Spectroscopic Studies of Keto–Enol Equilibria. VIII. Schiff Base Spectroscopic Correlations

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Two correlations of the spectroscopic properties of a number of β-amino α,β-unsaturated ketones and esters are presented. The first involves the NH proton chemical shift *vs.* the NH infrared stretching frequency and the second involves the NH proton chemical shift *vs.* the chelated carbonyl infrared stretching frequency. Both correlations are compared with ones previously described for enols such as hydrogen-bonded phenols and those derived from β-diketones and β-keto esters.

The keto–enol equilibria of divers β-amino α,β-unsaturated ketones and esters have been discussed in previous papers of this series.[1–3] To a great degree, the presence of the hydrogen bond, although duly noted, was not explored in detail.

Many correlations involving a variety of spectroscopic properties of hydrogen bonds have appeared in the literature.[4] Reeves, Allan, and Strømme[5] related the p.m.r. chemical shift of the acidic proton of substituted phenols with the hydroxyl stretching frequency. Their work was particularly valuable, for it indicated that both spectroscopic methods responded concurrently to changes in hydrogen bonding. Merrill[6] studied this dependence in some related compounds. Forsén and Nilsson[7] noted that the hydroxyl proton resonance position was also related to the carbonyl stretching frequency in certain β-triketones and *o*-hydroxybenzaldehydes. Recently the correlation was extended to enolic β-keto esters by Burdett and Rogers[8] as well as by Hay and Williams.[9]

Since these correlations of the "oxygen" compounds emphasize the regularity and interrelationships among the various parameters of a hydrogen-bonded system, it is useful to apply some of the concepts to Schiff bases, to observe the regularities and to ascertain the significance of the exceptions. Furthermore, information from the "nitrogen" derivatives would provide additional information concerning the generality of the correlations previously proposed.

Experimental

Proton resonance spectra were obtained as previously described.[1,2] Infrared spectra were taken on a Cary-White 90 infrared spectrometer. The instrument was operated at 2-cm.$^{-1}$ resolution in the 3000-cm.$^{-1}$ region and 1.5-cm.$^{-1}$ resolution in the 1600-cm.$^{-1}$ region. The results are good to ±1 cm.$^{-1}$ except when band width precluded such accuracy.

Carbon tetrachloride was reagent grade and deuteriochloroform was supplied by Merck Sharp and Dohme of Canada. Compounds have either been previously described,[1–3] or else have been donated by Dr. Emily Pitcher Dudek.

Results

Figure 1 is a plot of the NH infrared stretching frequency *vs.* the proton resonance position of the same group (the data are in Table I). The results of the previous investigators are also included on the diagram (*vide infra*). It is apparent from Figure 1 that, as with the phenols studied by Reeves, *et al.*,[5] the two NH parameters are related in the hydrogen-bonded Schiff bases.

When possible, the compounds were studied in carbon tetrachloride solution, but, for reasons of solubility, many were studied in deuteriochloroform. The same solvent was used for both the p.m.r. and infrared spectra of each compound. Both spectra of ethyl β-aminocrotonate were also studied in the neat liquid since the proton resonance bands were very broad in carbon tetrachloride solution.

Generally the infrared and p.m.r. absorptions of chelated protons are insensitive to the solvent used, and this insensitivity includes concentration effects.[1,3,6] On the other hand, a nonchelated proton, such as one of the amino protons of an amino group, is sensitive to its environment; hence, compounds containing nonchelated protons were studied at two or more concentrations and the chemical shifts extrapolated to infinite dilution.[3,6] If the change in chemical shift was large, additional points were taken to ensure accuracy. The chemical shift is given to only 0.1 p.p.m. since in all cases the bands were broad.

In the infrared spectra of the acetylacetone derivatives, the amino hydrogen could not be located with certainty. A strong, broad band about 3100–2900 cm.$^{-1}$ was present, but due to the CH stretching bands in this region, the NH location was obscured.[6] Accordingly, the errors in this region are much larger.

It is important to compare the correlation for the Schiff bases with the three previously reported studies for the phenol derivatives. The derived units of $\Delta\delta$ and $\Delta\nu$ used by Reeves, Allan, and Strømme[5] were not advantageous here since the variety of compounds studied require numerous reference points. Furthermore, retaining the data in the original units simplifies its usage by others. Therefore all chemical shifts given in ref. 5 were converted back into p.p.m. with tetramethylsilane as the origin (the δ-scale).[10] The infrared stretching frequencies were likewise converted back into band positions for inclusion in Figure 1. Merrill's data was converted into p.p.m.

It is seen that the entire mass of data fits *one* line (Figure 1). Near 3500 cm.$^{-1}$, the wave-length region

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[1] Part VII: G. Dudek and E. P. Dudek, *J. Am. Chem. Soc.*, **86**, 4283 (1964).

[2] G. Dudek and G. P. Volpp, *J. Org. Chem.*, **30**, 50 (1965).

[3] G. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **84**, 2691 (1962); G. Dudek and G. P. Volpp, *ibid.*, **85**, 2697 (1963).

[4] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

[5] L. W. Reeves, E. A. Allan, and K. O. Strømme, *Can. J. Chem.*, **38**, 1249 (1960); E. A. Allan and L. W. Reeves, *J. Phys. Chem.*, **66**, 613 (1962).

[6] J. R. Merrill, *ibid.*, **65**, 2023 (1961).

[7] S. Forsén and M. Nilsson, *Acta Chem. Scand.*, **13**, 1383 (1959); **14**, 1333 (1960); **16**, 583 (1962); S. Forsén and B. Akermak, *ibid.*, **17**, 1907 (1963).

[8] J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964).

[9] R. W. Hay and P. P. Williams, *J. Chem. Soc.*, 2270 (1964).

[10] The value of C_6H_{12} *vs.* tetramethylsilane was measured as 1.43 p.p.m. (in CCl_4 solution).

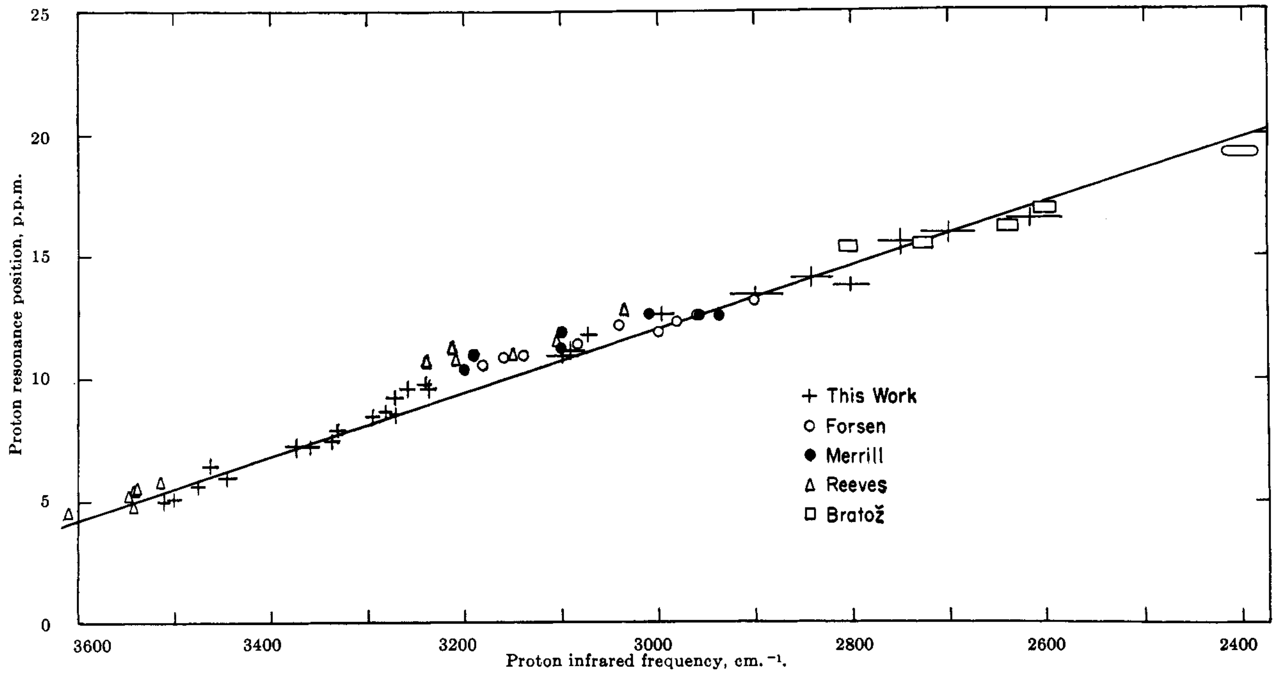


Figure 1.—The infrared stretching frequency of a hydrogen bonded NH or an OH group *vs.* its proton resonance position. The work of Forsén is ref. 7; Merrill, ref. 6; Reeves, ref. 5; and Bratož, ref. 13.

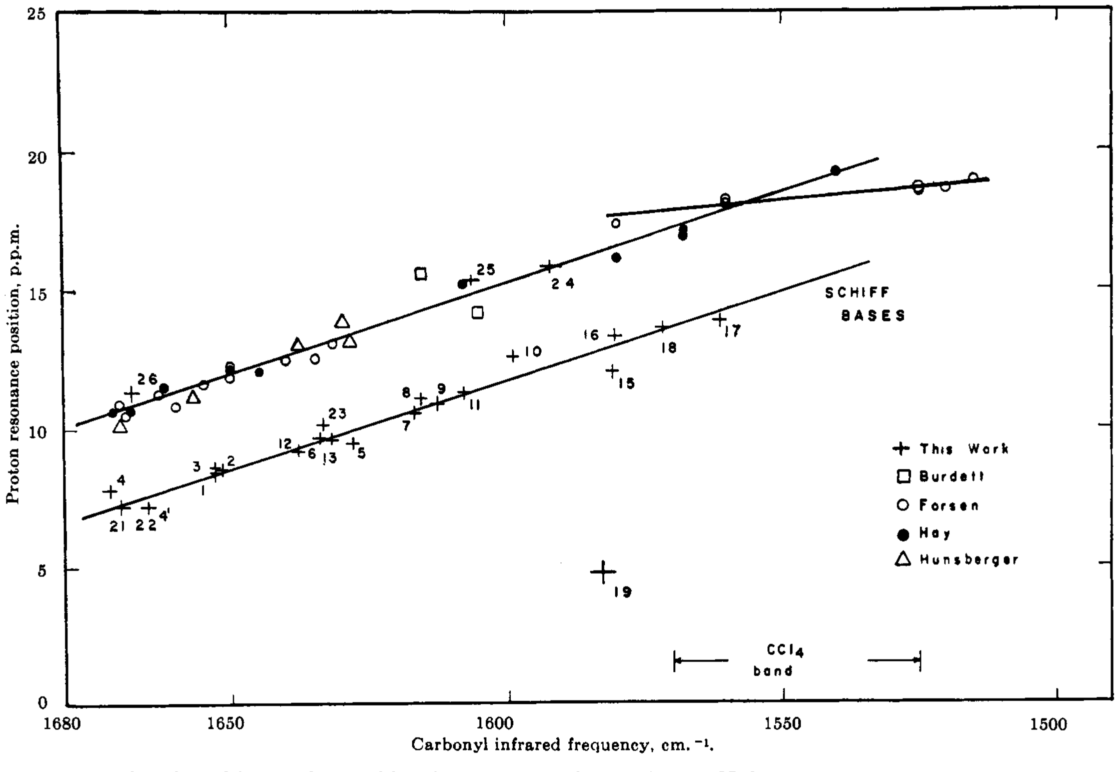


Figure 2.—The chelated carbonyl infrared stretching frequency *vs.* the contiguous NH or OH proton resonance position in hydrogen-bonded systems. The work of Burdett is ref. 8; Forsén, ref. 7; Hay, ref. 9; and Hunsberger, ref. 18 (and also ref. 15).

characteristic of weak hydrogen bonds, distinct hydroxyl and amino functions do exist; however, below 3000 cm.$^{-1}$, many of the compounds studied are tautomeric systems with the distinction between hydroxyl and amino blurred. The fact that one line will serve means, within the accuracy of the data and the correlation, the response of a hydroxyl or amino group to electron delocalization from hydrogen bonding is similar. It is also possible that a given point on the line does not represent the same hydrogen-bond strength for all types of structures. This could only be determined by accurate thermodynamic data on strengths of hydrogen bonds in a variety of compounds.

The Canadian workers made a correction in the hydroxyl chemical shift for the ring-current anisotropy of the adjacent aromatic nucleus. The correction has been ignored here for several reasons. The most compelling one is that the correlation of Figure 1 and the one of Figure 2 both appeared to be little affected by the presence or absence of such a correction. Furthermore,

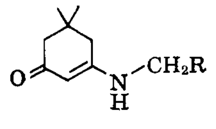
TABLE I

INFRARED AND PROTON RESONANCE DATA

			NH		
No.	Compound	Solvent[a]	δ, p.p.m.	Cm.$^{-1}$	C=O, cm.$^{-1}$
1	Ethyl N-methyl-β-aminocrotonate	CCl_4	8.4	3295	1653
2	Ethyl N-ethyl-β-aminocrotonate	CCl_4	8.6	3283	1653
3	Ethyl N-isopropyl-β-aminocrotonate	CCl_4	8.5	3271	1652
4	Ethyl β-aminocrotonate	Neat	5.9[b] 7.4	3444 3338	1660[b]
4	Ethyl β-aminocrotonate	CCl_4	5.0[b,c] 7.8	3512 3332	1672
5	N,N^1-Dibenzyl-β-aminocrotonamide	$CDCl_3$	5.1[c] 9.5	3448 3258	1628
6	Acetylacetonimine	CCl_4	5.1[c] 9.7	3240 3501	1634
7	N-Methylacetylacetonimine	CCl_4	10.6	3100[d]	1617
8	N-Benzylacetylacetonimine	CCl_4	11.1	3100[d]	1616
9	N-(2-Cyanoethyl) acetylacetonimine	$CDCl_3$	10.9	3100[d]	1613
10	N-Phenyl acetylacetonimine	CCl_4	12.6	3000	1598[e]
11	3-Methylamino-1,3-diphenyl-2-propen-1-one	CCl_4	11.3	3000[d]	1608[f]
12	2-Carbamoyldimedone	$CDCl_3$	5.6[c] 9.2	3476 3273	1638
13	N-Methyl-2-carbamoyldimedone	CCl_4	9.6		1632[g]
14	N-Phenyl-2-carbamoyldimedone	CCl_4	11.7	3070	. .
15	2-Acetiminodimedone	$CDCl_3$	6.4[c] 12.0	3462 3074	1581
16	N-Methyl-2-acetiminodimedone	CCl_4	13.3	. .	1581
17	N-Phenyl-2-acetiminodimedone	CCl_4	15.2	2760	1563
18	N-Isopropyl-2-acetiminodimedone	CCl_4	13.6	2900[d]	1572
19	3-Benzylamino-5,5-dimethyl-2-cyclohexenone	$CDCl_3$	4.7[c]	3434	1589[e]
20	3-Methylamino-5,5-dimethyl-2-cyclohexenone	$CDCl_3$	4.8[c]	3452	1589[e]
21	N-Benzylacetoacetamide	$CDCl_3$	7.2	3360	1670
22	N-Methyl-4,4-dimethyl-3-oxovaleramide	$CDCl_3$ CCl_4	7.2 *h*	3374 3380	1665
23	Phenyl(β-methylamino)vinyl ketone	$CDCl_3$	10.1	*h*	1634
24	8-Hydroxy-1-phenalenone	$CDCl_3$	15.5	2750	1592
25	2-Acetylcyclohexanone	$CDCl_3$ CCl_4	15.8	2670[d]	1610[b] 1608[b]
26	5-Nitrosalicylaldehyde	$CDCl_3$	11.5	. .	1668
27	2-(N-Methylacetimidoyl)-1-naphthol	$CDCl_3$	15.9	2700	*e*
28	2-(N-Methylacetimidoyl)phenol	$CDCl_3$	16.3	2600	*e*
29	1-(N-Methylformimidoyl)-2-naphthol	$CDCl_3$	14.3	2900	*e*
30	1-Hydroxy-2-acetonaphthone	$CDCl_3$	14.0	2810	. .

[a] For both the infrared and p.m.r. spectra. [b] Broad. [c] Extrapolated to infinite dilution. [d] Approximate. [e] Ambiguous assignment. [f] To 1630 cm.$^{-1}$ upon deuteration. [g] Carbonyl (to OH) at 1590 cm.$^{-1}$. [h] Insoluble.

in compounds with a possibility of ready tautomeric proton interchange, such as salicylaldehydes and Schiff bases derived therefrom, the amount of nonaromatic form present in the equilibrium mixture may be considerable, as evident by the large downfield shift of the enolic proton resonance (*vide infra*). The ring current in the nonaromatic tautomer should be much smaller, if it exists at all. In systems such as the ones being studied here, with several hetero atoms adjacent to the aromatic nucleus, the ring current may also be damped by the presence of a large, nonuniform charge distribution both in and adjacent to the ring. These factors would tend to reduce the anisotropy correction from an average of ~0.6 p.p.m. (calculated by Reeves, *et al.*[5]) to a much smaller value. Because of these uncertainties, the anisotropy correction was not used, but it is possible that part of the scatter of the points is due to a variation in the magnitude of the ring current.



In Figure 1, two nonhydrogen-bonded compounds were included, both dimedone derivatives (Table I, **19**, R = H; **20**, R = C_6H_5). The points for these compounds appear to be about 1 p.p.m. below the line of Figure 1. Jackman[11] indicated the anisotropy of the carbonyl bond is of such a magnitude; this could explain the failure of the open-chain compounds to obey the relationship. The same may be true of the two amides (**21** and **22**).

The strong enols from acetylacetone and dibenzoylmethane are of importance in establishing the generality of the correlation. In these enols, the OH stretch is greatly increased in intensity and is shifted below the 3000–2900-cm.$^{-1}$ CH bands.[12,13] Concurrently, the bands become broad and their exact positions are difficult to establish. In Figure 1, the data for several enols are plotted; the infrared data is from Bratož[13];

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(11) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry," Section 7.3, Pergamon Press, Oxford, 1959.

(12) See ref. 4, p. 96.

(13) S. Bratož, D. Hadzi, and G. Rossmy, *Trans. Faraday Soc.*, **52**, 464 (1956)

the p.m.r. data is from Burdett and Rogers[8] and also Hay and Williams.[9] Except for a few compounds, ~3200 cm.$^{-1}$, the fit to the line is excellent. Possibly the correlation line is not straight but curves slightly; additional data could confirm such a change in slope.[14]

The second correlation is that between the carbonyl stretching frequency and the contiguous NH proton resonance signal (Figure 2). The parameters used here result in a major advantage over the previous correlation (Figure 1) involving the NH (or OH) infrared stretching frequency. Usually an amino signal can be accurately located in a p.m.r. spectrum, but this is not true for an enolic hydroxyl or amino stretch in the infrared spectrum, especially when the proton is strongly hydrogen bonded.

The data from several other investigators covering β-diketones and β-keto esters are included in Figure 2. In gathering and combining data for the second line, changes were made which can be conveniently discussed here.

Several of the values for chemical shifts listed by Hay and Williams[9] were replaced by those from ref. 4 and ref. 15, since the latter values were measured in dilute solution in an inert solvent. In all cases the change in resonance position was small. A few β-diketones were added to provide points in the region about 1600 cm.$^{-1}$. These values are entered in Table I and the points are numbered in Figure 2. When the carbonyl band fell below 1600 cm.$^{-1}$, deuteriochloroform was preferred over carbon tetrachloride as the solvent.[16]

Hay commented upon the failure of dibenzoylmethane and benzoylacetone to follow their correlation. Similar values for the spectra were also given by Burdett and Rogers.[8] The infrared spectra of these compounds were rechecked here in both carbon tetrachloride and deuteriochloroform solution. Two strong bands are present in the spectrum of dibenzoylmethane[13]: a "moderately sharp" one at 1600 cm.$^{-1}$ and a much broader and apparently more intense one at 1580 cm.$^{-1}$ (best seen in $CDCl_3$ solution).[16,17] Since aromatic and double-bond frequencies usually appear near 1600 cm.$^{-1}$, the carbonyl is here assigned to 1580 cm.$^{-1}$. The same situation appears true of benzoylacetone. The infrared spectra of the two compounds, however, should be checked in further detail, perhaps with the aid of isotopic substitution.

It was also noted that, if Hunsberger's infrared data[18] for the carbonyl frequencies of *o*-hydroxyacetonaphthones are combined with the p.m.r. data of ref. 15, the results fit the "oxygen" line. The effect of the aromatic ring current in these tautomeric systems again seems unimportant.

The scatter of the points in the Schiff base relationship (Figure 2) is small with the exception of 2-acetyldimedonimine. Since the N-substituted derivatives are normal, the difference is a peculiarity of the amino derivative. The slightly high value for the N-phenyl compound is expected, the aromatic ring current being the cause of the disparity. The open-chain compounds (Table I, **19** and **20**) are considerably off the line.[19] These compounds suggest that the amino group and the double bond effect the carbonyl frequency to a far greater degree than does the presence or absence of an intramolecular hydrogen bond.

In this correlation, the "oxygen" and "nitrogen" compounds differ by about 3.5 p.p.m. or 50 cm.$^{-1}$, but the two lines are parallel. It is interesting that approximately the same difference, namely 50 cm.$^{-1}$, separates the infrared carbonyl frequencies of an amide from that of an aliphatic ester. Although the correlations of the two groups of compounds are not colinear, the response of both systems to increased hydrogen bonding is similar. As pointed out by Burdett and Rogers,[8] the tricarbonyl enols studied by Forsén and Nilsson[7] seem to form a distinct group of their own. However the separate line for the tricarbonyl enol system may also be the result of a sharp inflection in the "oxygen" line at 1560 cm.$^{-1}$.

Discussion

Despite the deviations and exceptions, it is gratifying to see such agreement as in Figure 1. The graph covers nearly 50 compounds with a range of 15 p.p.m. in proton resonance shift and a remarkable 1200 cm.$^{-1}$ in infrared shift. The diversity of compounds is also large. Although Figure 2 is disappointing in that two (or more) lines are present, many compounds are encompassed by each line and a carbonyl shift of over 100 cm.$^{-1}$ is not a small effect.

In the infrared, the NH-"free" infrared stretching frequency differs appreciably from that of the "free" OH. However, Schneider, *et al.*,[20] found that, for a number of hydrides (such as methane, ammonia, and water), the difference between the "free" and "associated" H–Y stretching frequency was related to the proton's hydrogen bond chemical shift. Apparently this proportionality between the two spectroscopic properties of a hydrogen bond is responsible for the agreement of Figure 1.

Reeves, *et al.*,[5] by means of p.m.r. measurements, claimed that $-\Delta H$ for the hydrogen bond in *o*-chlorophenol is 2.35 kcal., in *o*-bromophenol it is 2.14 kcal., and in *o*-iodophenol it is 1.65 kcal. (all in CCl_4 solution). Jones and Watkinson,[21] using infrared techniques, reported for these compounds a $-\Delta H$ of 1.28, 1.86, and 0.99 kcal., respectively (all in C_2Cl_4 solution). Therefore, the data yield about 2 kcal./100 cm.$^{-1}$ infrared hydrogen bond shift (from Figure 1). For intermolecular hydrogen bonds, Gramstad[22] found a shift of about 1.2 kcal./100 cm.$^{-1}$, Joesten and Drago[23] reported 1.6 kcal./100 cm.$^{-1}$, and Jones and Watkinson[21] were higher with a value of 5 kcal./100-cm.$^{-1}$ hydrogen bond shift. From these values, acetylacetone possess a hydrogen bond strength of 10–18 kcal. for a

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(14) Comparing data from several investigators reveals the not too surprising fact that the errors are much larger than their estimates. *At best*, the infrared band positions are good to 10 cm.$^{-1}$ and the p.m.r. positions to 0.1 p.p.m.

(15) G. Dudek, *Spectrochim. Acta*, **19**, 691 (1963).

(16) The approximate location (less than 10% transmittance in an 0.2-mm. cell) of the carbon tetrachloride band is indicated in Figure 2.

(17) See also the assignment of G. S. Hammond, W. G. Borduin, and G. A. Guter, *J. Am. Chem. Soc.*, **81**, 4682 (1959).

(18) I. M. Hunsberger, *ibid.*, **72**, 5626 (1950).

(19) There is an ambiguity in the assignment of the carbonyl in these compounds. The strong 1589-cm.$^{-1}$ band possesses a broad shoulder at ~1610 cm.$^{-1}$. The latter could be the broadened carbonyl stretch underlying the carbon–carbon double-bond frequency. The reassignment would be of no consequence here.

(20) W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.*, **28**, 601 (1958).

(21) D. A. K. Jones and J. G. Watkinson, *J. Chem. Soc.*, 2366 (1964).

(22) T. Gramstad, *Spectrochim. Acta*, **19**, 829 (1963).

(23) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962).

800-cm.$^{-1}$ infrared hydroxyl shift (assuming a linear dependence). This is about the range of the other estimates.[3,4]

Although the thermodynamic data is not encouraging, the purpose in presenting it was to provide some numerical background for the correlations of Figures 1 and 2. Powell and West[24] recently commented on the renewed interest in the validity of the Badger–Bauer relationship[25] between $-\Delta H$ and $\Delta\nu$. When more information on this relationship is available, the thermodynamics of Figure 1 will be better understood. It should be remembered, however, that the validity of Figures 1 and 2 do not depend upon the validity of the Badger–Bauer relationship.

It is claimed that the electron density on carbon in hydrocarbons is related to the chemical shift on the adjacent proton by $\delta_{\text{p.p.m.}} = 10.6\rho$.[26] In the case of the strongest hydrogen bonds, which have a 15-p.p.m. chemical shift, either the factor for oxygen is larger than 10.6 or else other deshielding mechanisms are involved. The electron redistributions which alter the strength of the hydrogen bond by over 10 kcal. apparently weaken the bond and deshield the proton simultaneously, and do so over a remarkably large range of electronic interactions.

From the correlations, it is seen that the chemical shift of the acidic proton is an excellent guide to the extent of tautomeric interaction and resulting hydrogen bonding. According to Figures 1 and 2, the hydrogen bonding increases from the β-amino α,β-unsaturated esters to the β-amino α,β-unsaturated ketones to the β-amino α,β-unsaturated diketones which have the strongest hydrogen bonds. This order is expected for the system in terms of ease of tautomeric proton interchange. Here, as in the naphthalene Schiff bases,[1] the greater the ease of tautomeric proton interchange, the stronger the hydrogen bond.

Since strongly interacting hydroxyl and carbonyl bands are difficult to locate in the infrared spectrum, a proton resonance appearing at low fields can be the most convenient diagnostic tool for tautomeric systems. The only common interfering band will be from carboxylic acids (most likely dimeric) which appear about δ = 10–13 p.p.m.[27] When the range of validity of the Badger–Bauer relationship is better understood, not only will tautomeric systems be readily identified by their chemical shifts, but also an approximate ΔH for the hydrogen bonds will be obtained.

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(24) D. Powell and R. West, *Spectrochim. Acta*, **20**, 983 (1964).

(25) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937); R. M. Badger, *ibid.*, **8**, 288 (1940).

(26) H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961).

(27) N. S. Bhacia, L. F. Johnson, and J. N. Shoolery, "Varian Spectra Catalog," Vol. I, Varian Associates, Palo Alto, Calif., 1962, Group 12, Table II.

Application of the Hammett Equation to Nonaromatic Unsaturated Systems. III. Dipole Moments of *trans*-Vinylene and Vinylidene Sets

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Dipole moments of *trans*-vinylene ($\underset{/}{\mathrm{C}}{=}\overset{/}{\mathrm{C}}$), vinylidene (C=C<) and acetylene (—C≡C—) sets were correlated successfully with the Hammett equation. *trans*-Vinylene and acetylene sets gave best results with σ_p, vinylidene sets with σ_m. The magnitude of ρ appears to be independent of the nature of the group to which the substituent is attached.

We have for some time been engaged in the extension of the Hammett equation (shown in eq. 1 below),[1] to nonaromatic unsaturated systems. Equation 1 has been found applicable to rate and equilibrium constants for a number of *trans*-vinylene sets.[2,3] It seemed of interest to examine the extension of eq. 1 to physical properties which are a function of substituent effects. Such a property is the dipole moment.

$$Q_{\mathrm{X}} = \rho\sigma_{\mathrm{X}} + Q_{\mathrm{H}} \qquad (1)$$

The first attempt to correlate dipole moments with substituent constants was that of Taft,[1] who reported the correlation of the moments of alkyl cyanides, chlorides, iodides, and tertiary amines with eq. 1 using σ^*-constants. Kross and Fassel[4] have reported correlation of the moments of *para*-substituted nitrobenzenes with eq. 1 using the σ_p-constants.

Rao, Wohl, and Williams[5] have studied the correlation of dipole moments of disubstituted benzenes with eq. 1 and of monosubstituted benzenes with eq. 2. Van Beek[6] has examined the correlation of moments for

$$\mu_{\mathrm{X}} = \rho|\sigma_{p}.\mathrm{x}| \qquad (2)$$

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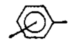
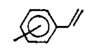
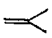
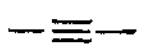
(1) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184; H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 565; V. Palm, *Russ. Chem. Rev.*, **31**, 471 (1961); P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(2) We will find it convenient to define these names of diradical groups.

trans-vinylene		phenylene	
cis-vinylene		styrylene	
vinylidene		*trans*-cyclopropylene	
acetylene		cyclopropylidene	

(3) M. Charton and H. Meislich, *J. Am. Chem. Soc.*, **80**, 5940 (1958); J. Hine and W. C. Bailey, Jr., *ibid.*, **81**, 2075 (1959); J. Hine and W. C. Bailey, Jr., *J. Org. Chem.*, **26**, 2098 (1961); P. B. D. de la Mare, *J. Chem. Soc.*, 3823 (1960).

(4) R. D. Kross and V. A. Fassel, *J. Am. Chem. Soc.*, **78**, 4225 (1956).

(5) C. N. R. Rao, W. H. Wohl, and E. J. Williams, *Can. J. Chem.*, **35**, 1575 (1957).

(6) L. K. H. van Beek, *Rec. trav. chim.*, **76**, 729 (1957).