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Intramolecular Hydrogen Bonds. XIV.[1] Correlation of the Hydroxyl and the Carbonyl Frequencies of Methyl Salicylates with Hammett's Substituent Constants

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The infrared OH and C=O stretching spectra of methyl 4- or 5-substituted salicylates have been measured in dilute carbon tetrachloride solutions, and the respective peak-frequencies have been correlated with ordinary Hammett's σ-constants. The best linear relationship has been established between the γ_{OH} and the $(\sigma_{OH}-0.38\sigma_{COOMe})$ values and between the $\gamma_{C=O}$ and the $(\sigma_{COOMe}-0.49\sigma_{OH})$ values, where σ_{OH} and σ_{COOMe} are the σ-constants of a substituent with respect to the OH and the COOMe group respectively. Besides, in other internally-bonded phenol systems, including *o*-bromophenols, *o*,*o*′-dihalophenols, and salicylic acids, the plotting of the OH frequencies against the $(\sigma_{OH}-A\sigma_X)$ values gave the best linear relationship, where A is a constant depending on the kind of proton acceptor, X. The value of A can be a measure of the electronic effects of the substituent, influencing the bonded OH frequency through X.

In general, the spectroscopic properties of ring-substituted aromatic compounds can be correlated with the electronic nature of the substituents. In unassociated phenols,[2] benzoates,[3] and benzoic acids,[4] for example, the respective infrared OH and C=O stretching frequencies have been correlated with Hammett's σ-constants.

In internally-associated phenol systems, such as *o*-hydroxybenzaldehyde-anils (mono-substituted in the anil moiety)[5] and *p*-substituted phenylglyoxylic acids,[6] the hydrogen-bonded OH and C=O frequencies change linearly with the σ-constants.

On the other hand, the additivity of electronic effects of substituents has been pointed out,[7] and these effects have been reported with the carbonyl stretching modes of substituted benzoic acids.[8] Accordingly, very interesting is a system of benzene compounds, each of which contains a substituent with electronic effects which contribute to the interaction between two other substituents, both attached to the same benzene ring. An infrared investigation has previously been reported on the substituent effect on the interaction between the OH and the C=O group in 2-hydroxy-5-substituted-acetophenones;[9] in this case, the observed spectral shift, $\Delta\gamma_{OH}$, was correlated with the term of $(\sigma_p+\sigma_m)/2$, suggesting that equal proportions of the two tautomeric structures contribute to the interaction. However, their bonded OH bands appeared in the complex C–H stretching absorption region, thus reducing the accuracy of the reported band frequencies.

The present investigation has been performed on the electronic effects of a substituent exerted on the hydrogen bonding in methyl 4- and 5-monosubstituted salicylates, the bonded OH bands of which can easily and reliably be assigned.[10]

A major work on the chelation in substituted salicylates has been performed by Brooks and his co-workers,[10] but their interest was primarily in the problem of the so-called *o*-effects of adjacent substituents on the chelation.

Another subject of this investigation is the correlation of the OH frequencies with Hammett's σ-constants in the systems of internally-bonded phenolic compounds, such as substituted *o*-halophenols and salicylic acids, which may be expected to have essentially the same mechanism of hydrogen-bond formation.

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[2] P. J. Stone and H. W. Thompson, *Spectrochim. Acta,* **10**, 17 (1957).

[3] J. L. Mateos, R. Cetina, E. Olivera and S. Meza, *J. Org. Chem.,* **26**, 2494 (1961).

[4] M. St. C. Flett, *Trans. Faraday Soc.,* **44**, 767 (1948).

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[6] A. Schellenberger and G. Oehme, *Tetrahedron Letters,* **1966**, 767.

[7] H. H. Jaffé, *Science,* **118**, 242 (1953).

[8] N. Fuson, M. L. Josien and E. M. Shelton, *J. Am. Chem. Soc.,* **76**, 2526 (1954).

[9] Z. Yoshida and M. Haruta, *Tetrahedron Letters,* **1964**, 2631.

[10] C. J. W. Brooks, G. Eglinton and J. F. Morman, *J. Chem. Soc.,* **1961**, 661.

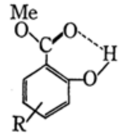
Experimental

Samples. All the esters, except for the 4-bromo-homologue, were known substances and were prepared by the methods described in the literature. The purified esters had almost, or completely, the same melting or boiling points as the reported values. The methyl 4-bromosalicylate was prepared by essentially the same method as the known 4-chloro-compound.

Infrared Measurement. This was carried out in almost the same manner as has been described in the preceding paper,[1] at an operating temperature of *ca.* 25°C, using a grating, double-beam spectrophotometer, Model DS-403G, of the Japan Spectroscopic Co., Ltd. The OH-stretching region was measured in a concentration of 0.002 mol/*l* or less in carbon tetrachloride, while the C=O stretching region was measured in a concentration of 0.001 mol/*l* or less. The cells used were 5.0 and 1.0 cm in optical path-length for the OH and the C=O measurements respectively. At those concentrations, no intermolecular hydrogen bonding was present, as has been described in the literature.[10]

Results and Discussion

The infrared OH and C=O spectra of three representative esters are shown in Fig. 1, while the spectral data of all the esters are summarized in Table 1. In the OH region, each of the esters shows only a very broad, intense, bonded OH band, with a distinct maximum in a frequency range from 3140 to 3222 cm^{-1}; the OH absorption begins near 3500 cm^{-1}, and the lower frequency side merges into the C–H absorption region. The carbonyl bands, which are sharp and, in most cases, almost symmetrical, appear near 1700 cm^{-1}; this frequency is lower than the 1730 cm^{-1} of methyl benzoate but much higher than the 1650 cm^{-1} of tautomeric *o*-hydroxyacetophenones.[9] The relatively small lowering of the carbonyl frequency from 1730 cm^{-1} suggests that the intramolecular hydrogen bonding in these esters can be explained by structure I, but not by a mixture of the two tautomeric structures I and II or by the meso-ionic structure III. In fact, the observation of the infrared spectra has shown none of the absorption bands to be expected for the quinoid-carbonyl (near 1650 cm^{-1}) and the C$\cdots$O half double bond (near 1400 cm^{-1}).



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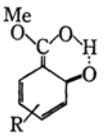

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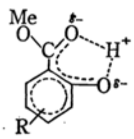


III

In these esters, therefore, the conformation of the carbonyl group*1 can be fixed by chelation with the phenolic OH group.[10] In this case, however, the coplanarity of the two substituents and

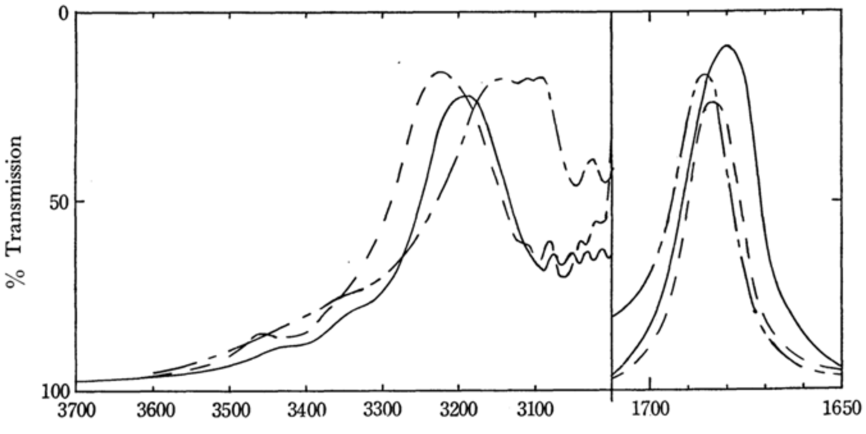


Fig. 1. Infrared OH (left) and C=O spectra (right) of methyl salicylate (——), methyl 5-methoxysalicylate (— — —) and methyl 5-nitrosalicylate (—‑—‑—).

[*1] In general, a carboxylate ester function itself, while strongly preferring a roughly planar conformation resulting from the resonance interaction between the alkoxy-oxygen and the carbonyl group,[11] may be exclusively in a *cis*-arrangement,[12] where both groups are *cis* in respect of the C–O bond, but not trans, because of the electrostatic repulsion of filled orbitals.[13] Accordingly, the *cis*-arrangement is the normally preferred one.[14]

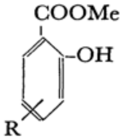
11) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, New York, N. Y. (1955), p. 99.

12) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, **1936**, 1383; R. Huisgen and H. Ott, *Tetrahedron*, **6**, 253 (1959).

13) D. Cooke, *J. Am. Chem. Soc.*, **80**, 49 (1958).

14) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York (1954), p. 88.

TABLE 1. THE PHYSICAL CONSTANTS AND THE INFRARED DATA OF METHYL SALICYLATES



R	Mp,°C (Bp, °C/mmHg)	ν_{OH}	$\nu_{C=O}$	σ_{OH}	σ_{COOMe}
H	(77/5)	3185	1680	0	0
4-CH_3	27.5—28 (88/3)	3188	1678	−0.069	−0.170
4-CH_3O	48—49	3163	1673	+0.115	−0.268
4-Cl	27 (91/3)	3160	1681	+0.373	+0.227
4-Br*	41—42 (97/2)	3155	1682	+0.391	+0.232
5-CH_3	(97—99/5)	3209	1680	—0.170	−0.069
5-CH_3O	(85/1.5)	3222	1684	−0.268	+0.115
5-NO_2	116	3140	1687	+0.778	+0.710

* Anal., Found: C, 3.18; H, 41.84%. Calcd: C, 3.03; H, 41.59%.

the benzene ring is not implied.

In substituted phenols[2] and benzoates,[3] the respective OH and C=O stretching frequencies become lower and higher respectively as the electron-withdrawing by the substituents increases. The substituent effects on both frequencies are interpreted in terms of the changes in the electronegativities of, respectively, the hydroxyl-oxygen and the carbonyl-carbon atom corresponding to the changes in the substituents. That is, as the electron-withdrawal by the substituents increases, the O–H bond of substituted phenols is weakened, resulting in a decreased OH stretching frequency, while the carbonyl double-bond character of substituted benzoates is increased (the contribution of the polar structure, $\overset{+}{C}$–$\overset{-}{O}$, to the resonance is decreased), resulting in an increased C=O stretching frequency.

In the case of the present salicylates, a substituent is expected to have electronic effects on the characteristics of the O–H and the C=O bond, both being involved in the hydrogen-bonding interaction, and thus to have an effect on the interaction itself. For example, the interaction will be strengthened by the increase in the polarity of the O–H bond and will simultaneously be weakened by the decrease in the polarity of the C=O bond, as the electron-withdrawal by the substituent increases. The sum of the two effects, reversely influencing the interaction in this way, is reflected by the observed bonded OH and C=O frequencies. In the above case, for example, the frequency of the OH group involved in the interaction will be decreased with an increase in the O–H polarity and will be simultaneously increased as a result of the interaction being weakened by the decrease in the C=O polarity.

On the basis of the above considerations, the observed OH and C=O frequencies were plotted against the respective ordinary Hammett's σ-

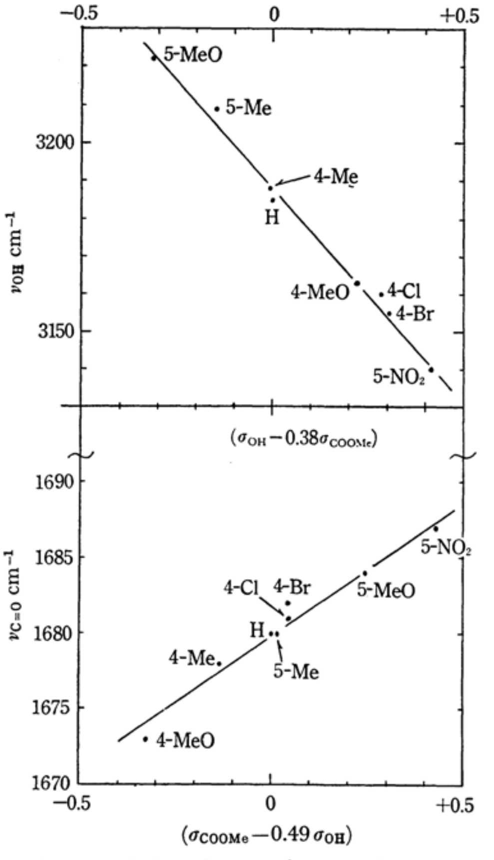


Fig. 2. Correlation of ν_{OH} and $\sigma_{C=O}$ with σ-constant in methyl salicylates.

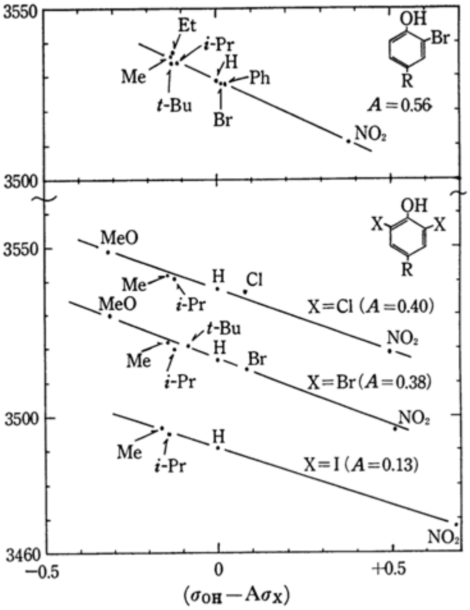


Fig. 3. Correlation of ν_{OH} with σ-constant in *o*-bromophenols and in *o,o'*-dihalophenols.

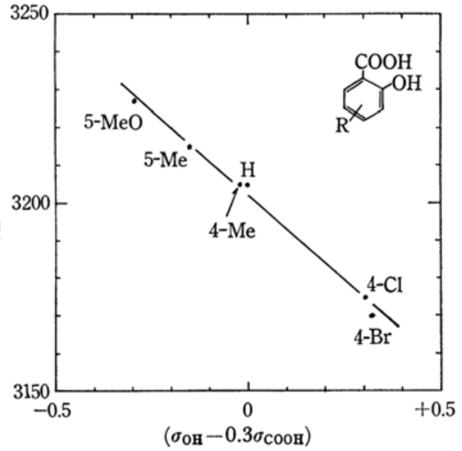


Fig. 4. Correlation of ν_{OH} (phenolic) with σ-constant in salicylic acids.

constants.[15] The best linear relationship has been established between the values of γ_{OH} and ($\sigma_{OH} - 0.38\sigma_{COOMe}$) and between those of $\gamma_{C=O}$ and ($\sigma_{COOMe} - 0.49\sigma_{OH}$), as is shown in Fig. 2, where σ_{OH} and σ_{COOMe} are the Hammett σ-constants of a substituent with respect to the OH and COOMe groups respectively. In the former relationship, the factor of 0.38 seems to be a measure of the electronic effect of the substituent on the bonded OH frequency, operating through the proton-accepting carbonyl group, while the factor of 0.49 in the latter is a similar measure of the substituent effect influencing the bonded C=O frequency through the proton-donating hydroxyl group.

In some systems of phenolic compounds, including substituted *o*-bromophenols,[16] *o,o'*-dihalophenols,[17] and salicylic acids,[1] a linear relationship has been further obtained between the values of γ_{OH} and ($\sigma_{OH} - A\sigma_X$),[*2] as is shown in Figs. 3 and 4, where the OH frequencies used in the plotting are those reported in the literature. However, the reported OH frequencies of *o*-hydroxyacetophenones[9] have not provided a linear relationship. Accordingly, the intramolecular hydrogen bonding in the former three systems of compounds can probably be explained in terms of essentially the same structure as that of the methyl salicylates.

In the cases of the *p*-substituted *o,o'*-dihalophenols, each forming a similar 5-membered ring through the hydrogen bonding, the OH frequency can be determined by the constant of *A*, which increases with the halogens in the order: I (0.13)<Br(0.38)<Cl(0.40), which is equivalent to the order of their electronegativities. It is well known[18] that, in *o*-halophenols, the spectral shifts, $\Delta\gamma_{OH}$, increase with the halogens in the order: F<Cl<Br<I, which is the reverse of the order of the electronegativities and is different from that of the hydrogen bond enthalpies. However, the disagreement in the orders has not yet been elucidated. Though the present investigation does not deal with this problem, the value of *A* seems to imply the operation of another significant factor in the hydrogen-bond formation.

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

[*2] The value of *A* is a constant depending on the kind of proton-acceptor, X, and the terms of σ_{OH} and σ_X are ordinary Hammett σ-constants of a substituent with respect to the OH and X group respectively.

[16] I. Brown, G. Eglinton and M. Martin-Smith, *Spectrochim. Acta,* **18**, 1593 (1962).

[17] A. W. Baker, H. O. Kerlinger and A. T. Shulgin, *ibid.*, **20**, 1477 (1964).

[18] For example, A. W. Baker and A. T. Shulgin, *Can. J. Chem.*, **43**, 650 (1965); D. A. K. Jones and J. G. Watkinson, *J. Chem. Soc.*, **1964**, 2366, and the references cited therein.