

Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. XV.¹ Monosubstituted Ethylenes²

A. R. Katritzky, R. F. Pinzelli, M. V. Sinnott, and R. D. Topsom

Contribution from the School of Chemical Sciences, University of East Anglia, Norwich England, and the School of Physical Sciences, La Trobe University, Melbourne, Australia. Received January 14, 1970

Abstract: Integrated intensities for the $\nu_{C=C}$ mode of 62 monosubstituted ethylenes are tabulated, together with σ_R° values for the substituents, derived by the relation: $\sigma_R^\circ = [(A - 80)/27,100]^{1/2}$. The resulting σ_R° (irE) values are in good agreement with the corresponding σ_R° (irPh) values from the integrated intensities of monosubstituted benzenes, but are more reliable for values of small magnitude.

The study of electronic interactions in aromatic species has been the subject of much attention.³ The major approaches to the effect of a substituent on a benzene ring have been derived either from the Hammett equation or from MO treatment. The separation of Hammett substituent constants (σ) into inductive field (σ_I) and resonance components (σ_R) by Taft⁴ has proved fruitful; in eq 1 the σ_I component is treated as a constant, but σ_R changes when variable amounts of direct resonance interaction with the reaction site are involved.

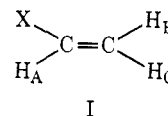
$$\sigma = \sigma_I + \sigma_R \quad (1)$$

For cases where no additional resonance interaction occurs over that normally found between the substituent and the benzene ring, the resonance component is denoted σ_R° .

The quantities σ_I and σ_R° measure the tendency of a substituent to interact, and they should be applicable to other classes of compounds in addition to benzenes. Indeed, the relationship of σ_I to inductive constants derived from aliphatic systems, such as σ^* is well known. However, much less attention has been given to intramolecular electrical interaction in substituted ethylenes. In particular it is not evident if the tendency of a substituent to conjugate with a benzene ring, as measured by its σ_R° value, is also indicative of its conjugation with a carbon-carbon double bond. The σ_R° values for substituents attached to benzene can be obtained⁵ from nmr and infrared measurements as well as from reaction rate and equilibrium data and we first briefly consider analogous information on substituted ethylenes.

A limited amount of work has been done on the acidities of substituted acrylic acids.⁶ The pK_a values of the trans acids give a good linear Hammett plot against normal aromatic para-substituent constants. This suggests that the substituents conjugate with the double bond in an analogous way to that when they are substituted in benzene. Similar results are found⁷

for the rates of esterification of trans-substituted acrylic acids.



The pmr spectra of substituted ethylenes (I) also provide⁸ information about electron densities. Thus the quantity $\delta_A - 1/2(\delta_B + \delta_C)$, where δ is the substituent chemical shift, has been shown⁹ to follow Taft's resonance parameter¹⁰ for the substituent X. The shifts of protons B and C can also be related to the group dipole moment of X^{8,11} or to Hammett σ constants.¹² A similar relationship holds¹² for 1,2-trans-disubstituted ethylenes where one substituent is invariant.

The geminal proton-proton coupling constants seem to give a measure of the substituent effect^{8,13} and should¹⁴ be capable of giving information of π -electron densities. Changes in vicinal proton-proton coupling constants are said¹⁵ to be dominated by σ electron effects. The trans J_{HH} values have also been suggested to depend linearly on the substituent electronegativity in mono- and 1,2-disubstituted¹⁶ ethylenes.

Very little work⁸ has been done on ¹³C and ¹⁹F shifts, both of which have proved very useful probes in the investigation^{3,5} of aromatic systems. α ¹³C-H coupling constants in monosubstituted ethylenes do, however, correlate linearly with those of the corresponding monosubstituted methanes¹⁷ which suggest that they would provide little guide to π -electron effects. The β ¹³C-H coupling values seem¹⁷ to be very little affected by change in substituent.

There have been a number of results published on dipole moments¹⁸ and ultraviolet spectra^{19,20} which

(7) W. C. Bailey and J. Hine, *ibid.*, **81**, 2075 (1959).

(8) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, Oxford, 1966.

(9) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

(10) R. W. Taft, *J. Amer. Chem. Soc.*, **79**, 1045 (1957).

(11) J. H. Goldstein, L. Mandell, and G. S. Reddy, *ibid.*, **83**, 1300 (1961).

(12) J. Niwa, *Bull. Chem. Soc. Jap.*, **40**, 1512 (1967).

(13) S. J. S. Formosinho-Simoes and V. M. S. Gil, *Mol. Phys.*, **15**, 639 (1968).

(14) H. Günther, *Tetrahedron Lett.*, 2967 (1967).

(15) R. Ditchfield and J. N. Murrell, *Mol. Phys.*, **15**, 533 (1968).

(16) J. Niwa, *Bull. Chem. Soc. Jap.*, **40**, 2192 (1967).

(17) L. Lunazzi and F. Taddei, *Spectrochim. Acta, Part A*, **25**, 533 (1969).

(18) C. P. Smythe, "Dielectric Behaviour and Structure," McGraw-Hill, New York, N. Y., 1955.

(1) Part XIV: A. R. Katritzky, H. J. Keogh, S. Ohlenrott, and R. D. Topsom, *J. Amer. Chem. Soc.*, **92**, 6855 (1970).

(2) Preliminary communication of part of this work: J. M. Angelelli, A. R. Katritzky, R. F. Pinzelli, M. V. Sinnott, and R. D. Topsom, *ibid.*, **91**, 4013 (1969).

(3) (a) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964); (b) S. Ehrenson, *ibid.*, **2**, 195 (1964).

(4) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

(5) A. R. Katritzky and R. D. Topsom, *Angew. Chem., Int. Ed. Engl.*, **9**, 87 (1970).

(6) M. Charton and H. Meislich, *J. Amer. Chem. Soc.*, **80**, 5940 (1958).

indicate contributions from resonance effects of substituents joined directly to the double bond in substituted ethylenes. However in neither case has it been possible to produce a more quantitative result.

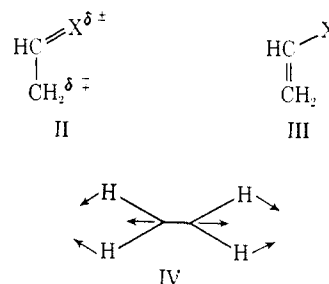
Many investigations have been concerned with the ability of an olefinic linkage to transmit electric effects when conjugated with a substituted benzene ring. Results such as ionization constants,²¹ hydrolysis rates,²² and pmr shifts²³ of cinnamic acid and derivatives, and pmr^{8,24} and ¹³C shifts^{8,25} of substituted styrenes, suggest that conjugative effects between a substituent and a benzene ring are fairly effectively transmitted to an atom or group (probe) situated trans to an ethylenic linkage.

The infrared spectra of substituted ethylenes have been well studied but mainly with regard to frequency measurements;²⁶⁻³⁰ thus the stretching frequency of the carbon-carbon double bond at approximately 1640 cm⁻¹ is altered by both the degree and geometry of substitution of the ethylene and the electrical and steric nature of the substituent itself. This has to date mainly been used to diagnose the number and geometrical arrangement of substituents relative to the double bond, particularly in hydrocarbons. It is important^{27,31} to minimize variations in bond angles and substituent masses if the results are to reflect charge distribution effects. In cases where this is done the frequency has been related²⁷ to the electronegativity of the substituent group. Further the frequency can be related to the heats of hydrogenation of the double bond. Variations of ν_{OH} in compounds where a hydroxy group is hydrogen bonded to ethylene π electrons are also dependent on the nature of the substituents on the ethylene,²⁷ as are the frequencies of CH₂ wagging and C=C twisting vibrations in substituted ethylenes.^{32,33} The frequency of the twisting vibration seemed to be related to inductive effects of the substituent while the wagging mode apparently gave a measure of π -electron effects. The identities derived have been used³⁴ to assess Hammett constants

of further substituents but these results may not be reliable. Some measurements have been previously made of the intensities of the carbon-carbon stretching vibration; the limited accurate results are discussed below. Russian workers have investigated the frequencies and intensities of a series of substituted vinyl ethers²⁷ and vinyl esters³⁵ and claim that the integrated intensities of the carbonyl and ethylenic stretching frequencies in the vinyl esters are proportional to the electrical effects of the substituents in the ester grouping. Some results for the Raman intensities of halo substituted ethylenes have also appeared.³⁶ No systematic investigation appears to have been made, however, of the intensities of the double bond stretching vibration in a series of simple substituted ethylenes.

$$A_{\text{mono}} = 17,600(\sigma_R^\circ)^2 + 100 \quad (2)$$

We have shown that³⁷ the integrated intensity A_{mono} ³⁸ of the ν_{16} mode near 1600 cm⁻¹ of monosubstituted benzenes is related to σ_R° by eq 2. This was justified by a VB treatment³⁷ and it was shown³⁹ that a MO treatment could be used to calculate the intensities. There is a considerable formal similarity between the C=C stretching band in ethylenes near 1640 cm⁻¹ and the ν_{16} vibration of benzenes: both are forbidden in the parent compound (and in certain symmetrically substituted derivatives, e.g., para or trans disubstituted) and derive their intensity from the influence of the substituent(s). On the VB formulation, interaction of the type II will be greatest in the stretched state, whereas III depicts the compressed state.



The 1640-cm⁻¹ vibration in monosubstituted ethylenes arises from the ν_2 (Herzberg's notation) vibration in ethylene which appears in the Raman but is not allowed in the infrared spectrum; it has the form IV. In a monosubstituted ethylene the overall symmetry drops to C_s even where the substituent is of high symmetry, and the vibration appears in the infrared spectrum. Normal coordinate and force-field analyses of some simple monosubstituted ethylenes^{30,40} suggest

(19) C. N. R. Rao, "Ultra-violet and Visible Spectroscopy," 2nd ed, Butterworths, London, 1967.

(20) C. A. Coulson and E. Stewart in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, London, 1964.

(21) R. Fuchs and J. J. Bloomfield, *J. Org. Chem.*, **31**, 3423 (1966); D. N. Kursanov, Z. N. Parnes, and V. I. Zdanovich, *Dokl. Akad. Nauk SSSR*, **165**, 566 (1965).

(22) J. J. Bloomfield and R. Fuchs, *J. Org. Chem.*, **26**, 2991 (1961); A. B. Thigpen and R. Fuchs, *ibid.*, **34**, 505 (1969).

(23) T. A. Wittstruck and E. N. Tachtenberg, *J. Amer. Chem. Soc.*, **89**, 3803 (1967); F. W. Wehrli, E. Pretsch, and W. Simon, *Helv. Chim. Acta*, **50**, 2189 (1967).

(24) Gurudata, J. B. Stothers, and J. D. Talman, *Can. J. Chem.*, **45**, 731 (1967); G. K. Hamer and W. F. Reynolds, *ibid.*, **46**, 3813 (1968); J. E. Dubois, J. P. Doucet, and J. A. Miller, *J. Chim. Phys., Physicochim. Biol.*, **63**, 1283 (1966); J. E. Dubois and J. P. Doucet, *ibid.*, **64**, 1145 (1967).

(25) K. S. Dhama and J. B. Stothers, *Can. J. Chem.*, **43**, 510 (1965).

(26) L. J. Bellamy, "The Infrared Spectra of Complex Organic Molecules," 2nd ed, Methuen, London, 1958.

(27) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1968.

(28) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963.

(29) W. Brugel, "An Introduction to Infrared Spectroscopy," Methuen, London, 1962.

(30) N. Sheppard and D. N. Simpson, *Quart. Rev., Chem. Soc.*, **6**, 1 (1952).

(31) S. Bank, W. D. Closson, and L. T. Hodgins, *Tetrahedron*, **24**, 381 (1968).

(32) W. J. Potts and R. A. Nyquist, *Spectrochim. Acta*, **15**, 679 (1959).

(33) D. B. Cunliffe-Jones, *ibid.*, **21**, 245 (1965).

(34) J. Knizck, H. Horak, and V. Chvalovsky, *Collect. Czech. Chem. Commun.*, **28**, 3079 (1963).

(35) L. A. Kotorlenko, *et al.*, *Zh. Prikl. Spektrosk.*, **5**, 366 (1966); *Teor. Eksp. Khim.*, **4**, 438 (1968); *Opt. Spectrosc. (USSR)*, **24**, 495 (1968); S. Higuchi, S. Tanaka, and H. Kamada, *Nippon Kagaku Zasshi*, **89**, 22 (1968).

(36) M. G. Borisov and L. M. Sverklov, *Opt. Spectrosc. (USSR)*, **17**, 459 (1964); V. S. Kukina, S. M. Kats, and K. M. Sverdlov, *ibid.*, **23**, 229 (1967).

(37) R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, **90**, 1757 (1968).

(38) Expressed in IUPAC practical units; *C. R. Vingtieme Conf. Munich*, 187 (1959). The A values are $1/cl \int \log (I_0/I) d\nu$ integrated over the whole band; some authors employ the symbols B or E for this quantity and use A for the quantity $1/cl \int \ln (I_0/I) d\nu$, that is, the values 2.303 greater than those in the present series.

(39) R. T. C. Brownlee, A. R. Katritzky, M. V. Sinnott, M. Szafran, R. D. Topsom, and L. Yakhontov, *J. Amer. Chem. Soc.*, **92**, 6850 (1970).

(40) See for example, L. M. Sverdlov, *et al.*, *Chem. Abstr.*, **53**, 859

Table I. Infrared Spectra and σ_R° Values of Monosubstituted Ethylenes^a

Subst	ν, cm^{-1}		$\nu_{\text{C}=\text{C}}$ vibration			Lit. σ_R°		
	b	c	ϵ_A^d	Lit. ϵ_A	A^e	$10F^f$	irPh ^g	σ_R° irE
OEt	1612	1652 1638	155	112 ^h	5149	-0.43 ⁱ	0.439	0.431
OBu	1612	1652 1636	154	110 ^h	5263		0.425 ^j	0.435
OCOMe	1648		253	90 ^h	2115	-0.21	0.235	0.272
Br	1597		147		1640	-0.16	0.231	0.239
I	1587		149		1209	-0.14	0.221	0.204
SMe	1584		147		1675	-0.17	0.250	0.242
SO ₂ Me	1617		9		204 ^k	+0.16	0.069	0.072
SO ₃ Me	1614		6		227		0.087	0.073
NCO	1629	1666	234		4384	0.17	0.403	0.397
<i>n</i> -Pr	1641				470 ^l		0.109	0.119
<i>i</i> -Pr	1639		39		482		0.115	0.121
<i>sec</i> -Bu	1641				460 ^l		0.115	0.118
<i>t</i> -Bu	1641		43		512	-0.17	0.125	0.126
SiMe ₃	1594		27		298	0.04 ^m	0.00 ^m	0.088
SiCl ₃	1618		33	24 ⁿ	301		0.088 ⁱ	0.090
SnMe ₃	1582		1.7		23	0.01 ^m		0.00
CH(CH ₂) ₂	1638		46		528		0.128	0.128
CH ₂ CN	1646		28	26 ^h	310	-0.08	0.090	0.092
CH ₂ Ph	1638		35		359	-0.08	0.117	0.101
Ph	1630		33		339	-0.09	0.096	0.097
CH ₂ OH	1646		11	10 ⁿ	177 ^k	-0.07	0.00	0.060
CH ₂ OMe	1648		10		127		0.054	0.041
CH ₂ Cl	1642	1646	8	8 ⁿ	123	-0.03	0.00	0.037
CHCl ₂	1636		7		81	+0.02 ^o	0.00	0.005
CN	1608	1650	4	3.5 ^h	117	+0.21	0.085	0.037
CHO	1618		9		177	+0.27	0.244	0.060
COMe	1616	1648 ^p	50	90 ^h	669	+0.19	0.219	0.147
COEt	1620	1650 ^p	59	48 ^h	948		0.206 ^j	0.178
COOH	1637	1618	137	90 ^h	2304	+0.21	0.292	0.285
COOMe	1635	1622	42	45 ^h	733		0.155	0.155
COOEt	1638	1622	63	38 ^h	887	+0.19	0.180	0.172

^a For CCl₄ solution unless otherwise stated. ^b Frequency of main band. ^c Frequency of subsidiary bands or shoulders. ^d ϵ_A is the peak extinction coefficient. $\epsilon_A = A_{\text{max}}/cl$ where A_{max} is the absorption at the main peak maximum, c is in moles and l is in centimeters. ^e A is integrated absorption intensity of the main and subsidiary bands taken together, in $\text{l. mol}^{-1} \text{cm}^{-2}$. ^f Taken from R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 3146 (1963), unless otherwise stated. ^g Taken from ref 37 unless otherwise stated. ^h Reference 50. ⁱ Value for OMe. ^j This work, see Table III. ^k Determined in CHCl₃ solution. ^l Taken from ref 51. ^m J.-M. Angelelli, T. R. C. Brownlee, A. R. Katritzky, R. D. Topsom, and L. Yakhontov, *J. Amer. Chem. Soc.*, **91**, 4500 (1969). ⁿ Taken from ref 34. ^o Private communication from R. W. Taft. ^p These two shoulders do not enter in the calculation of the integration.

that the form of the vibration is substantially as for ethylene except that the substituent does not move significantly. The variation of the frequency is difficult to predict²⁶ and obviously depends²⁶ on a combination of chemical and physical parameters.

We therefore measured the integrated intensities of this vibration for monosubstituted ethylenes for which σ_R° values were available to establish if any relationship existed with the resonance effect of the substituents.

Experimental Section

Chemicals and Solvents. Most of the compounds studied were commercial specimens purified by standard methods. Spectroscopic grade carbon tetrachloride was stored over molecular sieve. The following compounds were prepared by the literature methods indicated: vinyl iodide, bp 57° (lit.⁴¹ 56–56.5°); methyl vinyl sulfide, bp 70° (lit.⁴² 69–70°); methyl vinyl sulfone, bp 112° (13 mm) (lit.⁴² 115–117° (19 mm)); methyl ethenesulfonate, bp 95° (20 mm) (lit.⁴⁴ 90–91° (15 mm)); vinyl isocyanate, bp 40° (lit.⁴⁵ 38–39°); 3,3-dichloro-1-propene, bp 82° (lit.⁴⁶ 82°); N,N-

dimethylallylamine, bp 62° (lit.⁴⁷ 64°); allyl methyl ether, bp 46° (lit.⁴⁸ 46°); allyl ethyl ether, bp 62° (lit.⁴⁸ 62.5°). The identity and purity of all these compounds were confirmed by the nmr and ir spectra.

Vinyltrimethylstannane, tetravinylstannane, and vinyltriethoxysilane, were kindly donated by Professor J. C. Maire (Marseilles).

Spectroscopy. The spectra were recorded on a Perkin-Elmer Model 125 spectrometer in sodium chloride cells using carbon tetrachloride (or CHCl₃) as solvent. The cell path length was determined by the interference method.⁴⁹ The solvent absorptions were balanced in a variable path length cell, using the $\nu_{\text{C}-\text{Cl}}$ overtone peak (1549 cm^{-1}) of the CCl₄ and the $\nu_{\text{C}-\text{H}}$ overtone peak (2400 cm^{-1}) of the CHCl₃. The concentrations were adjusted to give peaks of between 20 and 70% transmission: for the strong $\pm\sigma_R^\circ$ values, $c = 0.15 \text{ M}$; medium, $c \approx 0.8 \text{ M}$; small $c \approx 1$ or 1.5 M .

For every compound the spectrum was recorded twice for each of two different concentrations: the recorded values are an average of the four integrations. The transmission values obtained were converted to absorbance values every two wave numbers. The integrated intensity³⁸ was calculated using $A = 1/c \int a dv$ (A in $\text{l. mol}^{-1} \text{cm}^{-2}$), where l = path length in centimeters (0.00924), c is in moles/liter, and a is the absorbance value corrected for the base

(1959); *ibid.*, **59**, 12303 (1963); J. R. Scherer and W. J. Potts, *J. Chem. Phys.*, **21**, 1691 (1959); R. Myer and Hs. H. Günthard, *Spectrochim. Acta, Part A*, **23**, 2341 (1967); E. M. Popov and G. I. Kagan, *Opt. Spectrosc. (USSR)*, **12**, 102 (1962).

(41) J. Spence, *J. Amer. Chem. Soc.*, **55**, 1290 (1933).

(42) R. Brown and R. C. G. Moggridge, *J. Chem. Soc.*, 816 (1946).

(43) G. C. Buckley, J. L. Charlsh, and J. D. Rose, *ibid.*, 1514 (1947).

(44) W. F. Whitmore and E. F. Landau, *J. Amer. Chem. Soc.*, **68**, 1797 (1946).

(45) R. Hart and A. E. van Dormael, *Bull. Soc. Chim. Belg.*, **65**, 291 (1956).

(46) W. H. King and H. A. Smith, *J. Amer. Chem. Soc.*, **72**, 3459 (1950).

(47) A. C. Copc and P. H. Towle, *ibid.*, **71**, 3423 (1949).

(48) F. K. Beilstein, "Handbuch der Organischen Chemie," Band I, Edwards Brothers, Ann Arbor, Mich., 1943, p 438.

(49) W. J. Potts, "Chemical Infrared Spectroscopy," Vol. 1, Wiley, New York, N. Y., 1963, p 117.

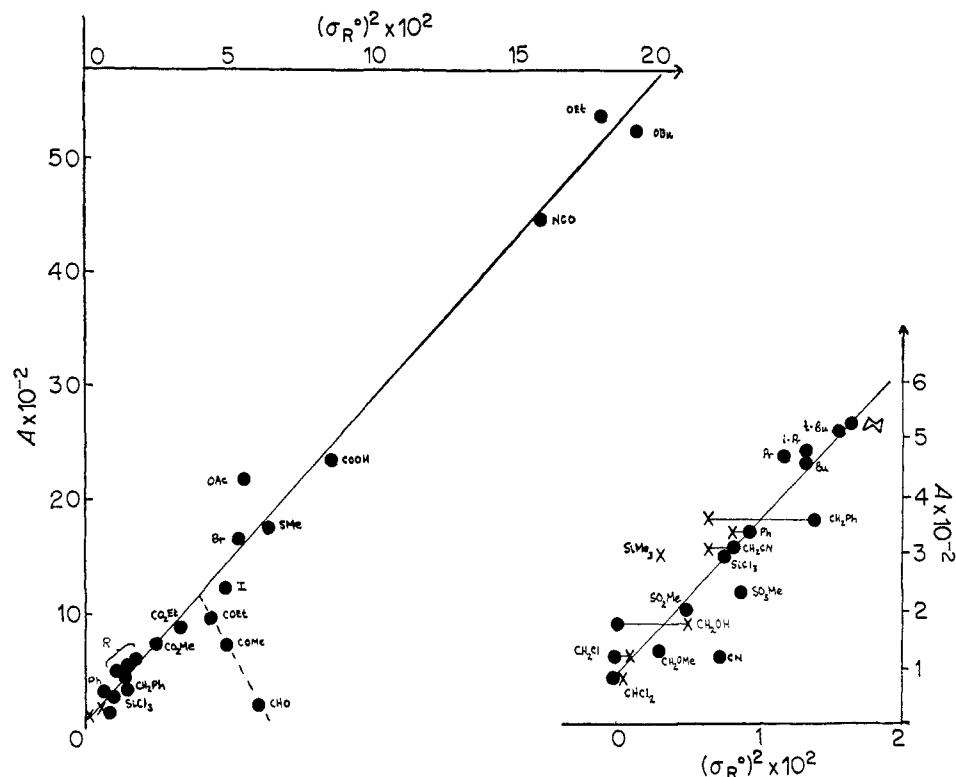


Figure 1. Integrated intensity of the infrared C=C stretching vibration for monosubstituted ethylenes plotted against $(\sigma_R^\circ)^2$: ●, ir derived σ_R° values; ×, ^{19}F derived σ_R° values; A, large σ_R° values; B, small σ_R° values.

line. The bands were integrated over the whole absorption, including any small side bands (see below) for most compounds. However in the case of the few carbonyl compounds, the shape of the high frequency end of the absorption was estimated to separate it from the carbonyl stretching absorption.

The extinction coefficients were obtained for each absorption (or the main one for a complex system) using the formula: $\epsilon_{\text{max}} = \Delta a / cl$, where Δa is the difference between the observed absorbance at the maximum and the base line.

Results and Discussion

Comparison of Measured Intensities with Literature Values. The apparent extinction coefficients for $\nu_{\text{C}=\text{C}}$ of many of the compounds investigated can be compared with values from Davison and Bates⁵⁰ (solutions in CCl_4 , 0.5 mol l., cell 0.2 mm, Grubb-Parsons single beam spectrometer) and from ref 34 (solutions in CCl_4 , cell from 0.17 to 0.081 mm, double Beam Reiss-Jena LIR 10 spectrophotometer). The overall agreement is fair (cf. Table I) considering the differences in conditions.

The more significant comparison, with previously measured integrated areas, is possible in fewer cases (Table II). Wexler reported⁵¹ precise integrated intensities for the $\nu_{\text{C}=\text{C}}$ of some 1-alkenes: our values for 1-hexene and styrene are in good agreement, as are our values for acrolein, and methyl and ethyl vinyl ketones with those found by Mecke and Noack.⁵² Recently Czech workers⁵³ studied 19 compounds of type $\text{CH}_2=\text{CH}-(\text{CH}_2)_n\text{X}$ with $n = 1, 2, 3$. We have measured four of these compounds; the agreement in intensity is poor for the CH_2OH substituent (which may

be due in part to association) and only fair for the other values.

Correlation of Measured Intensities with σ_R° . The integrated intensities of all the monosubstituted ethylenes for which σ_R° values were available (Table I), are plotted against $(\sigma_R^\circ)^2$ in Figure 1 to check for an iden-

Table II. Comparison of Measured Integrated Intensities for Monosubstituted Ethylenes with Literature Values

Subst	ν, cm^{-1}		$A, \text{l. mol}^{-1} \text{cm}^{-2}$		Ref
	This work	Lit.	This work	Lit.	
CHO	1618	1620	177	190	a
COMe	1616	1618	669	690	a
COEt	1620	1619	948	1240	a
Ph	1630		339	400	b
<i>n</i> -Pr		1641		470	b
<i>i</i> -Pr	1639		480		
<i>n</i> - C_4H_9	1640		505	500	b
<i>n</i> - C_5H_{11}		1642		604	c
CH_2Cl	1642	1643	123	179	c
CH_2Br	1638	1640	87	200	c
CH_2OH	1646	1646	177	532	c
CH_2CN	1646	1647	310	448	c

^a Reference 52. ^b Reference 51. ^c Reference 53; the literature A values have been divided by 2.303 as log values were used for the calculation.

tity analogous to that found (eq 2) for monosubstituted benzenes. For the plot σ_R° values derived³⁷ from monosubstituted benzenes by the ir method were used except that ^{19}F derived values are also shown for the substituents which have low (<0.09) values of σ_R° for the determination of which the monosubstituted benzene method is not reliable. Experimental data

(50) W. H. T. Davison and G. R. Bates, *J. Chem. Soc.*, 2607 (1953).
 (51) A. S. Wexler, *Spectrochim. Acta*, 21, 1725 (1965).
 (52) R. Mecke and K. Noack, *Chem. Ber.*, 93, 210 (1960).
 (53) M. Podzimeková, M. Procházka, and M. Paleček, *Collect. Czech. Chem. Commun.*, 34, 2101 (1969).

Table III. Spectral Data^a for Monosubstituted Benzenes and Calculated^b Values of σ_R°

Subst	$\pm \sigma_R^\circ$ calcd	1600 band		1585 band		<i>A</i>
		ν	ϵ_A	ν	ϵ_A	
OBu	0.425	1602	190	1588	97	3282
COEt	0.206	1598	53	1584	44	852
SiCl ₃	0.088	1594	38			238

^a Infrared solvent was CCl₄. ^b Calculated using eq 1.

required for the determination of new σ_R° values from monosubstituted benzenes are given in Table III: σ_R° values found for OBu and COEt resemble, as expected, the values³⁷ for OMe and COMe. The relation between the integrated intensity for 18 monosubstituted ethylenes and σ_R° irPh (OEt, OBu, Br, I, SMe, NCO, *n*-Pr, *sec*-Bu, *t*-Bu, CH(CH₂)₂, COOH, COOMe, COOEt) or σ_R° ¹⁹F (CH₂CN, Ph, CH₂OH, CH₂Cl, CHCl₂) is defined by eq 3 with a correlation coefficient of 0.998. The values of σ_R° calculated

$$A_{\text{eth}} = 27,100(\sigma_R^\circ)^2 + 80 \quad (3)$$

from this equation (and designated irE to distinguish from irPh values for monosubstituted benzene) are in good agreement with the irPh (Table I). Equation 3 represents a small refinement of the one which was published in our preliminary communication² and which was derived from ten substituted ethylenes only.

Equation 3 is the same form as eq 2 which governs monosubstituted benzenes.³⁷ For the latter compounds, the constant of 100 represents the contribution to the intensity of an overtone of the CH out-of-plane bending modes, similarly, we believe that an overtone causes the constant of 80 units for the monosubstituted ethylenes. Previous workers have suggested^{27, 35, 54} that complexities in band shapes in this region (vinyl ethers, vinyl acetate) are due to interference by overtones. The overtone of the CH₂ out-of-plane wagging mode occurs^{32, 55} at 1600–1650 cm⁻¹ in vinyl ethers and is of the right symmetry to allow Fermi interaction with $\nu_{\text{C}=\text{C}}$; however this wagging overtone occurs³² above 1800 cm⁻¹ for most of the compounds reported here. The first overtone of the CH₂ in-plane rocking mode, the fundamental of which absorbs at 810 cm⁻¹ in the Raman spectrum of ethylene itself,⁵⁶ may also be involved. Another feature leading to more complex spectra is the presence of rotational isomerism in some of the compounds (see below). The total absorption was integrated in each case. Acrylonitrile shows distinct bands at 1650 and 1608 cm⁻¹, *A* = 74 and 43 units. The complication of rotational isomerism is absent here. The higher band may^{57, 58} be a combination between ν_{CH_2} deformation at 1416 cm⁻¹ and a $\nu_{\text{C}=\text{C}=\text{N}}$ band at 242 cm⁻¹; two other possible combination tones are⁵⁹ 972 + 683 cm⁻¹ and 955 + 683

(54) E. M. Popov, N. S. Andreev, and G. I. Kagan, *Opt. Spectrosc. (USSR)*, **12**, 17 (1962).

(55) N. L. Owen and N. Sheppard, *Trans. Faraday Soc.*, **60**, 634 (1964).

(56) D. H. Rank, E. R. Shull, and D. W. E. Axford, *J. Chem. Phys.*, **18**, 116 (1950); R. L. Arnett and B. L. Crawford, Jr., *ibid.*, **18**, 118 (1950).

(57) F. Halverson, R. F. Stamm, and J. J. Whalen, *ibid.*, **16**, 808 (1948); H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 597 (1944).

(58) We are indebted to one of the referees for this suggestion.

(59) R. D. McLachlan and R. A. Nyquist, *Spectrochim. Acta, Part A*, **24**, 103 (1968).

cm⁻¹. Thus the higher band would seem to be the overtone and its intensity gives some support for the value of 80 units in eq 3 although Fermi resonance is possible here. The value *A* = 81 for the CHCl₂ substituent, which is known to have a very low σ_R° value also gives support to the increment of eq 2.

Application of Eq 3 to the Calculation of σ_R° Values. Equation 2 is unsuited to the calculation of σ_R° values below 0.1 because of the large influence of the overtone correction of 100 ± 50 units. The relative importance of the overtone correction in eq 3 is much less: assuming a value of 80 ± 40 gives the following possible errors for σ_R° as 0.1 ± 0.007, 0.07 ± 0.009, 0.05 ± 0.015. The corresponding errors for the determination from monosubstituted benzenes are 0.1 ± 0.015, 0.07 ± 0.025, and 0.05 ± 0.05. Therefore eq 3 is of unique value in the determination of small σ_R° values. In addition, for certain classes of compounds, the substituted ethylene is considerably more readily available than the substituted benzene, and for others the substituted ethylene must be used because of band overlap in the substituted benzene (*e.g.*, aryl groups as substituents).

In the light of these considerations, we first discuss the irE σ_R° values of Table I, for which literature data are available for comparison. Agreement between the irPh and irE values is good for several cases where discrepancies between the irPh and ¹⁹F values were previously³⁷ noticed, *i.e.*, the d-orbital acceptors Br, I, SMe, and the donor-acceptor group NCO.¹ For the substituents of low σ_R° , good agreement with the ¹⁹F value is generally found; this holds for CH₂CN, CH₂Ph, CH₂OH, CH₂Cl. The irE σ_R° value for the groups CH₂OMe, SO₃Me, and SO₂Me are considered to be more reliable than the previously published irPh data. Apart from those substituents with σ_R° of low magnitude, poor agreement between irPh and irE occurs only for certain substituents with a carbonyl group directly attached to vinyl (CHO, COMe, COEt); this is attributed to rotational isomerism and it will later be shown that a quantitative assessment of such isomerism is possible by the ir method (the moderate discrepancy found for OCOCH₃ may be due to a similar cause). Rotational isomerism also appears to occur in vinyl ethers²⁷ and allyl halides.⁵⁶ For the cyano group, the discrepancy between ¹⁹F (0.21) and irPh (0.085) is exacerbated by the irE result (0.037), this group is under scrutiny.

We have measured previously unknown values for the substituents of the compounds recorded in Table IV. Together with the values recorded in Table I, a considerable number of σ_R° values for substituents of the type CH₂X are now available. Except for the anomalous cyano group, a rough correlation exists between σ_R° for CH₂X and σ_1 for X; this is shown in Figure 2. Statistically, eq 4 holds with a correlation coefficient of

$$\sigma_R^\circ(\text{CH}_2\text{X}) = 0.128 - 0.224\sigma_1(\text{X}) \quad (4)$$

0.926. No simple relation could be expected to give a precise correlation: the influence of X will depend not only on its influence on the hyperconjugation of the remaining allylic hydrogen atoms, but also on its own ability to hyperconjugate, and on steric factors which will influence rotamer populations.

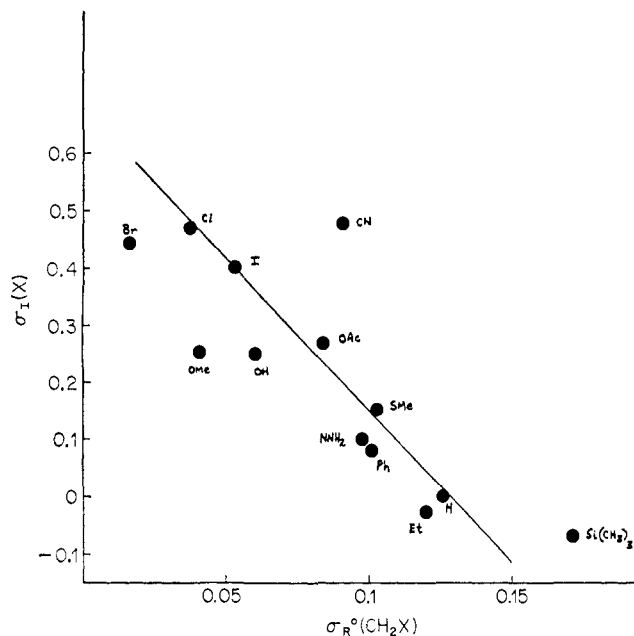


Figure 2. Plot of $\sigma_I(X)$ against $\sigma_R^o(\text{CH}_2\text{X})$ for substituted ethylenes.

Values of σ_R^o for substituents of type $\cdot\text{CH}_2\text{CH}_2\text{X}$ and $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{X}$, calculated from data of ref 53 are compared in Table V with those for the analogous CH_2X substituents. The variations are expected to, and do, become less as the chain length increases:

Table IV. New σ_R^o Values Calculated for Monosubstituted Ethylenes

Subst	ν, cm^{-1}		ϵ_A	A	σ_R^o (irE)
	a	b			
<i>n</i> -Bu	1640		43 ^c	505	0.124
<i>n</i> -C ₈ H ₁₇	1642			604 ^d	0.139
CH ₂ N(Me) ₂	1644		22	341	0.097
CH ₂ OCOMe	1652		19	272	0.082
CH ₂ Br	1638	1646	8 ^e	87	0.016 ^d
CH ₂ I	1638	1642	16	161	0.052
Si(OEt) ₃	1599		35	174	0.083
CH ₂ SiMe ₃	1629		84	938	0.177 ^h
SO ₂ CH:CH ₂	1612		14	109 ^f	0.032
CH ₂ SMe	1636		31	364	0.102
CH ₂ SBu ^g	1637		7.8	183 ^d	0.055
CH ₂ SO ₂ Bu ^d	1641		13.2	280 ^d	0.086
NCH(CH ₂) ₅ ^d	1644		23.5	807 ^d	0.163
CH ₂ OEt	1648		11	184	0.062
CH ₂ NCO	1650		14	165	0.057
CH ₂ NCS	1650		19	215	0.070
Sn(CH:CH ₂) ₃	1582	1642 ^g		27 ^f	0.00
<i>p</i> -C ₆ H ₄ Cl	1630	1652	41	586	0.136
<i>p</i> -C ₆ H ₄ Br	1630	1652	49	644	0.144
<i>p</i> -C ₆ H ₄ Me	1632	1652	38	620	0.140
<i>p</i> -C ₆ H ₄ OMe	1630	1656	104	680	0.148

^a Frequency of main band. ^b Frequency of subsidiary bands or shoulder. ^c Reference 34 gives $\epsilon_A = 40$. ^d From ref 53 (see also c Table II). ^e Reference 34 gives $\epsilon_A = 7$. ^f A value per vinyl group. ^g This shoulder does not enter in the calculation of the integration. ^h R. W. Taft, privately communicated ¹⁹F results of 0.02 for CH₂Br and 0.20 for CH₂SiMe₃.

Table V. σ_R^o Values for Substituents of Type $(\text{CH}_2)_n\text{X}$

X	$n = 1^a$	$n = 1$	$n = 2$	$n = 3$
<i>n</i> -Pr	0.124			
<i>n</i> -Bu		0.139		
NMe ₂	0.097			
NCH(CH ₂) ₅		0.163		
OCOMe	0.083			
Cl	0.037		0.103	0.126
Br	0.016			0.117
I	0.052			
OH	0.060	0.128	0.161	0.135
OMe	0.041			
OEt	0.062			
SMe	0.102			
SBu		0.055	0.130	0.146
SO ₂ Bu		0.086	0.229	0.137
NCO	0.057			
NCS	0.070			
CN	0.092	0.116	0.110	0.119
Ph	0.102			

^a Calculated from intensity data of this work; all others from data of ref 53.

indeed, we doubt if the variation found within each of these series exceeds the experimental error.

para-Substituted Styrenes. Spectral data for para-substituted styrenes are recorded in Table IV ($\nu_{\text{C}=\text{C}}$) and

Table VI. Spectral Data^a for para-Substituted Styrenes

Subst	ν_{ring}	ϵ_A	A	\bar{R}_p^b	$\pm\sigma_R^o$ (subst)	σ_R^o (CH=CH ₂) ^c
Cl	1602	15	374	0.131	0.217	-0.099 ^d
Br	1590	30	407	0.141	0.231	-0.086 ^d
OMe	1608	160	1965	0.390	0.428	-0.045 ^e
Me	1610	9	<i>f</i>	<i>f</i>	0.099	<i>f</i>

^a Infrared solvent was CCl₄. ^b $\bar{R}_p = [(A - 170)/11,800]^{1/2}$ [P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, **90**, 1767 (1968)]. ^c $\sigma_R^o(\text{CH}=\text{CH}_2) = -0.03$ [from R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davies, *ibid.*, **85**, 3146 (1968)], and ± 0.05 from ref 37. ^d Calculated using the equation $A = 11,800 [\sigma_R^o(1) - \sigma_R^o(2)]^2 + 170$. ^e Calculated using eq 9 from P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, **90**, 1767 (1968). ^f No calculation possible because of the big overlap with the $\nu_{\text{C}=\text{C}}$ band.

Table VI (ν_{ring}). The variation of σ_R^o with X for the substituent group C₆H₄X is small indicating that direct resonance interaction between the para substituents is also small. The intensity of the ring vibration (Table VI) affords a method for estimating the σ_R^o value of the CH₂:CH group.

Conclusions

The conjugative interaction between substituents and an adjacent carbon-carbon double bond seems to parallel that between substituents and benzene rings. (This result is in agreement with recent CNDO/2 calculations.⁶⁰) The results reported here are also useful in estimating weak interactions.

(60) R. T. C. Brownlee and R. W. Taft, to be published.