bonded forms of salicylic acids.

The appearance of the two OH bands gives evidence of the preferential existence of Form I, since there are no other detectable absorptions corresponding to any of the interacted phenolic and carboxyl OH groups in the other forms. These findings agree completely with those based on the carbonyl data; in the monomeric C=O region these acids show a single absorption due to the internally bonded, *cis*-carboxyl C=O group, but there are no absorptions which correspond to the free carbonyl groups in Forms II and III. The very weak shoulder appearing at 1702 cm^{-1}, which is observed in all the salicylic acids, can not definitely be assigned at the present time.

Mandelic Acids (13—19). In the monomeric OH region, these acids show an intense band at 3535 cm^{-1} and a broadened part centered at *ca.* 3565 cm^{-1}. Apart from these, a very weak absorption band appears near 3445 cm^{-1} with a relative intensity of *ca.* 0.015.

These acids can take the three internally-bonded forms, IV, V, and VI, shown in Fig. 5, where the values in parentheses are the frequencies of the

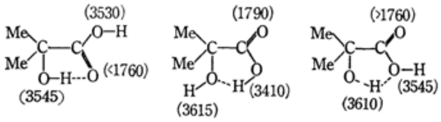


Form IV Form V Form VI

Fig. 5. Internally-bonded forms of mandelic acids.

corresponding groups which would be expected on the basis of the spectral data of the reference compounds, including *α*-methoxyphenylacetic acid (20), methyl mandelate (21), and methyl *α*-methoxyphenylacetate (22). According to these comparisons, only Form IV can reasonably explain the appearance of the two overlapped, strong bands. The very weak band of the lowest frequency can be due either to the carbonyl overtone or to a minor amount of the *trans*-carboxyl group, judging from both the relative intensity and the position at which it appears. However, the carbonyl overtone seems responsible for it, since the observation of carbonyl spectra shows the presence of no *trans*-carboxyl group. The carbonyl spectra each contain only two bands, which correspond to the *cis*-carboxyl and the dimeric carboxyl group; there is no absorption of the *trans*-carboxyl group, which could be expected to appear near 1790 cm^{-1}.

***α*-Hydroxyisobutyric Acid (23).** In the monomeric OH region, this acid shows four bands, at 3623 (weak), 3575 (strong), 3534 (strong), and 3436 cm^{-1} (weak). On the basis of a comparison of these data with those of *α*-methoxyisobutyric acid (24) and ethyl *α*-hydroxyisobutyrate (25), the two strong bands can be assigned to the bonded alcoholic and the *cis*-carboxyl OH group in Form VII (see Fig. 6, in which the frequencies in parentheses are those expected).



Form VII Form VIII Form IX

Fig. 6. Internally-bonded form of *α*-hydroxyisobutyric acid.

As for the last band, its intensity is too high for it to be that of a carbonyl overtone; therefore, it may be predominantly due to a *trans*-carboxyl absorption overlapped with the carbonyl overtone. The first weak band may be assigned to either or to both of the two, free and bonded, alcoholic OH species in Forms VIII and IX. In view of the appearance of the weak, *trans*-carboxyl OH and CO band, however, the assignment to the free OH species in Form VIII is rather more reasonable.

In the monomeric C=O region, the acid shows a weak and a strong band at 1788 and 1755 cm^{-1}; these bands can be assigned to the *trans*-carboxyl group in Form VIII and to the *cis*-carboxyl group in Form VII respectively. The precise proportion of the *trans*-carboxyl group to the whole can not be calculated because the respective molecular absorption coefficients are unknown. From the intensity ratio of the apparent bonded OH bands, however, it can be calculated to be approximately 0.16.

It is interesting that the acid takes the *trans*-

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6) C. J. W. Brooks, G. Eglinton and J. F. Morman, *J. Chem. Soc.*, **1961**, 661.

7) C. J. W. Brooks, G. Eglinton and J. F. Morman, *ibid.*, **1961**, 106.

8) M. Ōki, and M. Hirota, This Bulletin, **37**, 213 (1964).

9) N. Mori, Y. Tanaka and Y. Tsuzuki, *ibid.*, **39**, 1490 (1966).

10) N. Mori, S. Ōmura, N. Kobayashi and Y. Tsuzuki, *ibid.*, **38**, 2149 (1965).

carboxyl structure VIII to a significant extent, while mandelic and salicylic acids take no such structures. The difference can not decisively be explained at the present time, but it seems attributable to some unknown factors other than steric effects, because the latter two acids, rather than the former, would be expected to meet the steric requirements for taking the *trans*-structures for the following reasons: (1) α-hydroxyisobutyric acid may involve the steric repulsion between the two α-methyl groups and the free alcoholic OH group in the *trans*-structure (such a repulsion has already been proposed in the cases of α,α-dialkylethyleneglycols[11]) and, therefore, it may prefer the *cis*-Structure VII, which involves no such repulsion, while (2) mandelic and salicylic acids may not involve steric effects strong enough to make the presence of *trans*-structures II and VI completely impossible, since even α-methoxyphenylacetic and *o*-methoxybenzoic acids prefer the *trans*-structures to an appreciable extent.

Substituent Effects on the OH Frequencies. The alcoholic and carboxyl OH frequencies of mandelic acids are almost constant irrespective of the substituent, while those of salicylic acids change depending on the substituent. The correlation with the ordinary Hammett σ-constant[12] is shown in Fig. 7, where the ordinate is the difference in frequency between unsubstituted (γ^{H}_{OH}) and substituted acid (γ^{R}_{OH}), and the abscissa, the Hammett σ-constant. In the case of salicylic acids, the relatively large deviation of some phenolic OH plots from the straight line would not be due to the inexactness of the frequencies, but, rather, due mainly to the electronic effects of the substituent, influencing the hydrogen bonding through the carbonyl-oxygen atom. A detailed study of this problem is in progress and will be reported in the next part of this series of studies.

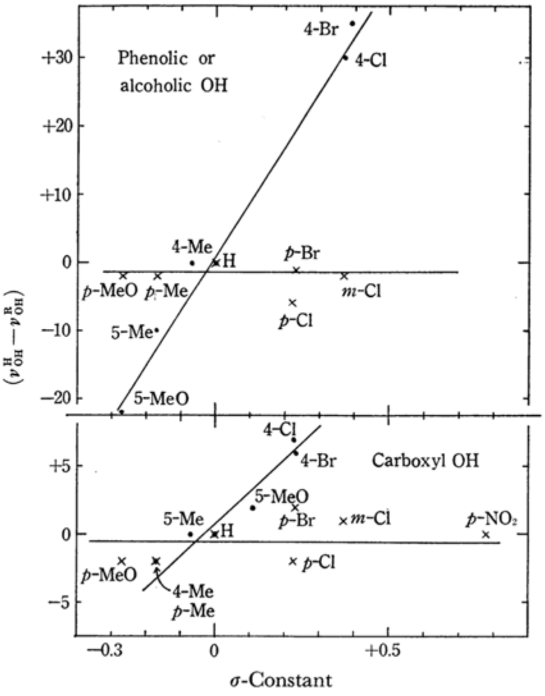

Fig. 7. Correlation of ν_{OH} with Hammett σ-constant in salicylic (—•—) and mandelic acids (—×—).

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[11] L. P. Kuhn, *J. Am. Chem. Soc.*, **80**, 5950 (1958).

[12] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).