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Intramolecular Hydrogen Bonding. II. The Determination of Hammett Sigma Constants by Intramolecular Hydrogen Bonding in Schiff's Bases

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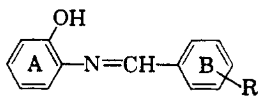
The intramolecular hydrogen bonding in *o*-hydroxy aromatic Schiff bases has been investigated. This has permitted the direct physical determination of Hammett σ-constants of *ortho*, as well as *meta* and *para* substituents. The *ortho* values are found to be similar to the *para* values.

In paper I[1] of this series, we have shown that intramolecular hydrogen bonding effects can be used to measure the basicity of certain π-orbital electrons. For example, in compounds such as *o*-allylphenol, an intramolecular hydrogen bond exists between the phenolic hydroxyl and the π-electrons of the allyl group. As the electron environment adjacent to the double bond is altered, the basicity of the π-electrons changes and, consequently, there is a corresponding change in the strength of the hydrogen bond. Electron attracting groups reduce both the electron density in the double bond and the $\Delta\nu_{OH}$ shift of the hydrogen bond. Oppositely, electron donating groups increase the electron density and the $\Delta\nu_{OH}$ shift. These effects were clearly, although only qualitatively, shown by substituting groups of varying electronegativities directly on the double bond of the allyl group.[2] In this paper we propose to show that intramolecular hydrogen bonds can also be used as sensitive "internal probes" to measure the changes in basicity of available electrons caused by exchange of groups further removed from the point of hydrogen bond formation. In particular, changes in basicity of the lone-pair electrons of nitrogen in Schiff bases of type A are examined as a function of the polar properties of the group R substituted in each of the three possible positions in ring B These changes are correlated with the Hammett σ-values of the substituent groups, showing that a *linear* relationship exists between the shift in frequency of the vibration of the associated OH group ($\Delta\nu_{OH}$, measured with respect to a hydrogen substituent) and the electron density at the point of bonding. Therefore, invoking Badger's rule[3] which states that $\Delta\nu_{OH}$ is proportional to the energy of the hydrogen bond, we conclude that the data quantitatively prove the linear relationship between basicity of the donor atom and the energy of the hydrogen bond.



A

We have considered the possibility that the acidity of the OH group is markedly affected by electronegative substituents. However, we feel that the major effect must be due to a change in the basicity of the lone-pair orbital of the nitrogen for these various reasons. This orbital probably is affected more than is the orbital bonding the nitrogen to ring A because it is almost certainly more polarizable. Moreover, the electronic changes must be passed on through two more bonding orbitals in order to alter the electron density in the OH bond. Also, the resonance stabilization in ring A would tend to minimize the effect on a particular ring position and probably would tend to distribute the electron density changes around the ring. Finally, a given polar effect would decrease the basicity of the nitrogen but would increase the acidity of the OH, thus producing opposite effects

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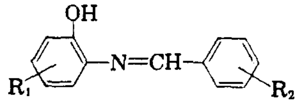
[1] A. W. Baker and A. T. Shulgin, THIS JOURNAL, **80**, 5358 (1958). This paper henceforth will be referred to as "Intramolecular Hydrogen Bonding I. Hydrogen Bonds to π-Electrons and Other Weakly Basic Groups."

[2] The groups were substituted in the *trans* position in order to avoid any complications due to steric effects.

[3] R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

TABLE I

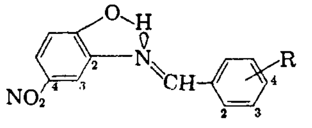


Compound R1	Compound R2	Method	Crystn. solvent	M.p., °C.[a]	Description
H	H	1	EtOH-H_2O (norite)	89–91[b]	Tan crystals
H	2-F	1	EtOH-H_2O	101–104	Brown-tan solids
H	3-F	1	50% MeOH	75–75.5	Tan crystals
H	4-F	1	50% MeOH	86–88[c]	Sand-colored crystals
H	2-Cl	1	90% MeOH	92.5–94[d]	Yellow crystals
H	3-Cl	1	MeOH-H_2O	82–84	Tan crystals
H	4-Cl	1	EtOH-H_2O (norite)	116–117[e]	Dull yellow solid
H	4-Br	1	EtOH	123.5–124.5	Fine brown crystals
H	2-NO_2	1	EtOH-H_2O	103–105[f]	Tent-green crystals
H	3-NO_2	1	MeOH-H_2O (norite)	132–133[g]	Yellow-green crystals
H	4-NO_2	1[h]	EtOH	159–160[i]	Gold-colored crystals
H	2-OCH_3	1[j]	MeOH	104–106	Tan crystals
H	3-OCH_3	2		Oil[k]	
H	4-OCH_3	1	MeOH-H_2O	89–92	Dull green crystals
H	2-OH	1	80% EtOH	184–186[l]	Brick-red crystals
H	3-OH	1[m]		Oil	
H	4-OH	1[m]		Oil[n]	
H	4-$N(CH_3)_2$	1	50% MeOH	117–119[o]	Green crystals
H	2-CH_3	1	EtOH-H_2O	51–52	Yellow-green crystals
H	3-CH_3	1		Oil[k,p]	
H	4-CH_3	2		Oil[q]	
4-NO_2	H	3	$CHCl_3$	193–194[r]	Yellow-tan crystals
4-NO_2	4-Cl	3	EtOH	187–188	Grey-green crystals
4-NO_2	4-Br	3	EtOH	190–192.5	Yellow crystals
4-NO_2	4-NO_2	3	EtOH	232 dec.[s]	Drab-green crystals
4-NO_2	4-OCH_3	3	50% EtOH	152–153.5	Light olive green solid
4-NO_2	4-$N(CH_3)_2$	3	CCl_4	187–188	Yellow crystals

[a] Melting points are uncorrected. [b] Melting point 89°, Pictet and Ankersmit, *Ann.*, **266**, 140 (1891). [c] Sensitive to light. M.p. 93°, Mayer and Mansa, *Ber.*, 54, 23 (1921). [e] M.p. 117°, Stephens and Bower, *J. Chem. Soc.*, 2971 (1949). [f] M.p. 104°, Mohlau and Adam, *cf. Beil.*, **13**, 368. [g] M.p. 131°, Mohlau and Adams, *cf. Beil.* **13**, 368. [h] 10% ethanol was added to the warmed mixture prior to treatment with sodium acetate. [i] M.p. 161°, Mohlau and Adams, *cf. Beil.*, **13**, 368. [j] The hydrochloride of this base crystallized out of the reaction mixture prior to the addition of sodium acetate. Washing with ether leaves an olive-green solid, m.p. 189–190° dec. [k] The oil obtained was sufficiently free of starting aldehyde (determined by infrared) to be used without further purification. [l] M.p. 175°, Haegele, *Ber.*, **25**, 2755 (1892). [m] Obtained from aldehyde-contaminated product by cold CH_2Cl_2 extraction. Decomposes on standing. [n] Smets and Delvaux, *Bull. soc. chim. Belg.*, **56**, 106 (1947), report a m.p. 98°. [o] M.p. 119°, Mohlau and Adam, *cf. Beil*, **14**, 34. [p] Singleton and Pollard, THIS JOURNAL, **62**, 2288 (1940), report m.p. 105°. [q] Singleton and Pollard, *ibid.*, **62**, 2288 (1940), report m.p. 108°. [r] M.p. 189°, Raiford and Linsk, *ibid.*, **67**, 878 (1945). [s] M.p. 239–240°, Stephens and Bower, *J. Chem. Soc.*, 1722 (1950).

on the $\Delta\nu_{OH}$ shift. Since the correlation is that which would be predicted for a change only in basicity, we feel that the above reasoning is valid. Nevertheless, for substituent groups which have large positive resonance contributions to their polar effect, such as for the *p*-NO_2 group, evidence presented below indicates that both the lone-pair orbital of the Schiff base nitrogen and the OH bonding orbital are being affected.

The acidity of the OH group can be directly altered by substituting groups of different electronegativities on ring A. This has been done for a series of compounds of type B in which ring A has a 4-NO_2 substituent. Again the $\Delta\nu_{OH}$-values of these compounds are linear with respect to the σ-values of the R groups and give a line which, within experimental error, is identical in slope to the line obtained from the compounds unsubstituted in ring A. The fundamental OH stretching frequencies have been decreased by a remarkable 30 cm.$^{-1}$ due to the increased acidity of the OH group, but this effect is constant and essentially independent of R.



B

Experimental

The fundamental data were obtained from infrared spectra recorded on a Beckman DK-II spectrophotometer. The stretching frequencies of the associated OH group at about 3500 cm.$^{-1}$ were observed directly and calibrated with the vapor spectrum of ammonia.[4] Although the OH bands are too broad and too asymmetric to allow resolution by the differential technique previously used,[5] the signal-to-noise ratio of this instrument is sufficiently large that the bands can be measured with an accuracy of about ±1 cm.$^{-1}$ or better in almost all cases. In a majority of cases, the precision was better than ±0.5 cm.$^{-1}$. To increase the apparent sharpness of the bands, the spectra were recorded in per cent. absorbance.

The spectra of all samples unsubstituted in ring A were obtained from approximately 0.01 molar CCl_4 solutions in a 1 cm. cell. Those compounds having a 4-nitro group in

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(4) A. R. Downie, M. C. Magoon, T. Purcell and B. Crawford, Jr., *J. Opt. Soc. Am.*, **43**, 941 (1953).

(5) A. W. Baker, *J. Phys. Chem.*, **62**, 744 (1958).

ring A were insoluble in CCl_4 and, therefore, were run at equivalent concentrations in methylene chloride. Due to interfering solvent bands, the samples were compensated with pure methylene chloride in the reference beam of the double beam spectrophotometer. The wave length shift due to the difference in dielectric constants of the solvents was measured by the unsubstituted reference compound which was soluble in both solvents. This shift is 11.4 cm.$^{-1}$ to lower frequencies and probably can be applied unchanged to each compound.

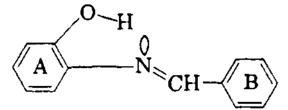
The chemicals employed in the course of this study were prepared by reaction between the appropriate *o*-aminophenols and benzaldehydes. Three methods were employed: (1) an aqueous 1 *M* solution of *o*-aminophenol hydrochloride was mixed with an equivalent amount of the proper aldehyde. The mixture was heated several minutes to effect a homogeneous solution. To the hot solution, a slight excess of aqueous sodium acetate was added, and the desired base was obtained as a solid or more often as a dark oil that solidified on cooling. (2) The aldehyde was fused with a large excess of aminophenol at a temperature that rapidly expelled the water formed. The cooled melt was then extracted with methylene chloride to obtain a solution of the desired base. (3) A hot saturated alcohol solution of the aminophenol was treated with an equivalent amount of the appropriate aldehyde. After a short period of heating, crystallization of the product was instigated by either cooling or by adding a few drops of water. Table I lists the compounds employed, their physical properties and methods of preparation.

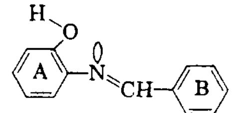
Discussion

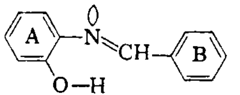
We have shown previously in paper I[1] of this series that for some types of intramolecular hydrogen bonds, the strength of the bonds will depend upon the size and favorable orientation of the orbital to which bonding occurs. In the Schiff bases under discussion, the valence orbitals of the nitrogen are hybridized approximately sp^2, with the orbital of the non-bonding pair of electrons being coplanar with the bonds to the two attached groups. This lone-pair orbital has a comparatively large electron density and is markedly polar, thus aiding the formation of a strong hydrogen bond to the *ortho* hydroxyl group. As noted in paper I, this orbital can form stronger intramolecular hydrogen bonds at greater distances than the orbitals on much larger atoms such as iodine. This is due in part both to the configuration of the orbitals and their electron density. The shape of the nitrogen lone-pair orbital is probably ellipsoidal with a comparatively small cross-sectional area, while the three non-bonding orbitals of the halogens combine to produce an effective field which is more nearly spherical; because of this latter point, orbital–orbital repulsive interaction between the halogen orbital and the OH bonding orbital is undoubtedly very important and appears to be a major contributor to the small energy of the intramolecular hydrogen bonds formed by halogens. This effect increases with the size of the halogen and may be particularly important for *o*-halophenols because the hydrogen bonds are not co-linear but are "bent" at considerable angles.[6]

The changes in the strength of the intramolecular hydrogen bonds in the Schiff bases are due to the transmission of inductive and resonance effects from the substituent group to the nitrogen orbital through a comparatively large number of intermediate atoms. It has been shown previously that Hammett σ-values[5,7] are linearly proportional to the change in electron density at the aromatic ring carbon *meta* or *para* to the substituent group. This electronic effect is then transmitted from ring B to the nitrogen by the same mechanisms which operate across the aromatic ring. This results in a contraction or expansion in the size of the lone-pair orbital or, equivalently, a decrease or increase in the electron density. This decreases or increases, respectively, the basicity of the electrons. Inasmuch as the changes in $\Delta\nu_{OH}$ are comparatively large, the size of the shift attests to the sensitivity of the hydrogen bond strength to slight changes in electron density (availability) at the donor atom.

The molecular structure of these compounds probably corresponds to that of *trans*-stilbene, thus allowing ring A to be coplanar with ring B. This ensures a considerable amount of resonance interaction through the extended structure and places the lone-pair electrons of nitrogen in an orientation favorable to bonding to the OH group. The association energy of the hydrogen bond stabilizes the molecules in structure I; as a result, no unassociated hydroxyl is observed which could be due to either structure II[8] or III.


I


II


III

In Table II, the OH stretching frequencies (ν_{OH}) of compounds unsubstituted in ring A are listed in decreasing order together with the frequency shift ($\Delta\nu_{OH}$) measured from the value of the unsubstituted compound, the corresponding σ-values obtained from the literature,[10–12] and the spectrographic values determined in this paper The decreasing frequencies indicate an increasing strength of the hydrogen bond. The linear relationship between the strength of the hydrogen bond and the basicity of the nitrogen atom is shown in Fig. 1 where the $\Delta\nu_{OH}$ shifts are plotted against the Hammett σ-values. Nearly all of the points fit the linear relationship within the experimental errors in both sets of data. In most cases, the σ-values are those published by both Brown[11] and Taft.[12] In the one instance of disagreement between these authors, the value chosen for the *m*-OH group was that given by Taft.[12] This value (0.00) probably is better than the higher value of +0.12 calculated by Brown from the

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[6] Data to be published.

[7] H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952); THIS JOURNAL, **76**, 5843 (1954).

[8] A *cis–trans* equilibrium such as occurs in *o*-halophenols[9] is not observed in these compounds.

[9] A. W. Baker, THIS JOURNAL, **80**, 3598 (1958).

[10] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

[11] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

[12] R. W. Taft, Jr., Fifth Natl. Org. Chem. Symp., June 17, 1957, Page 41, Abstracts.

TABLE II

ν_{OH} FREQUENCIES AND $\Delta\nu_{OH}$ SHIFTS OF SCHIFF BASES MONOSUBSTITUTED IN RING B

Substituent		ν_{OH}	$\Delta\nu_{OH}$	Chemical σ-values	Spectroscopic σ-values
1	3-NO_2	3466.2	+22.5	+0.71[11,12]	+0.75
2	2-NO_2	3463.1	19.4		
3	4-NO_2	3462.3	18.6	.78[11,12], $\sigma^* =$ 1.27[14]	
4	3-Cl	3455.5	11.8	.37[11,12]	.38
5	3-F	3453.3	9.6	.34[11,12]	.31
6	4-Br	3452.2	8.5	.23[11,12]	.25
7	2-Cl	3450.7	7.0		.22
8	4-Cl	3450.2	6.5	.23[11,12]	.20
9	2-F	3449.1	5.4		.17
10	4-F	3448.9	5.2	.06[11,12], 0.16[11]	.15
11	3-OCH_3	3445.4	1.7	.11[12]	.04
12	H	3443.7	0.0	0	0
13	3-OH	3442.5	−1.2	0.00[12]	−0.05
14	3-CH_3	3442.4	−1.3	−0.07[11,12]	− .07
15	4-CH_3	3440.2	−3.5	− .17[11,12]	− .14
16	2-CH_3	3440.2	−3.5		− .14
17	4-OCH_3	3436.2	−7.5	− .27[11,12]	− .28
18	4-OH	3435.0	−8.7	− .33,[9] −0.36,[8] − .37[11]	− .32
19	2-OCH_3	3434.3	−9.4		− .34
20	4-$N(CH_3)_2$	3420.9	−22.8	− .83[11]	− .80

data of Dippy.[13] Added weight is given to this conclusion by the σ-values of the CH_3O-group[11,12] which are −0.27 *para* and +0.12 *meta*, whereas the value for the *p*-OH is −0.33 to −0.37. It appears unlikely that the values for the two *meta* compounds can be equal when those for the *para* compounds are so dissimilar. Jaffé[14] also is in agreement with the lower value for the *meta* isomer. On the other hand, Dippy's[13] value of −0.33 for the *p*-OH group is in better agreement with our data than the values accepted by Taft[12] (−0.36) or Brown[11] (−0.37) although all of these values are within the quoted probable error of 0.04 unit. In agreement with the infrared value, several other reactions listed by Jaffé[14] likewise yield values close to the lower limit. Finally, it is interesting to note that the σ-value given by Brown[11] for the *p*-F group (0.06) puts the correlation outside of the infrared experimental error, but that the value of Kuhn and Wasserman[15] (0.16) obtained from thermodynamic data, is in good agreement with the value of 0.15 obtained from the curve in Fig. 1.

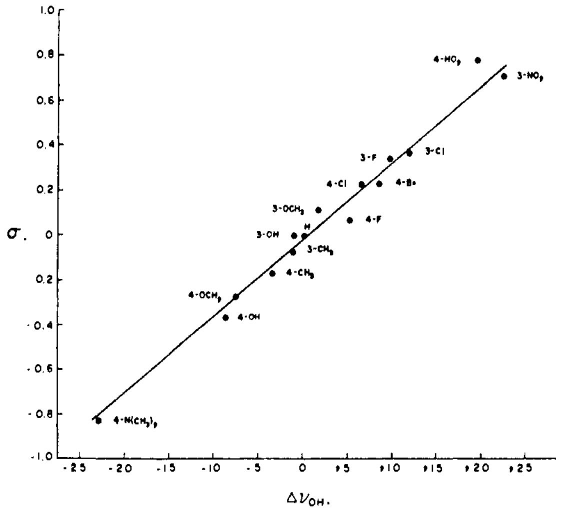

Fig. 1.—Comparison of hydroxyl frequency shifts with literature σ-values for Schiff bases unsubstituted in ring A.

Two points of particular interest are those due to the *p*-NO_2 and *p*-F group. The *p*-F group is interesting because it falls within experimental error (σ-value) of the line for this correlation. It is electron withdrawing and shows the expected decrease in total polar effect from *p*-Cl because of its greater resonance tendency. However, in a previous correlation of the OH stretching frequencies of *p*-substituted phenols,[5] the value of ν_{OH} (*p*-F) was anomalous since it was shown to be even greater than that for unsubstituted phenol; in contrast, the frequencies were smaller for all of the other halogens. This was interpreted to mean that due to the larger resonance effect of fluorine,[12] a *p*-F group is electron donating to the hydroxyl group, although hybridization changes in the OH bond were suggested as a secondary explanation. Despite the apparent conflict in the two sets of data, we believe for the reasons outlined below that the first explanation is valid and that the observed increase in ν_{OH} reflects an increase in the electron density of the OH bond.

Taft[12] lists the contributions to the total polar effect for a *p*-fluoro group as +0.50 induction and −0.44 resonance. These two balance so nearly to zero that it is not surprising that the net result varies to some extent in different compounds. For example, it is interesting to note that a *p*-F group is activating for some electrophilic reactions[16–20] and that Brown has assigned an electro-

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(13) L. G. Bray, J. F. J. Dippy, S. R. C. Hughes and L. W. Laxton, *J. Chem. Soc.*, 2405 (1957).

(14) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(15) R. Kuhn and A. Wasserman, *Helv. Chim. Acta*, **11**, 31 (1928).

(16) H. G. Kuivala and L. E. Benjamin, This Journal, **77**, 4834 (1955).

philic σ_p^+ value of -0.07 to fluorine.[20] Such reactions are believed to proceed through a carbonium ion intermediate in which resonance contributions from a *para* substituent are particularly important and are increased because of the electron demands from the electron-deficient center in the transition state. However, since the values of ν_{OH} pertain only to the conditions existing in the electronic ground state, we feel that our data show that some variations in the net value of the σ-constants are due primarily or in part to ground-state changes in the static electronic distribution. We can conclude that for some substituent groups in such systems sigma is multivalued and need not be accurately transferrable between compounds.[21]

Chemical support for our data on phenols is given by the *Ka* values for *p*-substituted phenols obtained by Baddeley, *et al.*[19] These values are listed in Table III and show that a *p*-F group is slightly acid weakening while all of the other halogens are acid strengthening.

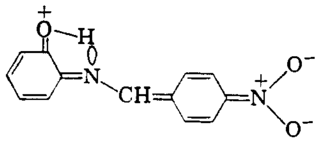
TABLE III

Ka VALUES OF *p*-SUBSTITUTED PHENOLS

Substituent	$Ka \times 10^{10}$
p-F	0.26
H	0.32
p-Cl	1.32
p-Br	1.55
p-I	2.19

Furthermore, Brown, *et al.*,[23] have observed an enhancement in the rates of solvolysis of the halophenyldimethylcarbinyl chlorides for a *p*-F group. The relative order exhibited by *para* halogens is F>H>Cl>Br<I, the rate for *p*-F being more than twice that for H.

On the other hand, the value of ν_{OH} for the *p*-NO₂ compound is inconsistent because it is lower than that for the *m*-NO₂ compound by about 4 cm.$^{-1}$ and, therefore, falls off the curve in Fig. 1 by much more than the experimental error. Since the correlation for the *m*-NO₂ compound is satisfactory, the difference in behavior is probably due to the increased resonance effect of the *p*-NO₂ compound. This increased resonance interaction very likely carries the electronic effect through the Schiff base nitrogen atom and on to the OH group as indicated by the valence bond resonance structure



This increases the strength of the hydrogen bond over the expected value because of the greater acidity of the OH group.

Taft[12] separates the total polar effect of the *m*- and *p*-NO₂ groups into an inductive effect of +0.63 (equal for both isomers) and a resonance effect of +0.15 (*p*-NO₂) and +0.08 (*m*-NO₂). Since the very small resonance value of 0.08 for the *meta* isomer does not affect its correlation, it is probable that the actual value for *p*-NO₂ is much larger than +0.15 for these compounds. This would be consistent with the fact that σ^*-values must be used for *p*-NO₂ substituted phenols and anilines because of resonance structures involving the single aromatic ring similar to the one above. If the difference between σ- and σ^*-values is due only to resonance effects, then the value to be applied to the *p*-NO₂ group in the Schiff bases would be nearer to +0.64 (1.27[10] minus 0.63) rather than to +0.15. Interestingly, large negative resonance contributions to the σ-value do not appear to affect the OH acidity; this is paralleled by the fact that resonance structures reverse to the one drawn above are unknown and, therefore, σ^*-values do not pertain to such substituents.

As mentioned in the Introduction, the acidity of the OH group (and, therefore, the strength of the hydrogen bond) can be changed by substituting electronegative groups on ring A. This is demonstrated by the series of compounds, listed in Table IV, in which ring A has a 4-NO₂ substituent. Allowing for the change in solvents, the frequency of the OH vibration has been decreased by about 30 cm.$^{-1}$ for each compound. This again shows the remarkably large effect of a *p*-NO₂ group and the need for using σ^*-values with phenols. The NO₂ group is *meta* to the Schiff base nitrogen and affects the basicity of its lone-pair electrons to a much smaller extent than it affects the acidity of the OH group. For the isomeric 5-NO₂ compound, on the other hand, we would expect a sharp reduction in the strength of the hydrogen bond.

The frequency shifts in Table IV are shown in Fig. 2 plotted against the Hammett σ-values of the substituents. The slope of the line is essentially identical to that in Fig. 1, thus demonstrating that

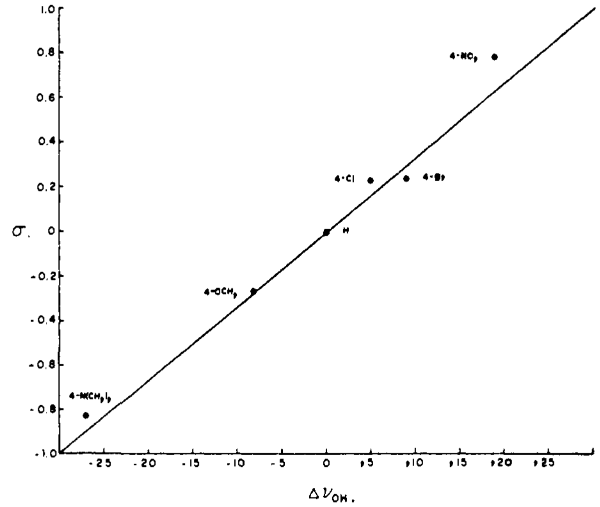


Fig. 2.—Comparison of hydroxyl frequency shifts with literature ρ-values for Schiff bases containing a 4-NO₂ group in ring A.

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(17) A. G. Evans, J. A. G. Jones and G. O. Osborne, *Trans. Faraday Soc.*, **50**, 470 (1954).

(18) C. Eaborn, *J. Chem. Soc.*, 4858 (1956).

(19) G. Baddeley, G. M. Bennett, S. Glasstone and B. Jones, *ibid.*, 1827 (1935).

(20) H. C. Brown and Y. Okamoto, THIS JOURNAL, **79**, 1913 (1957).

(21) It is of interest here to note that other substituents have shown variable σ-values depending upon the precise nature of the compound in which they occur.[22]

(22) H. H. Szmant and G. Suld, THIS JOURNAL, **78**, 3400 (1956).

(23) H. C. Brown, Y. Okamoto and G. Ham, *ibid.*, **79**, 1906 (1957).

the OH frequency of each compound has been shifted by an equal amount. Other 4-position substituents probably could be selected, such as the halogens, which would affect the basicity of the nitrogen to a greater extent than the acidity of the OH group. Whichever group is affected more will control the strength of the hydrogen bond.

TABLE IV

ν_{OH} FREQUENCIES AND $\Delta\nu_{OH}$ SHIFTS OF SCHIFF BASES CONTAINING A 4-NITRO GROUP IN RING A

Substituent	ν_{OH}	$\Delta\nu_{OH}$
4-NO_2	3421.1	+18.6
4-Br	3411.5	9.0
4-Cl	3407.4	4.9
H	3402.5	0
4-OCH_3	3394.4	−8.1
4-$N(CH_3)_2$	3375.5[a]	−27.0

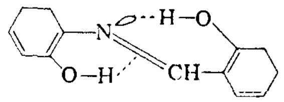
[a] This band is close to a band of methylene chloride. The instrument slits are widening so rapidly that the frequency may be in error by several cm.$^{-1}$.

The data of Table I also show small but significant differences between the effects of an *ortho* and a *para* substituent. The trend is for both the inductive and the resonance effects to be greater in the *ortho* position than in the *para*. For example, in the fluoro and chloro compounds, the *ortho* isomer has a frequency 0.2 to 0.5 cm.$^{-1}$ higher than that of the *para:* this is due to the predominance of the inductive effect and to its increase as the interacting groups approach each other. However, for the methoxy compounds, the situation is reversed since the *ortho* isomer has a lower frequency than the *para* by 1.9 cm.$^{-1}$. This is due to a much larger resonance effect and shows that the difference in inductive effects, which would cause the frequencies to be reversed is much less than the difference in resonance effects.

Very little has as yet been published concerning the evaluation of *ortho* substituent polar values by reaction rates or equilibria. This is due to the difficulties of obtaining chemical data not subject to interfering steric effects. However, Taft[24] has investigated a few such systems and has concluded that the *ortho* substituent constants are essentially equal to the Hammett σ-values for the corresponding *para* substituents. The above spectroscopic data indicate that these conclusions are approximately valid, but that there are appreciable differences for some groups. For example, we would expect the resonance effect of the amino group to cause even a larger difference between *ortho* and *para* values than for the CH_3O-group.

The *ortho* and *para* nitro isomers are interesting because the frequency of the *ortho* compound is higher than that of the *para* by 0.8 cm.$^{-1}$. The resonance and inductive contributions to the σ-value for a 4-NO_2 group are nearly identical but, as discussed above, the inductive effect primarily changes the basicity of the Schiff base nitrogen, while the resonance effect is propagated into ring A to the hydroxyl group. The shorter range inductive effect then appears to dominate and causes ν_{OH} to increase. It is possible that a slight steric effect is also present although molecular models indicate that this can be neglected.

π-Type Hydrogen Bonds.—The correlation of the 3- and 4-hydroxy groups is very satisfactory considering the inaccuracies in the literature σ-values. The compounds are not stable, however, and decompose on standing. The 2-hydroxy compound, on the other hand, is very stable and gives an OH spectrum quite unlike those of the other isomers. There is no observable frequency near the frequencies of the above compounds; instead, there are two widely separated frequencies, one at 3545.8 cm.$^{-1}$ and the other outside the range of the Beckman DK-II at approximately 2730 cm.$^{-1}$. The latter frequency is undoubtedly due to the ring B OH group which preferentially forms an intramolecular hydrogen bond to the nitrogen. Since this OH group can bond to the nitrogen by forming a 6-membered ring, the strength of the resultant bond is much greater than that formed by the OH group in ring A. Therefore, the ring B OH group completely displaces the ring A OH group from bonding to the nitrogen lone-pair orbital. However, reminiscent of the allyl and propenyl compounds discussed in paper I, the ring A OH group can, and does, bond to the π-electron system at the N=CH double bond. Due to the configuration stabilization of the double hydrogen bonding, the ring A OH group is mainly in the bonded state. The following structure is representative of the dihydroxy compound. We intend to discuss a more or less complete series of such compounds in a forthcoming paper because they will indicate the behavior of π-electrons to substituent effects. This would be most interesting in comparison with he above data.



Multiple Substituents in Ring B.—The Schiff bases provide an excellent system for investigating the total polar effects of multiple substituents. Such an evaluation has been difficult to obtain by chemical means, in part, because of the steric interference from *ortho* substituents. Taft[25] has investigated a limited number of compounds and has concluded that the polar effects are roughly additive. However, he pointed out that in some systems the resonance effects might not be additive both because of steric interaction between the groups and because resonance effects may lead to non-additivity through "saturation." Within these limits the present technique appears to be straightforward with no interfering side effects.

At present, only one disubstituted compound has been made, but we plan a complete series for a future paper. The compound contains chlorine in the 2- and 4-positions in ring B. The $\Delta\nu_{OH}$ values for the monosubstituted chloro compounds are 2-Cl, +7.0 cm.$^{-1}$; and 4-Cl + 6.5 cm.$^{-1}$. The combined shift to be expected if the polar effects are strictly additive is 13.5 cm.$^{-1}$. The measured value of 13.4 cm.$^{-1}$ is well within the

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(24) R. W. Taft, Jr., THIS JOURNAL, **74**, 3120 (1952).

(25) R. W. Taft, Jr., *ibid.*, **79**, 5075 (1957).

experimental error, showing that the polar effects for such substituents are additive. This may not be true for disubstituted compounds in which one of the groups is electron donating while the other is electron attracting.

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[CONTRIBUTION FROM THE GENERAL ENGINEERING LABORATORY, GENERAL ELECTRIC COMPANY]

On the Role of the Gaseous Phase in Solid State Reactions[1]

BY HANS J. BORCHARDT

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The early work on reactions between powdered solids has been questioned recently by a group of Russian investigators. These workers claim that many of the reactions previously reported to proceed by solid state diffusion processes occur in reality by a vaporization mechanism. They conclude that solid state reactions between powders do not generally occur except at very high temperatures since the contact area between the particles presents too small a cross section for rapid diffusion. The ambiguities associated with the experimental methods used to differentiate between solid state and gas phase mechanisms are discussed briefly. Criteria are developed whereby it is possible to determine conclusively when a vaporization mechanism *cannot* be the principal mode of mass transport. These are applied to a number of reactions between powdered solids which occur rapidly at low temperatures. It is found that a vaporization mechanism is untenable for at least two of these reactions and that the above generalization as regards powder reactions is questionable.

In reactions between powdered solids such as the reaction

$$MgSO_4(s) + CaO(s) \longrightarrow CaSO_4(s) + MgO(s)$$

it is generally difficult to determine whether the reaction proceeds by solid state diffusion processes or whether mass transport through the gaseous phase ($SO_3(g)$) is involved. This question was the subject of heated controversy between European investigators some thirty years ago (for example, refs. 2, 3). The conflicting viewpoints regarding mechanism apply to numerous reactions, all of which are listed by Hedvall,[4] who has tabulated most "solid state" reactions studied prior to the 1940's. The reactions in question involve reactants where either vaporization (dissociation) is *possible* or where liquid phases *can* form. Another characteristic is that the reactions all proceed rapidly at relatively low temperatures (approximately 500°, some lower). The question that was basic to the entire controversy is whether solid state reactions can occur at all at such low temperatures.

The viewpoint that the reactions in question are, for the most part, purely solid state reactions apparently predominated, as evidenced by statements in the more recent literature and texts on the subject.[4–6]

In the last several years, Ginstling and co-workers have re-examined several of these reactions and claim to have shown that they proceed by transport of molecules through the gaseous phase.[7–9] These investigators have reverted to the viewpoint that solid state reactions between powdered solids are unlikely processes except at very high temperatures. Their reasons for this belief are, however, quite different from the reasons previously presented. They fully accept reactivity in the solid state as a fact, but offer the contention that the contact area between powder particles offers so small a cross section for diffusion that appreciable mass transport will only occur when diffusion coefficients are very large, *i.e.*, at high temperatures. They, therefore, conclude that the reactions studied by Hedvall, Tammann, Jander and co-workers are really not solid state reactions at all and these workers misinterpreted their results.

The reason that this question has not been resolved is that no means have been available up to the present whereby solid state and other mass transport processes may be unambiguously differentiated in powder compacts. Consider the experiments of Ginstling and co-workers where the reactants are separated so that there is no direct contact at all. The fact that the reaction is observed to proceed under these conditions led the authors to conclude that some of the so-called "solid state" reactions are not solid state reactions at all but that they proceed by dissociation of the salt followed by a gas–oxide interaction. Although this experiment demonstrates dramatically that gas phase mass transport is taking place under the experimental conditions, it *does not* disprove Hedvall's contention that mass transport by solid state diffusion is occurring under a different set of conditions, namely, when the reactants are in intimate contact in a powder compact. Since solid state reactions, particularly powder reactions, are quite sensitive to experimental conditions, any experiment designed to elucidate the mechanism which requires *changing* the conditions, immediately assumes an uncertainty.

In the present communication, criteria are developed whereby it is possible to gain knowledge regarding the mechanism of a reaction without disturbing the system. These considerations are limited to the determination of what is *not* occurring; specifically, it will be shown that in certain instances the possibility of a mechanism involving a vaporization step can be ruled out completely.

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(1) Presented in part at the 134th Meeting of the American Chemical Society, Chicago, Illinois, September, 1958.

(2) D. Balarew, *Z. anorg. Chem.*, **160**, 92 (1927).

(3) G. Tammann, *ibid.*, **160**, 101 (1927).

(4) J. A. Hedvall, "Einfuhrung in die Festkorperchemie," Friedr. Vieweg. Braunschweig, 1952, p. 169 ff., p. 257 ff.

(5) W. E. Garner, "Chemistry of the Solid State," Butterworths, London, 1955, p. 307.

(6) G. Cohen. *Chem. Revs.*, **42**, 527 (1948).

(7) A. M. Ginstling, *J. App. Chem. USSR*, **24**, 629 (1951) (transl.).

(8) A. M. Ginstling and T. R. Fradkina, *ibid.*, **25**, 1199, 1325 (1952) (transl.).

(9) M. E. Pozin, A. M. Ginstling and V. V. Pechkovsky, *ibid.*, **27**, 261. 404 (1954) (transl.).