The Steric Requirements and the Nature of the Intramolecular Hydrogen Bonding of o-Methoxybenzoic Acid[*1]

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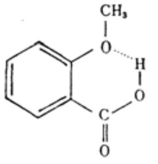
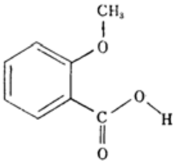
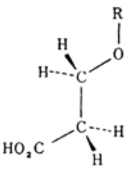
(Received August 19, 1963)

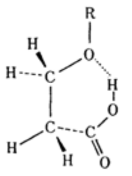
The existence of the six-membered intramolecular hydrogen bonding in *o*-aryloxybenzoic acids[1] and in *o*-methoxybenzoic acid[2] has already been established, but the reason why the six-membered hydrogen bonding is present in *o*-aryloxy- and *o*-alkoxybenzoic acids but not in β-phenoxy- and β-alkoxybenzoic acids has not yet been explained.

An answer to this question may be given by the entropy difference between the two systems. That is, the intramolecular hydrogen bonding is forced in *o*-alkoxybenzoic acids (such as I), while the rotational isomerism around the C–C single bond reduces the probability of the intramolecular hydrogen bonding in β-alkoxypropionic acid, since the most stable rotamer is IIa if there is no stabilization by the hydrogen bond formation.


Ia


Ib


IIa

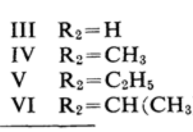

IIb

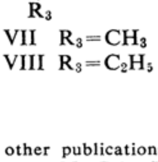
An alternative answer to this question may be that the intramolecular hydrogen bonding in *o*-alkoxybenzoic acids is stabilized by resonance, since this kind of stabilization is present in many hydrogen bond systems, such as the enol form of acetylacetone and salicylaldehyde. The resonance-stabilized hydrogen bond systems usually have a characteristic electronic spectra in the ultraviolet region. Ultraviolet spectral studies of the intramolecular hydrogen bonding have been carried out with many ortho-substituted phenols by Burrawoy and his co-workers,[3] who concluded that the intramolecular hydrogen bonding causes a remarkable red shift of the so-called B-bands, which have the longitudinal transition moment. On the other hand, the ultraviolet spectral measurement is also a very useful tool for the estimation of the steric hindrance; extensive study in this field has been reported by Braude and his co-workers.[4]

Thus, the ultraviolet spectral technique, as well as the infrared spectral measurement, has been employed in order to study the nature of the intramolecular hydrogen bonding of *o*-alkoxybenzoic acid derivatives, and the spectral data have been interpreted from the stand-point of steric hindrance and that of the characteristic absorption of the conjugated system.

Experimental

Preparation of the Materials. — *Substituted 2-Methoxybenzoic Acids.* — To a solution of 25 g. of 2,4-dimethylanisole in 150 ml. of chloroform, an equi-molecular amount (29.5 g.) of bromine was added at such a rate that the large excess of bromine did not remain unreacted in the reaction mixture. The mixture was left to stand for 10 min. after the addition was over; then the solvent distilled off, and the residual liquid was distilled under reduced pressure. The liquid, which boiled at 130 ~134°C/15 mmHg, was almost pure 6-bromo-2,4-dimethylanisole. Yield: 32 g. (81%).


III $R_2=H$
IV $R_2=CH_3$
V $R_2=C_2H_5$
VI $R_2=CH(CH_3)_2$


VII $R_3=CH_3$
VIII $R_3=C_2H_5$

[*1] Presented at the Symposium on Molecular Structure and Spectroscopy, IUPAC, Tokyo, September, 1962. The preceding paper: M. Ōki and M. Hirota, This Bulletin, 37, 209 (1964).

1) M. Ōki and M. Hirota, ibid., 35, 1048 (1962).

2) M. Davies, "Hydrogen Bonding—Papers Presented at the Symposium on Hydrogen Bonding Held at Ljubljana, 29 July—3 Aug., 1957" (Pergamon Press, 1959), p. 393.

3) A. Burawoy, ibid., p. 259, and other publications by the same author, such as A. Burawoy, M. Cais, J. T. Chamberlain, F. Liversedge and A. R. Thompson, *J. Chem. Soc.*, 1955, 3721.

4) E. A. Braude and F. Sondheimer, ibid., 1955, 3754, and other publications by the same authors. See also E. A. Braude and E. S. Waight, "Progress in Stereochemistry," Ed. by Klyne, Butterworth, London (1954), p. 126.

TABLE I. SUBSTITUTED 2-METHOXYBENZOIC ACIDS

Substituent	Yield	M. p., °C	Calcd., %		Found, %	
			C	H	C	H
3, 5-Dimethyl	64	90	66.65	6.71	66.78	6.73
3-Ethyl-5-methyl	45	135	68.02	7.27	68.13	7.35
3-Isopropyl-5-methyl	70	87.5	69.21	7.74	69.24	7.81
6-Methyl*	75	138	65.21	6.18	65.05	6.07
6-Ethyl	—	110	66.65	6.71	66.57	6.70

* The preparation of this compound had been reported[5] by means of the hydrolysis of the corresponding nitrile. However, the hydrolysis was found to be very slow and the reported melting point did not agree with the present results.

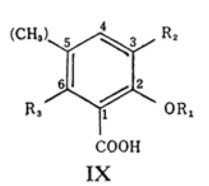
A solution of 32 g. of 6-bromo-2, 4-dimethylanisole in 50 ml. of dry ether was added to 3.6 g. of magnesium in 100 ml. of ether, while the flask was externally heated to the boiling point. The heating was continued for 2 hr. after the completion of the addition; then the Grignard reagent was cooled to room temperature and treated with a large excess of solid carbon dioxide until the reaction mixture was saturated with carbon dioxide. The mixture was kept overnight and decomposed with hydrochloric acid. The ether layer was collected and, after washing with water, extracted with an aqueous sodium bicarbonate solution. The solution was heated to remove the ether in the solution and then acidified. The solid was dried and recrystallized from a xylene-petroleum mixture to give 17 g. (64%) of 2-methoxy-3, 5-dimethylbenzoic acid (m. p. 90°C).

Other subtituted 2-methoxybenzoic acids were prepared in a similar manner; the results are tabulated in Table I.

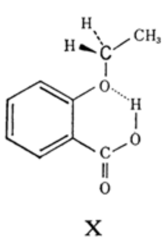
Spectral Measurement.—Ultraviolet spectra were measured with a Beckman model DU spectrophotometer, the samples being dissolved in an appropriate solvent to make up ca. 3×10^{-4} mol./l. solution. The details of the infrared spectral measurement have been reported elsewhere.[6]

Results and Discussion

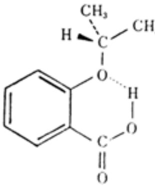
To investigate the steric effect of the intramolecular hydrogen bonding of *o*-methoxybenzoic acid, various alkyl substituents were introduced to the oxygen atom at the 2-position (R_1 in IX), to the 3-position (R_2), and to the 6-position (R_3).[*2]



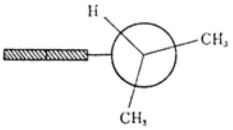
IX



X



XI



XII

The *O*-alkyl group R_1 is introduced to test the effect of the steric interference between the alkyl substituent and the hydrogen atom at the 3-position. The steric interference could be reduced if the alkyl substituent exists as an appropriate rotational isomer, as shown by X and XI. The infrared O–H stretching absorption spectra in the 3 μ region and the near-ultraviolet absorption spectra of 2-methoxy-, 2-ethoxy- and 2-isopropoxy-benzoic acids are shown in Tables II and III.

The results show that these acids apparently have two absorption bands in the O–H stretching region. One absorption at the higher frequency (about 3530 cm^{-1}) was assigned to the

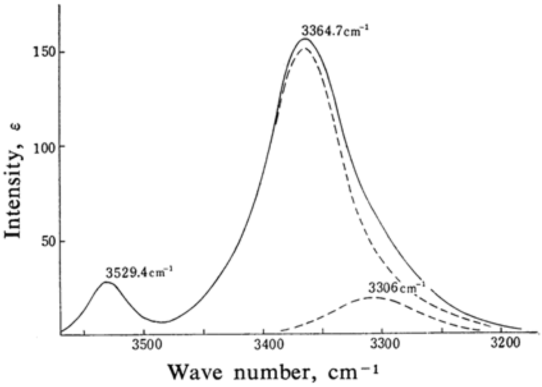


Fig. 1. The infrared ν_{O-H} spectrum of 2-methoxybenzoic acid.

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5) G. P. Gibson, *J. Chem. Soc.*, **123**, 1269 (1923).

6) M. Ōki and M. Hirota, *Spectrochim. Acta*, **17**, 583 (1961).

[*2] In this report, 2-methoxybenzoic acid derivatives are always named on the basis that carboxyl and methoxyl groups occupy the 1- and 2-positions respectively (see formula IX).

TABLE II. INFRARED ν_{O-H} ABSORPTION SPECTRA OF SUBSTITUTED 2-ALKOXYBENZOIC ACIDS

Benzoic acid		ν_{max}, cm^{-1}	ε_{max}	$\Delta\nu_{1/2}$	$A\cdot10^{-3}$	A_t/A_c
2-Methoxy	cis	3529.4	27.8	38.2	3.83	11.02
	trans	3364.7 3305.1	151 19.4	77.6 77.5	42.3 5.43	
2-Ethoxy	cis	3530.6	19.6	38.7	2.74	13.82
	trans	3351.4 3275.0	125 23.5	83.8 76.0	37.8 6.45	
2-Isopropoxy	cis	3531.1	19.2	38.4	2.66	12.41
	trans	3320.9 3255.0	104 30.4	88.2 80.4	33.12 8.82	
2-Methoxy-5-methyl	cis	3528.9	12.2	38.1	1.68	
	trans	3356.8 3290.0	98.7 13.8	76.2 65.6	27.2 3.27	
2-Methoxy-3, 5-dimethyl	cis	3532.9	28.6	36.6	3.78	8.48
	trans	3275.3	77.0	115.0	31.96	
3-Ethyl-2-methoxy-5-methyl	cis	3533.0	28.7	38.1	3.96	7.90
	trans	3275.0	79.4	108.9	31.22	
2-Isopropyl-2-methoxy-5-methyl	cis	3534.7	33.4	37.0	4.46	6.11
	trans	3273.3	69.5	108.6	27.3	
2-Methoxy-6-methyl	cis	3518.9	72.8	32.0	8.41	—
	trans	3331.8	27.2	*		
2-Methoxy-6-ethyl	cis	3518.6	89.1	30.8	9.91	—
	trans	3320	16.3	**		

* A small maximum in a broad absorption band.

** Shoulder.

TABLE III. ULTRAVIOLET ABSORPTIONS OF SUBSTITUTED 2-METHOXYBENZOIC ACIDS

Acid	Absorption maxima, mμ (extinction coeff.)		
	Heptane	Ethyl ether	Ethanol
2-Methoxybenzoic	286 (2480) 293 (2380)	291 (2970)	294 (3180)
2-Ethoxybenzoic	286.5 (2550) 294 (2450)	—	294.5 (3190)
2-Isopropoxybenzoic	288 (2760) 295 (2540)	292.5 (2770)	296 (2950)
5-Methyl-2-methoxybenzoic (III)	295 (2820) 302 (2540)	300 (3220)	302.5 (3180)
3, 5-Dimethyl-2-methoxybenzoic (IV)	287 (1860) 297 (2240)	295.5 (2230)	296 (2020)
3-Ethyl-5-methyl-2-methoxybenzoic (V)	287 (1900) 295 (2030)	—	294 (1960)
3-Isopropyl-5-methyl-2-methoxybenzoic (VI)	289 (1860) 294.5 (1940)	292.5 (2140)	291.5 (1830)
6-Methyl-2-methoxybenzoic (VII)	282 (1910)	279.5 (2030)	280 (2020)
α-Phenoxyisobutyric	264 (1420) 270.5 (1720) 276.5 (1280)	—	265 (1350) 271 (1680) 277 (1250)
Methyl 2-methoxybenzoate	295.5 (3160)	296 (4090)	300 (3530)

cis form, and the other at the lower frequency, ranging from 3364.7 cm^{-1} to 3320.9 cm^{-1}, to the trans form. The infrared ν_{O-H} spectra of 2-methoxybenzoic acid, as illustrated in Fig. 1, show a somewhat asymmetric band at the lower frequency. The band is divided into two absorptions by assuming that it is the overlap of two Lorentzian curves, the treatment being that carried out in the previous paper*1 with *o*-aryloxybenzoic acids. The ν_{O-H} frequencies of the cis forms are nearly constant throughout this series, but the ν_{O-H} frequencies of the trans forms shift to the lower frequency as the substituent becomes bulky, while the A_t/A_c intensity ratio are invariant throughout the series. The integrated intensity (A) of the cis and the trans forms should be proportional to the amount of the energy absorbed by each form of the acid molecule and related to the populations of the molecules existing as the assigned isomeric forms. However, the existence of the dimer, though its proportion to the rest is very small, prevents the exact discussion of the absolute intensity values and of the intensity ratio, which is supposed to be proportional to the population of the cis and the trans forms. The intensity ratio would be more reliable and could be an important element in comparing the relative population ratio existing in the two states of the acid if the effect of the dimer were negligible. However, the invariance of the A_t/A_c ratios indicates that the bulkiness of the *O*-alkyl substituent does not influence the equilibrium constant between the two forms.

Figures 2 and 3 show the ultraviolet spectra of these acids in heptane and ethanol respectively, together with the spectra of 2-methoxy-5-methylbenzoic acid and methyl 2-methoxybenzoate in the same solvents. The ultraviolet spectra of 2-methoxybenzoic acid and its 5-methyl derivative in ether are also shown in Fig. 4. From a comparison of these spectra, it becomes clear that the spectra of these acids in heptane differs from those in other polar solvents which are capable of hydrogen bond formation. The characteristic feature of the absorption curves in heptane is its two-peaked envelope, the maxima of which are located at 286~288 mμ and at 293~295 mμ with 2-alkoxybenzoic acids. The band envelope of the spectrum of methyl 2-methoxybenzoate in heptane is quite different from that of the parent acid, while those in ethanol are similar to each other except for a considerable red shift caused by the esterification.

The peak at the shorter wavelength is attributed to the ordinary B-band of 2-methoxybenzoic acid, and the one at the longer wavelength, to the intramolecular hydrogen-bonded

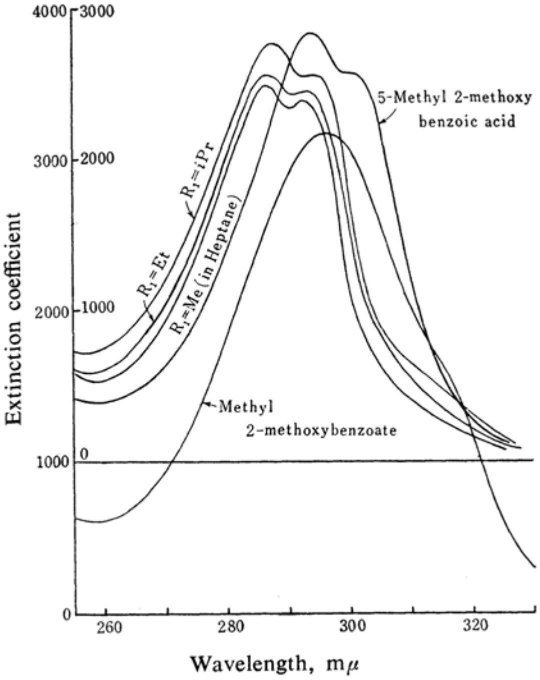


Fig. 2. The ultraviolet spectra of 2-alkoxybenzoic acids and related compounds in heptane.

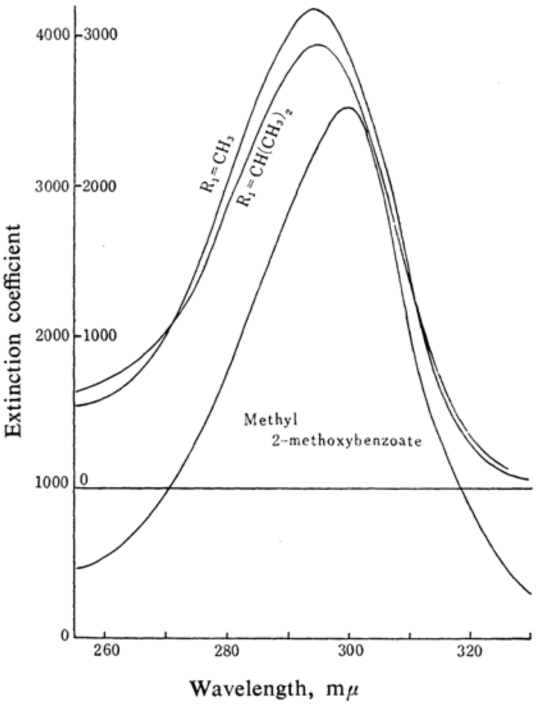


Fig. 3. The ultraviolet spectra of 2-alkoxybenzoic acids and methyl 2-methoxybenzoate in ethanol.

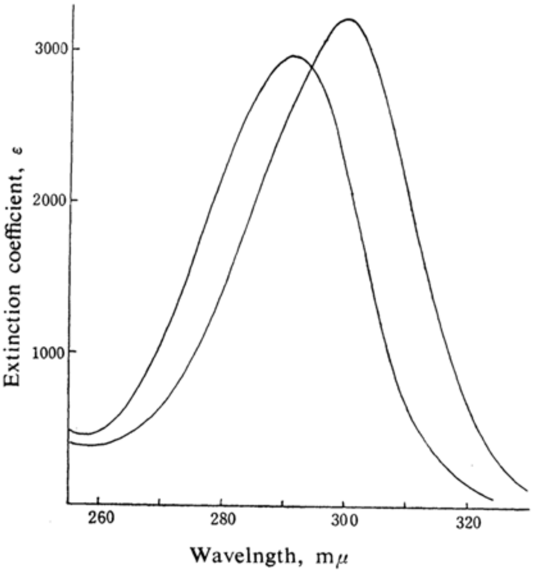
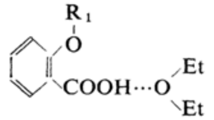


Fig. 4. The ultraviolet spectra of 2-methoxybenzoic acid (λ_{max} : 291 mμ) and its 5-methyl derivative (λ_{max} : 300 mμ) in diethyl ether.

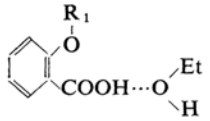
structure (Ia) ; these assignments will be discussed below. Thus, additional evidence for the intramolecular hydrogen bonding was given from the ultraviolet spectral measurement. This two-peaked absorption pattern disappears in ether and in ethanol ; this phenomenon is interpreted as stemming from the destruction of the intramolecular hydrogen bonding.

In ether, the intramolecular hydrogen bonded structure (Ia) is probably destroyed because intermolecular hydrogen bonding with ether is more favored than intramolecular hydrogen bonding. The enthalpy difference value for the intramolecular hydrogen bonding of 2-methoxybenzoic acid and for the association between acetic acid and dibutyl ether have been determined to be 3.3±0.5 kcal./mol.[2] and 4.56±0.3 kcal./mol.[7] respectively. Since the intermolecular hydrogen bonding enthalpy of this acid has not yet been obtained, the exact discussion cannot be given, but the above ΔH value for the intermolecular hydrogen bonding of carboxylic acid with ether and the advantage in entropy term in association (because the hydrogen acceptor is the solvent itselt) suggest the existence of the acid molecules as intermolecularly associated structures XIII.

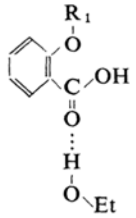
In ethanol, the acid can associate with the solvent both as a hydrogen donor (XIV) and as a hydrogen acceptor (XV and/or XVI). However it has not been clearly established whether either or both of these types of hydrogen bonding exists in the solution. Ito, Tsukioka and Imanishi[8] determined the ultraviolet spectra of benzoic and *o*-toluic acids in various solvents as functions of the temperature and of the concentration, but they could not reach a decisive conclusion on the type of hydrogen bonding. At any rate, it seems quite natural to conclude that the intramolecularly hydrogen-bonded structure Ia is destroyed in ether and in ethanol. Since the two-peaked absorption pattern disappears in these solvents, the assignment of the absorption to the intramolecularly hydrogen-bonded form is justified. This relation between ultraviolet spectra and intramolecular hydrogen bonding is also observed in other series of acids investigated.



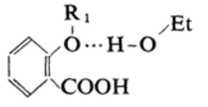
XIII



XIV



XV



XVI

A red shift upon the esterification of *p*-substituted cinnamic acids has been observed by one of the authors[9] and interpreted as arising from the unfavorable effect of the hydroxyl group on the electron-attracting property of the carboxylic carbonyl group ; a similar discussion is applicable in this case. The absorption band at ca. 300 mμ of 2-methoxybenzoic acid and its derivatives should be the B(benzenoid)-band according to the Gillam's classification.[10] From Burawoy's theory,[3] the B-band transition involves a charge migration from the terminal methoxyl group into the receiving termial carboxyl or methoxycarbonyl group in 2-methoxybenzoic acid and its methyl ester. In other words, the contribution of the polarized structure XVII plays an important role in this transition, although the electronegative character of the carboxylic hydroxyl group (the contribution of the structure XVIII) in the ground and ex-

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[7] M. Ōki and M. Hirota, This Bulletin, 36, 290 (1962).

[8] M. Ito, H. Tsukioka and S. Imanishi, *J. Am. Chem. Soc.*, **82**, 1559 (1952).

[9] Y. Urushibara and M. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 358 (1962).

[10] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Ltd., (1954), pp. 111, 116.

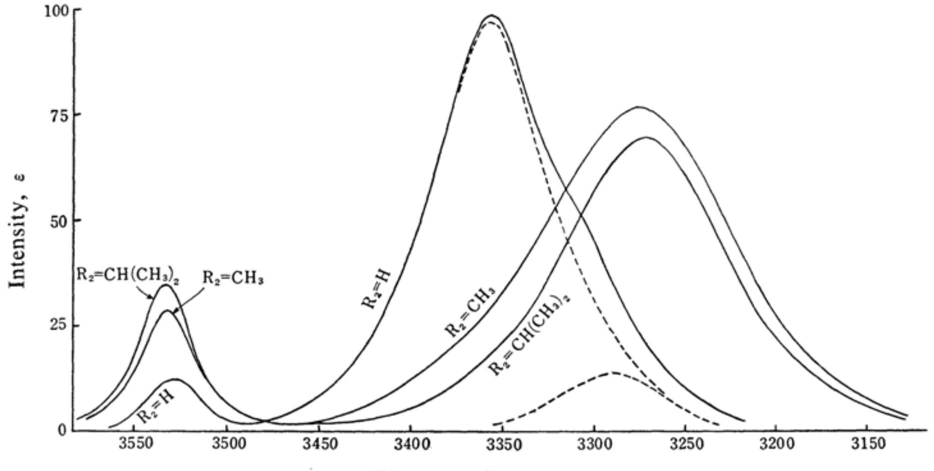
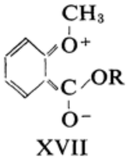
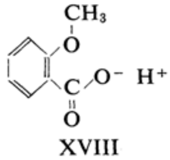


Fig. 5. The infrared ν_{O-H} spectra of 3-Alkyl-2-methoxy-5-methylbenzoic acids.

cited states of the acid does not favor the contribution of the structure XVII.



XVII



XVIII

The substituent at the 3-position is then introduced to test the necessity of the coplanarity of the methoxyl group with the benzene nucleus. Phenol and its derivatives are concluded to take the planar structure,[11,12] and the methoxyl group of 2-methoxybenzoic acid should take the S-trans configuration with respect of C_1, which carries the carboxyl group, in the absence of the steric hindrance created by the alkyl group at the 3-position. The slight steric effect on the resonance interaction of the methoxyl group with the 3-hydrogen atom is known[13], but it is estimated to be negligible by means of Braude's method[14] (XIX) for the estimation of the steric hindrance. On the other hand, a considerable steric hindrance is foreseen from the molecular chart (XX) by the introduction of the methyl group to the 3-position. The method uses covalent radii as a measure of the steric hindrance and so has a tendency to underestimate the steric hindrance.

The infrared ν_{O-H} absorption and near-ultraviolet absorption spectra of 2-methoxy-5-methylbenzoic acid (III) and its 3-alkyl(R_2)-derivatives (IV, V and VI) are listed in Tables II and III, together with those of other series of acids. The 5-methyl group is introduced for the convenience of synthesis. The infrared spectra of these compounds and their ultraviolet spectra in heptane are illustrated in Figs. 5 and 6 respectively. As is to be expected from the above consideration of the steric effect, the 3-alkyl group causes a considerable decrease in the A_t/A_c ratio, and it is concluded that an unfavorable effect is exerted by the 3-alkyl substituents. The A_t/A_c intensity ratios of 3-methyl (IV), 3-ethyl (V) and 3-isopropyl (VI) derivatives are 8.48, 7.91 and 6.11 respectively. This shows the gradual decrease in the A_t/A_c ratio as the substituent changes from methyl

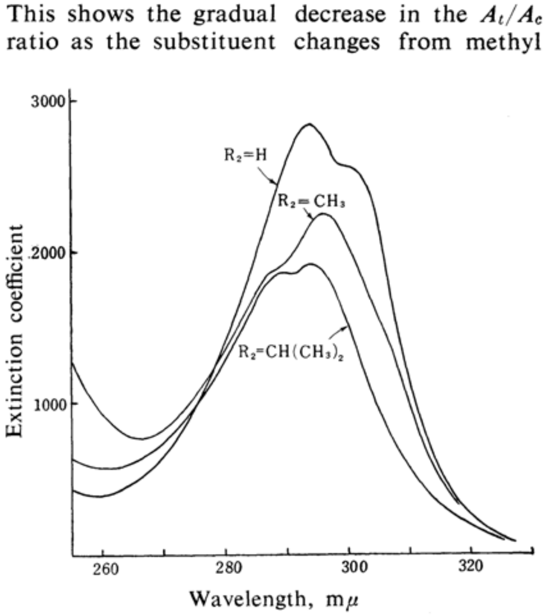


Fig. 6. The ultraviolet spectra of 3-alkyl-2-methoxy-5-methylbenzoic acids in heptane.

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[11] L. Pauling, *J. Am. Chem. Soc.*, **58**, 94 (1936).

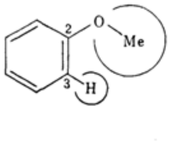
[12] O. R. Wulf, U. Liddel and S. B. Hendricks, ibid., **58**, 2287 (1936).

[13] G. Baddely, N. H. P. Smith and M. A. Vickars, *J. Chem. Soc.*, **1956**, 2455.

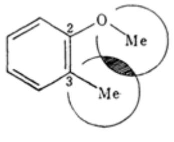
[14] E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richarson, F. Sondheimer and J. B. Toogood, ibid., **1949**, 1890.

to isopropyl; therefore, the unfavorable steric effect on a hydrogen-bonded structure like Ia increases in this order. The ultraviolet spectra of these compounds show a gradual decreases in the characteristic absorptions which have two peaks at about 295 mμ when the alkyl group R_3 is changed from hydrogen to isopropyl. This agrees with the infrared results. The introdction of the 3-*t*-butyl group would be very interesting since the very bulky *t*-butyl group would force the methoxyl group to take the S-cis configuration with respect to C_1, which carries the carboxyl group and so prevents the acid from existing as a hydrogen-bonded structure like Ia, but 3-*t*-butyl-2-methoxy-5-methylbenzoic acid has not been obtained in a pure state. Examining the frequency difference data $\Delta\nu(\equiv\nu_{max}^{cis}-\nu_{max}^{trans})$ in the ν_{O-H} region, it is concluded that the increase is caused by the larger bulk of the 3-alkyl substituents. In general, a parallel relation is expected between the $\Delta\nu_{max}$ and A_t/A_c values if the nature and steric conditions of the hydrogen bonding are similar.

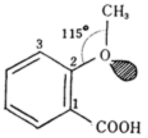
In this case, the 3-alkyl substituent hinders the coplanarity of the methoxyl group with respect to the benzene ring and destroys the conjugation between the p-π electrons of the methoxyl group and the π-electrons of the aromatic ring. The deviation from coplanarity causes, first, the alteration of the direction of the electron orbitals and, second, the localization of the electron on the oxygen atom, which is responsible for the higher electron density. On the other hand, the buttressing effect given by the 3-alkyl group causes the distance between the methoxyl oxygen and the carboxylic O–H group to be shorter than that in 2-methoxybenzoic acid. The C–O–H(C) angles of phenols and their alkyl ethers have been determined to be 115° from the dipole moment investigations[15]; the bond angle indicates that the alkoxyl oxygen takes a hybridized state between sp^2 and sp^3. Assuming that the oxygen atom takes a planar sp^2-like configuration, the four lone-pair electrons fill a p-π orbital which is perpendicular to the molecular plane and conjugate with the aromatic π-electrons and another sp^2-like orbital, the axis of which is planar with the other part of the molecule and divides the C_{Me}–O–C_{Ph} angle into two almost equal parts (XXI). The electron of the latter orbital is available to form a dative bond (hydrogen bond) with the carboxyl group. The steric hindrance is supposed to cause some twisting of the methoxyl group from the plane of the benzene ring without any appreciable change in hybridization. This twisting will reduce the probability of the hydrogen bond formation. The reduced probability of the hydrogen bonding and the shorter O···H–O distance are reflected in the decreased A_t/A_c ratio and in the larger $\Delta\nu_{max}$ values of the O–H stretching absorption bands. Another interpretation of the larger $\Delta\nu_{max}$ may be given by the increased electron density caused by the decreased contribution of the resonance form XXVII, resulting in the larger energy of hydrogen bonding. In any case, the introduction of the 3-akyl groups causes a considerable decrease in the relative population of the hydrogen-bonded species and an increase in $\Delta\nu_{max}$.



XIX



XX*3



XXI

The introduction of the methyl or ethyl group to the 6-position causes the disappearance of the O–H stretching absorption of the hydrogen-bonded trans isomer and of the characterstic ultraviolet absorptions. The infrared and ultraviolet absorption spectra of these acids (VII and VIII) are shown in Figs. 7 and 8.

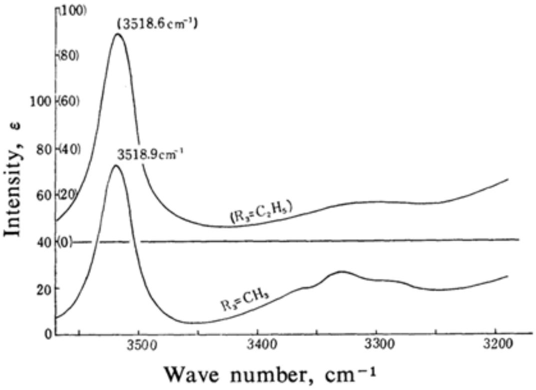


Fig. 7. The infrared ν_{O-H} spectra of 6-alkyl-2-methoxybenzoic acids.

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[15] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York (1954), p. 319.

*3 These molecular diagrams were drawn according to the method reported by Braude and his co-workers.[14] In these figures, the following dimensions were used: C-C (aromatic) 1.40 Å, C-H 1.98 Å, Me covalent radius 1.39 Å, =O covalent radius 1.10 Å, and C-O-C angle 115°.[15]

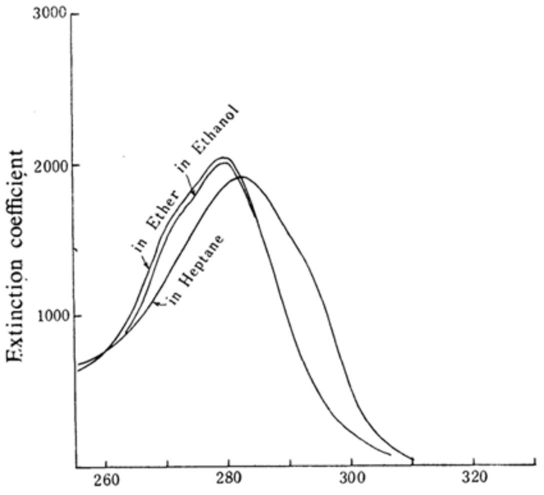
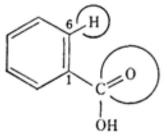


Fig. 8. The ultraviolet spectrum of 6-methyl-2-methoxybenzoic acid in various solvents.

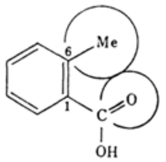
The ultraviolet spectrum of the 6-methyl acid VII in heptane and ether are almost identical, and, though the spectrum in heptane exhibits a small red shift, the band envelopes of the acid in every solvent investigated resemble one other. Consequently, it is concluded that the spectral behavior of 6-alkyl-2-methoxybenzoic acid differs from those of the acids of other series. A comparison of the infrared spectra of the 6-alkyl-2-methoxybenzoic acids indicates the existence of a broad and weak absorption in the hydrogen-bonded O–H stretching region when the alkyl group is methyl, but the characterization of the absorption band was impossible because of the low intensity, the diffuse band envelope and the very high background absorption, which is supposed to be the wing of either the C–H absorption or, less probably, the dimeric O–H absorption.

When the steric hindrance is estimated from the molecular diagram (XXIII) drawn by Braude's method,[14] a much smaller steric interaction is expected between the carbonyl oxygen and the 6-methyl group of 2-methoxy-6-methylbenzoic acid than the steric interference between the methoxyl and methyl groups of 2-methoxy-3-methylbenzoic acid (as is shown by XIX, XX, XXII and XXIII), but the actual steric effect is by far larger in the 6-alkyl acids. This indicates the important role of the planarity of the carboxyl group. In other words, the contribution of the resonance form XXV is much more important than that of the structure XXVII.

The importance of the resonance form XXV should be reflected in the polar C=O bond; the C=O stretching absorptions of these acids suggest this tendency. The infrared C=O stretching absorption data of some representative acids are tabulated in Table IV. The measurement of the spectra was carried out under almost the same conditions as that of the O–H spectra. The higher frequency of the



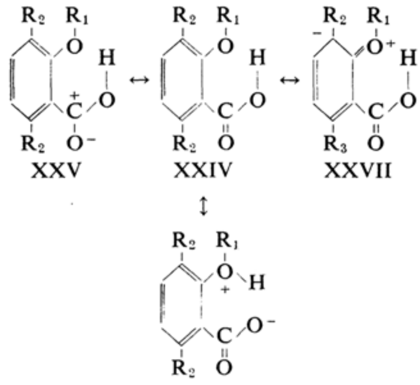
XXII



XXIII

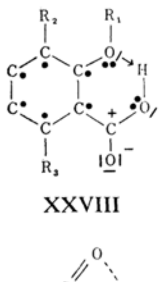
TABLE IV. THE INFRARED C=O STRETCHING ABSORPTION SPECTRA OF 2-METHOXYBENZOIC ACID AND RELATED COMPOUNDS

Acid	C=O Stretching bands, cm^{-1}		$\Delta\nu_{max}$ (C=O) cm^{-1}
	cis	trans	
α-Phenoxyisobutyric	1755	1786	31
2-Methoxybenzoic	1742	1750	7
3, 5-Dimethyl-2-methoxybenzoic	1739	1752	13
2-Toluic[16]	1740	—	—
Benzoic[16]	1742	—	—

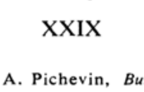


XXV XXIV XXVII

XXVI



XXVIII



XXIX

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[16] D. Peltier and A. Pichevin, *Bull. soc. chim. France*, **1960**, 1141.

$\nu_{C=O}$ absorption attributable to the trans isomer is explained in terms of the absence of the hydrogen bond-like interaction shown by XXIX.[17] The frequency shift ($\Delta\nu_{max}$) in the $\nu_{C=O}$ region caused by this four-membered ring interaction is as large as 32 cm^{-1} for α-phenoxyisobutyric acid, to which no resonance contribution of the polar C^+–O^- structure is expected on the formation of the intramolecular hydrogen bond as XXIX.[17] On the other hand, the $\Delta\nu_{max}$ (C=O)[*4] values for 2-methoxybenzoic and 3, 5-dimethyl-2-methoxybenzoic acids are 7 cm^{-1} and 13 cm^{-1} respectively, values being much smaller than that of α-phenoxyisobutyric acid. This implies the contribution of the polar structure C^+–O^-, even in the trans hydrogen-bonded isomer; as a result, the force constants of their C=O bond become less.

In view of the electronic theory, the results may be interpreted as follows. The structure of 2-methoxybenzoic acid may be expressed as the resonance hybrid of the canonical formulas XXIV, XXV, XXVI and XXVII when it takes the trans structure. The structure XXIV is the only structure without a charge separation, and its contribution is by far the greatest. Formulas XXV, XXVI and XXVII represent the canonical structures with the polarized carbonyl bond, with the charge transfer through the hydrogen bridge, and with the contribution of the electron-repelling property of the methoxyl group respectively. The strong hydrogen bond with a considerable lowering of the O–H stretching frequency is always accompanied by the weakening of the O–H bond to compensate the energy of the hydrogen bond, corresponding to the contribution of the charge transfer structure XXVI. The contribution of the polarized carbonyl structure XXV is concluded to be essential and to play a decisive part in the hydrogen bonding of this type. The importance of the structure XXV suggests that the stability of the planar hydrogen bond system in 2-methoxybenzoic acid is due to its pseudo-aromatic nature, which arises from the 10-π-electron system as illustrated by XXVIII, in which π-electrons are expressed by dots on the atoms to which the electrons originally belong.

The characteristic ultraviolet absorption bands for the intramolecularly hydrogen-bonded acids may be due to the electronic transition caused by this pseudo-aromatic system, but a more detailed investigation is needed before this hypothesis can be proven.

Summary

The infrared and ultraviolet absorption spectra of derivatives of salicylic acid with alkyl substituents at the 2-*O*-, 3- and/or 6-positions have been measured, and much information on the nature of the intramolecular hydrogen bonding has been obtained from these data. The infrared O–H stretching absorption measurement shows that a substituent at the 6-position inhibits the formation of hydrogen bonding and that a substituent at the 3-position has some unfavorable steric effects.

These data imply the importance of the coplanarity of the carboxyl group with the benzene nucleus; moreover, a consideration of these data, together with the infrared C=O streching and ultraviolet spectral data, leads to the conclusion that the structure of the hydrogen-bonded trans isomer Ia may be expresed as a resonance hybrid among XXIV, XXV, XXVI and XXVII, the contribution of XXIV being the most important and that of XXV the next most important.

The authors are indebted to Professor Saburo Nagakura and Dr. Haruo Hosoya for their valuable discussions throughout this work.

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[17] M. Ōki and M. Hirota, This Bulletin, 33, 119 (1960).

[*4] To distinguish the $\Delta\nu_{max}$ in the O–H region from that of the C=O region, $\Delta\nu_{max}$(C=O) is used for the frequency difference between the absorption maxima of the two $\nu_{C=O}$ absorptions assigned to the cis and the trans structures.