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.

Acknowledgment.—We wish to thank Dr. Emily Pitcher Dudek for several compounds and for helpful discussions and also the Milton Fund of Harvard University for generous financial support.

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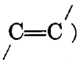
Dipole moments of *trans*-vinylene ( $\underset{/}{C}{=}\overset{/}{C}$), vinylidene (C=C<) and acetylene (—C≡C—) sets were correlated successfully with the Hammett equation. *trans*-Vinylene and acetylene sets gave best results with σ_p, vinylidene sets with σ_m. The magnitude of ρ appears to be independent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

$$Q_X = \rho\sigma_X + Q_H \qquad (1)$$

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

$$\mu_X = \rho|\sigma_{p \cdot X}| \qquad (2)$$

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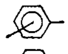
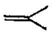
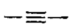
[1] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184; H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 565; V. Palm, *Russ. Chem. Rev.*,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

$$\log \frac{\mu_X}{\mu_H} = \rho\sigma_X \qquad (3)$$

disubstituted benzenes with eq. 3. Exner,[7] in a comprehensive discussion of the correlation of dipole moments of substituted alkanes and benzenes with substituent constants, has pointed out that eq. 3 must be inadequate as it fails for $\mu_X = 0$. Exner has proposed eq. 4 for the correlation of moments, where d_I is

$$\vec{\mu}_X = \vec{\rho_I d}_{I,X}\sigma_{I,X} + \vec{\rho_R d}_{R,X}\sigma_{R,X}^{\pm} + \vec{\mu}_0 \qquad (4)$$

the distance between charges due to the inductive effect and d_R the distance between charges due to "polar conjugation," also, $\sigma_R^{\pm}$ signifies the use of σ_R^{+} for +R substituents and σ_R^{-} for −R substituents. This relationship is based on the decomposition of μ into localized (μ_λ) and delocalized (μ_δ) moments, a concept

$$\mu = \mu_\lambda + \mu_\delta \qquad (5)$$

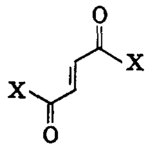
which is inherent in the mesomeric moments of Sutton.

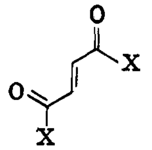
$$\mu_m = \mu_{ArX} - \mu_{AlkX} \qquad (6)$$

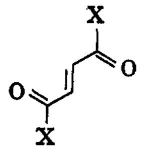
Sharp and Walker[9] have reported "good linear plots" of dipole moments of 3- or 4-substituted pyridines, pyridine N-oxides, and nitrobenzenes against $\mu_X - \mu_H$.

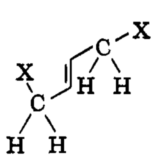
We have previously examined the application of eq. 1 to dipole moments of substituted acetylenes,[10] nitriles,[10] and cycloalkanes.[11] To determine the applicability of the Hammett equation to dipole moments of ethylenic systems, data taken from the literature were correlated with the σ_I-, σ_m-, and σ_p-constants as described by Jaffé.[1] The *trans*-vinylene sets examined include substituted ethylenes, 1-substituted propenes, 2′-substituted styrenes, 2-substituted bromoethylenes, 2-substituted chloroethylenes, 1-substituted 1-buten-3-ones, 3-substituted acrylonitriles, and 1-substituted 1,3-butadienes. Some vinylidene sets have also been studied, these include 2-substituted propenes, 1-substituted styrenes, and 2-substituted 1,3-butadienes. We have also examined for purposes of comparison, substituted allenes and some additional sets of acetylenes.

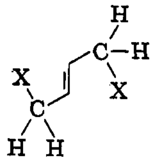
The data used are given in Table I. When available, moments determined from the Stark effect were used; otherwise values determined by other methods in the gas phase or in benzene solution were used. The σ_m- and σ_p-constants used are from the compilation of McDaniel and Brown[12] when possible. The σ_I-constants are generally from our compilation.[13] Substituent constants from other sources are given in Table II. Results of the correlations are given in Table III. Sets designated "a" include all of the data for each set given in Table I, sets designated "b" include only those substituents which are symmetric about the axis of the substituent–carbon bond. For these symmetric substituents, the group moment of the substituent lies on the substituent–carbon bond axis. It was thought that, as these substituents are free from conformational isomerism which might seriously affect the correlation, a comparison of the correlations obtained from sets "a" and sets "b" would provide a rough idea of the significance of conformation in determining dipole moments. Evidence that conformational effects are important may be obtained by comparing moments of *trans*-1,2-disubstituted ethylenes or of 1,2-disubstituted acetylenes with symmetric substituents against those with substituents capable of existing in conformations differing in dipole moment (Table IV). Thus, for example, compounds of type I are capable of existing in three planar conformations as shown below, and may also possibly exist in nonplanar conformations.[14] Compounds of the type II, may also exist in several conformations some of which are shown below. It should be noted that the correlations were made after the assignment of signs to the moments accounting for the direction of the moments. All sets studied may be written in the form XGY where Y is a constant substituent. For *trans*-vinylene and acetylene sets it was assumed that, for X = Y in the absence of conformational isomers, $\mu_{XY} = 0$. Those members of the set for which $\sigma_X > \sigma_Y$ were considered positive; those members for which $\sigma_X < \sigma_Y$ were considered negative. For the vinylidene sets those members of the set for which $|\sigma_X| > |\sigma_Y|$ were considered to have the sign of σ_X, those members for which $|\sigma_X| < |\sigma_Y|$ were considered to have the same sign as that of σ_Y.

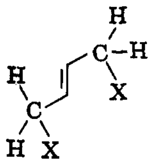

Ia
s-trans, s-trans


Ib
s-cis, s-trans


Ic
s-cis, s-cis


IIa

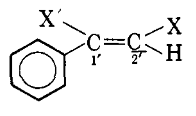

IIb


IIc

Results

trans-Vinylene Sets.—The results obtained, particularly those for the extensive sets, substituted ethylenes (1), 2′-substituted styrenes (2, IIIa), and 1-substituted propenes (3), are in accord with best correlation by σ_p. The "*t*" tests indicate that correlation with σ_p is significant at the 99.9% confidence level for sets 1a, 1b, 2a, 2b, 3a, 3b, 5b, 7a, and 8. In set 5c, the value for X = OMe was omitted since the value seemed dubious. Set 5b was also recalculated using −0.11 as the value for $\sigma_{m\text{-}SiMe_3}$, calculated from eq. 7. This was

$$\sigma_m = \frac{2\sigma_I + \sigma_p}{3} \qquad (7)$$


IIIa, X′ = H; set 2
b, X = H; set 10

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(7) O. Exner, *Collection Czech. Chem. Commun.*, **25**, 642 (1960).
(8) L. E. Sutton, *Proc. Roy. Soc.* (London), **A133**, 66j (1931).
(9) A. N. Sharpe and S. Walker, *J. Chem. Soc.*, 4522 (1961).
(10) M. Charton, *J. Org. Chem.*, **26**, 735 (1961).
(11) M. Charton, *J. Chem. Soc.*, 1205 (1964).
(12) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).
(13) M. Charton, *ibid.*, **29**, 1222 (1964).
(14) C. Beguin and T. Gaumann, *Helv. Chim. Acta*, **41**, 1376 (1958).

TABLE I

DIPOLE MOMENTS USED IN CORRELATIONS[a]

	Set[b]								
X[c]	1	2	3	4	5	6	7	8	9
H°	0	0.13	0.364	1.417	1.452	3.00	3.89	0	0.364
F°	1.427	1.36[d]	1.85						1.60
Cl°	1.44	1.41	1.97	0	0				1.69
Br°	1.417	1.56[d]	1.69	0	0				1.51
I°	1.27			0.39					
Me°	0.364	0.72	0	1.69	1.97	3.20	4.53	0.68	0.503
Et	0.37								0.50
Pr	0.37								
Bu	0.34								
$BuCH_2$									
t-Bu°									
C_2H_3	0		0.68				3.90	0.2	0.38
Ph°	0.13	0	0.72	1.41	1.41	3.31	4.17		0.76
C_2H	0.43[e]		0.94						
CH_2Cl	1.08	1.92			1.73				
CH_2Br	1.82								
CH_2I	1.62								
CF_3°	2.45								
OMe					1.6[f]				
OEt	1.27	1.69							
OBu	1.25								
OAc	1.79								
SEt	1.36[g]								
CHO	3.11	3.74	3.50						2.68
Ac	3.00	3.31	3.20						2.74
CO_2H		1.31	2.13						1.65
$CONH_2$		3.64							
CO_2Me		1.95							1.97
CO_2Et		1.86							2.15
CN°	3.89	4.17	4.53				0	3.90	3.69
$MeSO_2$	4.82	5.27							
$PhSO_2$	5.29	5.93							
NO_2°	3.44	4.54							
Me_3Si	0				1.71				
Me_2N						5.10			
Bz		3.03							

	Set[b]								
	10	11	12	13	14	15	16	17	18
H°	0.13	0	0.20	0.72	0.75	0			0
F°		1.417[h]							1.66
Cl°	1.93	1.43[i]		1.11					1.72
Br°		1.41[i]	1.50	0.86					1.72
I°				0.55					1.71
Me°	0.76	0.38	0.401						0.37
Et		0.45							
Pr									
Bu						1.09	0.76		
$BuCH_2$						1.06	0.81		
t-Bu°									0.70
C_2H_3				0.27	0.57				
Ph°	0.5			0		0.86	0.55		
C_2H									
CH_2Cl			2.02		2.17				
CH_2Br									
CH_2I									
CF_3									2.86
OMe					1.56				
OEt					1.69				
OBu									
OAc									
SEt					1.67				
CHO				3.39					
Ac				3.26					
CO_2H				2.31	2.14				
$CONH_2$									
CO_2Me									
CO_2Et				2.21					

TABLE I (*Continued*)

	Set^b								
X^c	10	11	12	13	14	15	16	17	18
CN$^\circ$				4.55		3.88	4.59		4.14
$MeSO_2$									
$PhSO_2$									
$NO_2$$^\circ$									4.22
Me_3Si									
Me_2N									
Bz									

[a] All data from A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963; unless otherwise noted. [b] 1, substituted ethylenes; 2, *trans*-2′-substituted styrenes; 3, *trans*-3-substituted propenes; 4, 2-substituted 1-bromoethylenes; 5, 2-substituted 1-chloroethylenes; 6, 1-substituted 1-buten-3-ones; 7, 3-substituted acrylonitriles; 8, 1-substituted 1,3-butadienes; 9, 2-substituted propenes; 10, 1′-substituted styrenes; 11, 2-substituted 1,3-butadienes; 12, substituted allenes; 13, 1-substituted 2-phenylacetylenes; 14, 1-substituted propynes; 15, 1-substituted 2-bromoacetylenes; 16, 1-substituted 2-iodoacetylenes; 17, 3-substituted propiolnitriles; and 18, substituted benzenes. [c] Substituents bearing a superscript ° are symmetric substituents used in the "b" sets of Table II. [d] V. N. Vasileva, K. A. Kocheskov, T. V. Talalaeva, E. M. Panov, G. V. Kazennikova, R. S. Sorokina, and O. P. Petrii, *Dokl. Akad. Nauk. SSSR*, **143**, 844 (1962). [e] G. A. Sobolev, A. M. Shcherbakov, and P. A. Akishin, *Opt. i Spektroskopiya*, **12**, 147 (1962). [f] Y. Mikawa, S. Morita, and S. Tsunokawa, *Bull. Chem. Soc. Japan*, **35**, 1109 (1962). [g] W. Drenth, G. L. Hekkert, and B. G. Zwanenburg, *Rec. trav. chim.*, **81**, 313 (1962). [h] D. R. Lide, Jr., *J. Chem. Phys.*, **37**, 2074 (1963). [i] A. A. Petrov, K. S. Mingaleva, and I. A. Maretina, *Tr. Leningr. Tekhnol. Inst. im. Lensoveta*, **60**, 75 (1960).

TABLE II
SUBSTITUENT CONSTANTS[a]

X	σ_I	σ_m	σ_p	X	σ_I	σ_m	σ_p
Pr		-0.07^b		Bu		-0.08^b	
$BuCH_2$		-0.08^b	-0.15^c	C_2H		0.32^b	0.270^g
CHO	0.36^d		0.42^e	$PhSO_2$		0.61^b	0.70^h
SEt		0.18^b		C_2H_3		0.05^b	-0.02^i
OAc	0.43^d			CH_2Cl		0.14^b	0.12^f
CH_2Br		0.16^b	0.12^f	CH_2I		0.14^b	0.09^f
$CONH_2$			0.36^e	Bz	0.29^d	0.343^e	
CN		0.615^e					

[a] From sources other than ref. 12 and 13. [b] From eq. 1. [c] From the equation $\sigma_{p\text{-XCH}_2} = m\sigma_{p\text{-X}} + n$. [d] From the equation $\sigma_I = (3\sigma_m - \sigma_p)/2$; ref. 15. [e] M. Charton, *J. Org. Chem.*, **28**, 3121 (1963), and references therein. [f] O. Exner and J. Jonas, *Collection Czech. Chem. Commun.*, **27**, 2296 (1962). [g] Calculated from the ionization constant of $HC_2CH{=}CHCO_2H$; see ref. 3. [h] H. H. Szmant and G. Suld, *J. Am. Chem. Soc.*, **78**, 3400 (1956). [i] From the equation $\sigma_{p\text{-XCH=CH}} = n\sigma_{p\text{-X}} + d$.

done since the value -0.04 given by Brown and McDaniel is less than σ_I or σ_p although it should lie between them. The results obtained from the recalculation are $\rho = 4.73$, $r = 0.927$, $s = 0.363$, $t = 4.953$, and $Q_H = -1.88$. Thus, set 5 gives best correlation with σ_p.

Vinylidene Sets.—The quantity to be correlated in these sets of structure XGY is not the observed moment μ_{obsd} but rather the moment of the X substituent μ_X. From the law of cosines, one may obtain eq. 8.

$$\mu_X = -\mu_Y \cos\theta \pm \sqrt{\mu_{\text{obsd}}^2 - \sin^2\theta\,\mu_Y^2} \tag{8}$$

For vinylidene sets, θ is almost 120° and

$$\mu_X = 0.5\,\mu_Y \pm \sqrt{\mu_{\text{obsd}}^2 - 0.75\,\mu_Y^2} \tag{9}$$

For Y with small moments, however,

$$\mu_X = \mu_{\text{osbd}} \tag{10}$$

The three vinylidene sets considered have constant substituents Y, with small moments [Y = Me, Ph (IIIb), C_2H_3]. The correlations have therefore been made on the basis of eq. 10. Good correlations are obtained with σ_m.

Acetylene Sets.—To provide further information on the variation of ρ with constant substituent Y, and the variation of ρ with G, we have examined several additional acetylenic sets, including 1-substituted phenylacetylenes (13), 1-substituted propynes (14), 1-substituted 2-bromoacetylenes (15), 1-substituted 2-iodoacetylenes (16), and 3-substituted propiolnitriles (17). For all sets except the propiolnitriles (which do not correlate at all with the σ-constants) good results are obtained with σ_p. The moments reported for 1-bromo- and 1-iodopropiolnitrile seem rather large. This may possibly be due to donor–acceptor complex formation between the 3-halopropiolnitriles and the benzene solvent.[16] If this is true, sets 15 and 16 are unreliable. The poor correlation in set 14 is probably due to conformational isomerism. All substituents in the set other than H are capable of this.

Allene Set.—What little data are available suggest that the best correlation is obtained with σ_p, but no definite conclusion can be drawn at present. Correlation of the set after deleting the CH_2Cl group gives best results with σ_m.

Significance of Conformational Isomerism.—The results obtained for the "b" sets including only symmetric substituents are generally better and at least as good as those obtained for "a" set . Conformational isomerism appears to be one of the factors which causes deviations from the correlation with the Hammett equation. Another factor which may be of importance as a cause of deviations is the formation of donor–acceptor complexes in solution. The use of moments determined in the vapor phase would remove this difficulty.

Discussion

Composition of Electrical Effects.—The results obtained for *trans*-vinylene and acetylene sets are in accord with previous findings. The electrical effects of substituents in these systems have a composition comparable to that of substituents in the *para* position of benzene. Thus, if we consider the electrical effects of these substituents to be composed of a localized effect σ_I and a delocalized effect σ_R, we may represent the substituent effect in the form

$$\sigma = \lambda\sigma_I + \delta\sigma_R \tag{11}$$

and describe the composition of the substituent effect by defining[17] as shown in eq. 12, p. 556. The

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(15) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

(16) S. Walker in "Physical Methods in Heterocyclic Chemistry," Vol. I, A. Katritzky, Ed., Academic Press, Inc., New York, N. Y., 1963, p. 189.

(17) M. Charton, *J. Am. Chem. Soc.*, **86**, 2033 (1964).

TABLE III

RESULTS OF CORRELATIONS

Set		ρ	r^a	s^b	t^c	Q_H	n^d
1a	I	5.44	0.800	0.948	6.668^e	0.118	27
	m	5.83	0.881	0.763	9.287^e	0.156	
	p	5.22	0.935	0.635	13.18^e	0.425	
1b	I	4.49	0.849	0.765	5.075^e	−0.101	12
	m	5.06	0.929	0.534	7.967^e	−0.189	
	p	4.34	0.935	0.512	8.348^e	0.286	
2a	I	6.81	0.741	1.25	4.544^e	0.0925	19
	m	7.13	0.844	0.996	6.499^e	0.0594	
	p	6.22	0.918	0.828	9.576^e	0.235	
2b	I	6.03	0.869	1.02	4.298^f	−0.478	8
	m	6.48	0.967	0.521	9.356^e	−0.403	
	p	5.62	0.987	0.334	14.88^e	0.306	
3a	I	4.89	0.743	0.968	3.508^f	0.370	12
	m	5.91	0.881	0.684	5.896^e	0.220	
	p	4.96	0.911	0.598	6.967^e	0.713	
3b	I	4.68	0.823	0.869	3.544^g	0.0921	8
	m	5.49	0.905	0.650	5.218^f	0.116	
	p	5.11	0.910	0.632	5.392^f	0.696	
4	I	3.23	0.988	0.134	12.74^e	−1.55	6
	m	3.64	0.986	0.143	11.92^e	−1.49	
	p	5.00	0.970	0.249	7.953^f	−1.14	
5a	I	3.04	0.864	0.424	4.213^f	−1.71	8
	m	4.10	0.924	0.321	5.940^f	−1.73	
	p	3.40	0.780	0.528	3.057^h	−1.26	
5b	I	3.27	0.975	0.216	8.754^e	−1.55	6
	m	4.15	0.995	0.0967	19.98^e	−1.58	
	p	5.28	0.988	0.151	12.66^e	−1.27	
5c	I	3.25	0.928	0.339	5.555^f	−1.64	7
	m	4.09	0.939	0.373	6.096^f	−1.68	
	p	4.70	0.861	0.461	3.792^g	−1.40	
6	I	−9.22	0.808	0.702	1.943^j	−3.77	4
	m	7.22	0.866	0.597	2.445^j	−3.25	
	p	2.42	0.977	0.253	6.517^h	−3.04	
7	I	7.24	0.978	0.449	8.120^f	−4.34	5
	m	6.70	0.991	0.293	12.61^f	−4.18	
	p	5.69	0.994	0.233	15.92^e	−3.82	
8	I	7.11	0.996	0.229	15.56^f	−0.247	4
	m	6.56	0.999	0.114	31.23^f	−0.122	
	p	5.71	0.996	0.201	18.17^f	0.0842	
9a	I	5.03	0.826	0.737	5.279^e	−0.0508	15
	m	5.64	0.919	0.515	8.415^e	−0.103	
	p	4.99	0.916	0.589	8.212^e	0.0653	
9b	I	4.70	0.872	0.709	4.364^f	−0.306	8
	m	5.31	0.923	0.558	5.870^f	−0.228	
	p	5.24	0.882	0.761	4.594^f	0.0934	
10	I	4.59	0.964	0.364	5.129^h	−0.146	4
	m	5.58	0.974	0.311	6.057^h	−0.0581	
	p	7.08	0.944	0.496	4.038^i	0.0518	
11	I	3.30	0.992	0.134	15.55^e	−0.166	6
	m	4.10	0.995	0.0998	21.00^e	−0.0864	
	p	4.91	0.917	0.420	4.593^g	0.407	
12	I	3.75	0.725	0.981	1.488^j	0.264	4
	m	4.33	0.757	0.931	1.638^j	0.279	
	p	5.82	0.860	0.726	2.387^j	0.515	
13a	I	6.21	0.672	1.29	2.724^h	−0.308	11
	m	7.33	0.830	0.970	4.458^f	−0.607	
	p	6.25	0.924	0.628	7.229^e	−0.108	
13b	I	6.32	0.790	1.26	2.578^i	−1.04	6
	m	7.02	0.879	0.977	3.687^h	−1.04	
	p	6.10	0.909	0.761	4.368^g	−0.104	
14	I	7.44	0.841	0.620	3.472^g	−0.142	7
	m	6.38	0.724	0.790	2.348^i	0.422	
	p	6.04	0.839	1.03	3.444^g	0.139	
15	I	7.61	0.979	0.484	8.285^f	−0.395	5
	m	6.86	0.979	0.480	8.345^f	−0.189	
	p	6.17	0.989	0.367	11.43^f	−0.244	
16	I	8.64	0.9996	0.0779	56.54^e	−0.404	4
	m	7.68	0.9988	0.155	28.39^f	−0.0964	
	p	6.74	0.991	0.442	10.29^f	0.0463	
17	I	−0.214	0.123	0.427	0.2483^j	4.15	6
	m	−0.159	0.0874	0.428	0.1755^j	4.17	
	p	−0.0962	0.0461	0.430	0.0923^j	4.18	
18	p	5.01	0.975	0.405	12.43^e	0.492	10

[a] Correlation coefficient. [b] Standard deviation. [c] "Student t" test. [d] Number of points in the set. [e] 99.9% significance level (s.l.). [f] 99% s.l. [g] 98% s.l. [h] 95% s.l. [i] 90% s.l. [j] Less than 90% s.l.

TABLE IV

DIPOLE MOMENTS OF *trans*-1,2-DISUBSTITUTED ETHYLENES AND 1,2-DISUBSTITUTED ACETYLENES

Symmetrical substituents		Asymmetrical substituents	
X	μ	X	μ
Ethylenes			
Cl	0	Vinyl	0.2
Br	0	CH_2Br	1.63
I	0	CO_2H	2.45
Me	0	CO_2Me	2.25
Ph	0	Ac	2.85
CN	0	CH_2OH	2.47
Me_3Si	0	Et	0
		Pr	0
Acetylenes			
Ph	0	CH_2Cl	2.08
Bu	0	CH_2OH	2.63
$BuCH_2$	0	C_2H_3	0–0.2

$$\epsilon = \frac{\delta}{\lambda} \tag{12}$$

values for ϵ of various groups G of sets XGY are given in Table V.

Results obtained for vinylidene sets show that the electrical effect of a vinylidene substituent is comparable to that of a substituent in the *meta* position of benzene.

TABLE V

VALUES OF ϵ

G	ϵ	G	ϵ
trans-Vinylene	1^a	*o*-Phenylene	1^c
Acetylene	1^a	*m*-Phenylene	$0.33–0.5^c$
Vinylidene	0.33–0.5	*p*-Phenylene	1^c
trans-Cyclopropylene	$0.33–0.5^b$	2-Pyridyl	$0–0.3^c$
Cyclopropylidene	1^b	3-Pyridyl	$0.33–0.5^c$
		4-Pyridyl	1^c

[a] This work. [b] Ref. 11. [c] Ref. 16.

ρ as a Function of G.—For correlations of rate and equilibrium data of XGY, ρ has been found to be highly dependent on G. It is convenient to describe the variation of ρ with G in terms of γ, where[10]

$$\gamma = \frac{\rho_G}{\rho_{G^\circ}} \tag{13}$$

In accord with previous usage we have chosen the phenylene group as G°. To provide a value for ρ_{G°, dipole moments of substituted benzenes in the vapor phase were correlated with σ_p. Only symmetrical substituents were included in the set. The data used are given in Table I, the results in Table III. Values of γ are given in Table VI. These values seem to

TABLE VI

VALUES OF γ

G	Dipole moments of XGH[a]	Ionization constants of $XGCO_2H$[b]
p-Phenylene	1	1
trans-Vinylene	0.87	2.23
Acetylene	0.94	1.89
Cyclopropylidene	1.05	5.36

[a] This work. [b] Ref. 11.

show that, for correlations of dipole moments, ρ is independent of G. The result is surprising. A dipole moment may be defined as the product of the distance between two charges and the magnitude of one of them. Thus, ρ would be expected to be a function of the distance separating the charges. Then, as all values of ρ obtained are about the same, the distance must be the same in all of the systems studied. This can be rationalized if the distance involved is the carbon–substituent bond length, which would have about the same average value for the systems considered.

The Variation of ρ with Y.—We have shown for equilibrium and rate data that for sets XGY where Y is a constant substituent, eq. 14 is obeyed.[18] Correlation

$$\rho_Y = m\sigma_Y + c \qquad (14)$$

of ρ for sets 1b, 2b, 3b, 4, 5b, and 7 with σ_p gave $r = 0.464$, $s = 0.487$, $t = 1.047$, and $m = 0.783$. Thus ρ-values for dipole moment correlations of *trans*-vinylene sets do not appear to follow eq. 14. Due to the uncertainty regarding sets 15 and 16, and the lack of correlation in set 17, no conclusion can be reached concerning the applicability of eq. 14 to acetylenic sets.

[18] M. Charton, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963, p. 46T.

Application of the Hammett Equation to Nonaromatic Unsaturated Systems. IV. Vinylidene and Heterovinylidene Sets

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The Hammett equation has been extended to the correlation of pK_a values of vinylidene (C=C<) and heterovinylidene (Z=C<) sets, including 2-substituted acrylic acids, 2′-substituted *cis*-cinnamic acids, 2′-substituted *trans*-cinnamic acids, substituted carbonylacetic acids, substituted carbonylpropanoic acids, and *anti*-substituted oximinocarboxylic acids. The σ_m-constants are preferred for correlation. The electrical effect of a vinylidene substituent is largely a localized electrostatic effect with a small but apparently significant resonance contribution. Sets bearing a constant *cis*-vinylene (∖C=C∕) substituent are more sensitive to vinylidene substituent effects than those bearing a constant *trans*-vinylene substituent. Vinylidene sets are very much more sensitive to substituent effects than are *trans*-vinylene sets.

We have for some time been interested in structure–reactivity relationships among nonaromatic π-bonded systems. In particular, we have considered the extension of the Hammett equation[1] to these systems.

$$Q_X = \rho\sigma_X + Q_H \qquad (1)$$

trans-Vinylene,[2,3] acetylene,[4] and cyclopropylidene[5] sets have been reported to be correlated by eq. 1 using the σ_p-constants. *trans*-Cyclopropylene sets are said to be correlated by the σ_m-constants.[5] It seemed of interest to extend those observations to vinylidene sets, I. Data from the literature for four vinylidene sets have therefore been correlated with the Hammett equation as described by Jaffé.[1] The correlations were made with the σ_I-, σ_m-, and σ_p-substituent constants in order to determine the nature of the electrical effect of vinylidene substituents. The sets studied are 2-substituted acrylic acids (1) (I, $R^1 = R^2 = H$); *cis*-2′-substituted cinnamic acids (2) (I, $R^1 = H, R^2 = Ph$); *trans*-2′-substituted cinnamic acids (3) (I, $R^1 = Ph, R^2 = H$); and 2-substituted 3,3-dimethylacrylic acids (4) (I, $R^1 = R^2 = Me$). Data used in the correlations are given in Table I. The σ_m- and σ_p-constants used are generally from the compilations of McDaniel and Brown[6]; the σ_I-constants are from our recent compilation.[7] Substituent constants from sources other than those cited above are given in Table II.

We have also examined several heterovinylidene sets in which the CR^1R^2 group in I is replaced by O (II) or NOH (III). These sets include substituted carbonylacetic acids (5) (II, $n = 1$); substituted carbonylpropanoic acids (6) (II, $n = 2$); substituted carbonylbutanoic acids (7) (II, $n = 3$); substituted carbonylpentanoic acids (8) (II, $n = 4$); and substituted oximinocarboxylic acids (9) (III). Data for these sets are also given in Table I. Data for all sets are taken from

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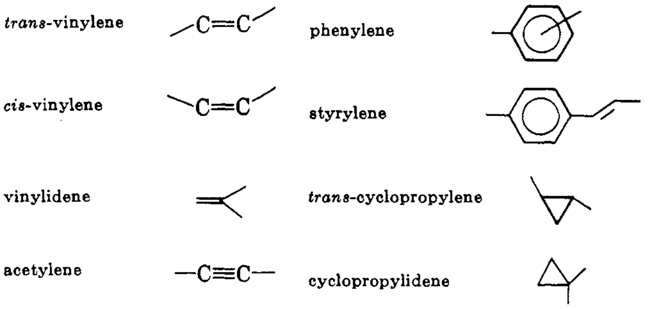
[1] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940; H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); V. Palm, *Russ. Chem. Rev.*, **31**, 471 (1961); P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

[2] We will find it convenient to define the following names of diradical groups.



[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).

[4] M. Charton, *ibid.*, **26**, 735 (1961).

[5] M. Charton, *J. Chem. Soc.*, 1205 (1964).

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

[7] M. Charton, *ibid.*, **29**, 1222 (1964).