Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. Part XXXII.[1] Conjugation of the Substituent and the Triple Bond in Monosubstituted Acetylenes

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The intensity of $\nu(C\equiv C)$ for monosubstituted acetylenes is determined by resonance interaction with the substituent, as measured by σ°_{R}. Previous literature on electronic interactions in acetylenes is reviewed.

THE intensity of the ν_8 (ν_{16} in Herzberg's notation) vibrations near 1600 cm^{-1} in monosubstituted benzenes,[2,3] expressed in equation (1), provides a direct measure of conjugative interaction between ring and substituent. The conjugative resonance parameter σ°_{R} also deter-

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[1] Part XXXI, T. B. Grindley, K. F. Johnson, A. R. Katritzky, H. J. Keogh, and R. D. Topsom, preceding apper.

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mines the intensity of the ν(C=C) stretching mode of monosubstituted ethylenes [equation (2)].[4,5]

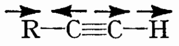
$$A_{\text{mono}} = 17{,}600(\sigma^{\circ}_{\text{R}})^2 + 100 \qquad (1)$$

$$A_{\text{eth}} = 27{,}100(\sigma^{\circ}_{\text{R}})^2 + 80 \qquad (2)$$

We have now studied the C≡C stretching band intensity of monosubstituted acetylenes. Less is known regarding intramolecular interactions in acetylenes than in either benzenes[3] or ethylenes.[4] The C≡C bond length appears to be virtually unaffected by substituents.[6] Studies[7] of the heats of hydrogenation of monosubstituted alkyl-, carboxy-, and aryl-acetylenes have indicated that inductive effects are more important here than for the corresponding ethylenes although resonance effects were also noted. A large number of dipole moment studies of monosubstituted acetylenes have been carried out[8,9] and correlation[10] of these data with dual parameter equations[11] indicates that resonance effects are about twice as important as inductive effects. Recently Rosenberg and Drenth[12] have summarised much of the evidence from n.m.r. chemical shifts and coupling constants about electronic interactions in acetylenes. The magnitudes of the chemical shifts appear to be determined chiefly by the inductive effects of the substituents although variable π-cloud and substituent anisotropy as well as resonance effects cause perturbations.

Some chemical evidence is also available on interactions in monosubstituted acetylenes, particularly in comparison with the appropriate ethylenes. Thus propiolic acid is decarboxylated more readily[13] and is more acidic[14] than acrylic acid, and its ester is hydrolysed more rapidly[15] than the corresponding acrylic ester, all of which indicates that C≡C is more electron withdrawing than C=C. The acidity of the terminal hydrogen atom is related to the electronegativity of the substituent.[16] The fact that bromine can be more readily added to ethylenes than acetylenes[17] has been quoted as evidence that the ethylenic bond is more polarisable, and this is supported by a report that the binding energy[18] of acetylenic π-electrons is greater than that of olefinic π-electrons. Plotting[8] the pK_a values of a limited range of 3-substituted propiolic acids against the normal Hammett *para*-substituent constants gives a good linear relation. All this evidence indicates that although the acetylenic bond is more inductively electron-withdrawing and apparently less polarisable than other π-systems, resonance effects are still important and Hammett relationships should apply. Very recently, Charton[19] has shown that many sets of equilibrium, reactivity, and spectroscopic data relating to monosubstituted acetylenes can be correlated by the extended Hammett equation, and that resonance effects do play an important role.

Infrared Results.—Force constant calculations[20] have shown that the C≡C stretching vibration (A-type) in monosubstituted acetylenes has the form (I). Mass effects for the vibration have been shown both experimentally[21] and theoretically[22] to be unimportant if the atomic weight of R is greater than 10. Although[21,23–25] Fermi resonance is unimportant for ν(C≡C) of most monosubstituted acetylenes, when the terminal hydrogen atom is replaced by deuterium, the C≡C and C–D stretching bands resonate strongly.[26] Because the C≡C stretch is well separated from other vibrations, a large number of authors have studied the effects of substituents on its frequency and intensity in a qualitative manner; however few quantitative studies are available. Nyquist and Potts[27] observed that conjugative effects lowered the frequencies of acetylenes and Alaune *et al.*[28] found that conjugation with C=O or C=C lowered the C≡C frequency and increased the intensity. Jouve[29]



(I)

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showed that the intensity of the ≡C–H stretching vibration and the chemical shift of the acetylenic proton were related by a smooth curve and suggested that both measurements reflect the change in electron density around the proton on change in substituents. d–π Interactions [26,30,31] or inductive effects [26] have been put forward as explanations for intensity changes for the C≡C stretching vibration for the compounds $R_3XC{\equiv}CH$ (X = C, Si, Sn, or Ge). The intensities obtained by previous investigators are given in Table 1 (converted to I.U.P.A.C. practical units).[32]

TABLE 1

Monosubstituted acetylenes: ν(C≡C) integrated intensities from the literature [a]

Substituent	Ref. to intensity	A_{obs} (original units)	Units	A_{obs}	$A^{1/2}$
$COPr^n$	*b*	5200	*h*	2260	47·5
Cyclohex-3-enyl-carbonyl	*b*	5640	*h*	2450	49·5
$SnEt_3$	*c*	0·10	*i*	430	20·7
$GeBu^n{}_3$	*d*	0·09	*i*	391	19·8
$GeEt_3$	*d*	0·107	*i*	465	21·1
$SiMe_3$	*c*	0·25	*i*	1090	33·0
Ph_2P	*c*	0·04	*i*	174	13·2
Ph_2As	*e*	0·05— 0·06	*i*	217— 261	14·7— 16·2
Cyclohexyl-$[CH_2]_2$·-CMeOH	*b*	227	*h*	99	9·9
Pr^nCHOH	*b*	220	*h*	96	9·8
Ph	*f*	436	*h*	189	13·7
Pr^n	*b*	583	*h*	253	15·9
Bu^n	*d*	0·067	*i*	291	17·1
	b	584	*h*	254	15·9
n-C_6H_{13}	*g*	683	*h*	297	17·2
Bu^t	*c*	0·06	*i*	260	16·1
CH_2GeEt_3	*d*	0·201	*i*	868	29·5
Ph_2PO	*e*	0·48— 0·58	*i*	2084— 2520	45·7— 50·2

[a] In CCl_4. [b] Ref. 28*a*. [c] E. A. Gastilovich, D. N. Shigorin, K. V. Zhukova, and I. S. Akchurina, *Russ. J. Phys. Chem.*, 1969, **43**, 1. [d] R. Mathis, M. C. Sergent, P. Mazerolles, and F. Mathis, *Spectrochim. Acta*, 1964, **20**, 1407. [e] R. Mathis, M. Barthelat, F. Mathis, and C. Charrier, *J. Mol. Structure*, 1967—1968, **1**, 481. [f] T. L. Brown, *J. Chem. Phys.*, 1963, **38**, 1049. [g] R. Romanet and B. Wojtkowiak, *Compt. rend.*, 1960, **251**, 364. [h] 1 mol^{-1} cm^{-2}, I.U.P.A.C. standard units. [i] 10^4 × 1 mol^{-1} cm^{-2}.

For benzenes [3] and ethylenes,[4] the interaction between the substituent and the multiple-bonded function has been shown to give rise, for ν_8 and ν_2 respectively, to an alternating dipole ($d\mu/dQ$) during the vibration; this is proportional to σ°_R. In the normal mode of the C≡C vibration for monosubstituted acetylenes, both the hydrogen atom and the substituent move in the same direction (see earlier). Treatment of σ°_R as a vector as previously [3] leads to the relationship (3) for monosubstituted acetylenes. The constant b is required because of the variation in the form of the normal vibration. The normal vibration remains relatively constant for all monosubstituted acetylenes, but is different for acetylene itself, and again different for the group of disubstituted acetylenes.[20,33,34] By comparison the form of the normal vibration changes little for substituted benzenes and ethylenes.[3,4]

$$A = K_1[\sigma^\circ_R(1) + b]^2 \qquad (3)$$

EXPERIMENTAL

The monosubstituted acetylenes were prepared by literature methods as outlined in Table 2 or were commercial samples purified by distillation. The purity of the compounds was checked by g.l.c. and/or m.p. determination and by i.r. and n.m.r. spectroscopy.

Spectroscopic grade carbon tetrachloride was stored over molecular sieves (4A). Chloroform was purified by passing it through alumina immediately prior to use. Methanol was dried with methylmagnesium iodide.[35] Dimethylformamide was purified by distillation from calcium hydride and was stored over molecular sieves.

The spectroscopic technique when carbon tetrachloride was solvent was as previously described.[36] When chloroform–methanol (9 : 1) was the solvent, the sodium chloride cells were used as previously described except that the 2401 cm^{-1} band of chloroform was employed for balancing. Although the measurement in dimethylformamide was carried out in calcium fluoride cells, the same technique as above was used. Integration procedures for all solvents were as previously described and reproducibilities of $A^{1/2}$ were ±1 for all compounds. Results are recorded in Table 2.

Molecular Orbital Calculations.—The observed i.r. intensity A of a band in I.U.P.A.C. practical units (l mol^{-1} cm^{-2}) is given [32] by equation (4), where c is the concentration in mol l^{-1} and l is the path length in cm. This intensity is related to the rate of change of dipole moment with the normal co-ordinate ($d\mu/dQ$ in e.s.u.) by equation (5).[37] It can be shown [38] that the working equation is equation (6), where $\Delta\mu$ is the change in dipole moment corresponding to the displacement at fractions of 10^{-9} of the normalised normal co-ordinates. Calculations were made with f at $\pm 2 \times 10^{-11}$ and $\pm 4 \times 10^{-11}$ of the normal co-ordinate to allow $d\mu/dQ$ to be estimated.

$$A = 1/cl \int \log_{10}(I_0/I) d\nu \qquad (4)$$

$$A = N\pi/(2{\cdot}303 \times 3000c^2)(d\mu/dQ)^2 \qquad (5)$$

$$d\mu/dQ = 776\Delta\mu \times f \qquad (6)$$

The calculations were performed on a PDP 9 computer of 16 K capacity by the standard CNDO/2 method [39] with the parameters suggested by Pople and Gordon. They were integrated to convergence within 0·0001 electron

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[30] (*a*) E. A. Gastilovich, D. N. Shigorin, K. V. Zhukova, and O. G. Yarosh, *Optics and Spectroscopy*, 1967, **23**, 304; (*b*) E. A. Gastilovich, D. N. Shigorin, N. V. Komarov, and O. G. Yarosh, *ibid.*, 1965, **19**, 162; E. A. Gastilovich, D. N. Shigorin, and N. V. Komarov, *ibid.*, 1964, **16**, 24.

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TABLE 2

Monosubstituted acetylenes: compounds examined

Substituent	M.p. or b.p.[a] (°C) [mmHg]	Lit. m.p. or b.p.[a] (°C) [mmHg]	Source	ν(C≡C)[b]			
				ν/cm^{-1}	ε_A[c]	A/ l mol^{-1} cm^{-2}	$A^{1/2}$
CO_2H	62 [22]	144 d[d]	*u*	2132	34	4211	64·9
COCl	70—74	72—75[e]	*v*	2120	224	3558	59·6
COPh	51 ‡	50—51[f] ‡	*f*	2101	154	2514	50·1
CO_2Et	57 [105]	119 [745][g]	*h*	2119	103	2477	49·8
COMe	86	84·5—86[f]	*f*	2100	154	2925	54·1
CO_2Me	48 [95]	102 [742][h]	*h*	2128	178	2621	51·2
CH_2Br	85	88—90[i]	*w*	2129	7	121	11·0
CH_2Cl	59	65[j]	*w*	2132	7	119	10·9
CHOHMe	110	108·5—110[k]	*k*	2113	4	94	9·7
CH_2OH	114—115	110—115[l]	*w*	2121	7	154	12·4
CHOHPh	49—101 [2]	115—116 [16][m]	*m*	2118	7	117	10·8
$CH_2N^+Me_3Br^-$	179—180 ‡	178—179[n] ‡	*n*	2126 2133sh	22	532[z]	23·1
$CH_2N^+H_3Cl^-,H_2O$	168 ‡	167—168[o] ‡	*o*	2124	24	264[aa]	16·2
CH_2NMe_2	80	82[p]	*x*	2197	2	97	9·8
Ph	141	142—143[q]	*u*	2111	10	137	11·7
Bu^n	73	71[r]	*r*	2119	13	208	14·4
Bu^t	39	37·8[s]	*s*	2135 2104	15	279	16·7
OEt	52	50[t]	*y*	2154	160	7607	87·2

[a] M.p. indicated by ‡. [b] Measured in CCl_4 unless otherwise noted. [c] $\varepsilon_A = a_{max.}/cl$ where $a_{max.}$ is absorbance at peak maximum, c = concentration in mol l^{-1}, l is cell path length in cm. [d] E. Baudrowski, *Ber.*, 1882, **15**, 2701. [e] F. C. Schaefer, U.S.P. 2,388,660/1945 (*Chem. Abs.*, 1946, **40**, 1868[8]). [f] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 39. [g] W. H. Perkin, jun., and J. L. Simonsen, *J. Chem. Soc.*, 1907, **91**, 834. [h] E. H. Ingold, *J. Chem. Soc.*, 1925, **127**, 1199. [i] L. Henry, *Ber.*, 1873, **6**, 728. [j] L. Henry, *Ber.*, 1875, **8**, 398. [k] R. B. Woodward and T. Singh, *J. Amer. Chem. Soc.*, 1950, **72**, 494. [l] L. Henry, *Ber.*, 1872, **5**, 569. [m] E. R. H. Jones and J. T. McCombie, *J. Chem. Soc.*, 1942, 733. [n] P. Marszak, J. P. Guermont, and R. Epsztein, *Mém. services chim. état* (*Paris*), 1951, **36**, 301 (*Chem. Abs.*, 1954, **48**, 8724*g*). [o] K. Sato, *Nippon Kagaku Zasshi*, 1955, **76**, 1404 (*Chem. Abs.*, 1957, **51**, 17,760*a*). [p] K. N. Campbell, F. C. Fatora, jun., and B. K. Campbell, *J. Org. Chem.*, 1952, **17**, 1141. [q] 'Beilsteins Handbuch der Organischen, Chemie,' eds. B. Prager and P. Jacobson, Springer-Verlag, Berlin, 1922, vol. V. p. 511. [r] B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.*, 1951, 893. [s] P. Ivitzky, *Bull. Soc. chim. France*, 1924, **35**, 357. [t] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, Chemical Rubber Co., Cleveland, Ohio, 1970, 51st edn., p. C-295. [u] From Ralph N. Emanuel Limited. [v] H. C. Brown, *J. Amer. Chem. Soc.*, 1938, **60**, 1325. [w] From B.D.H. Limited. [x] From Fluka AG. [y] J. F. Arens, *Rec. Trav. chim.*, 1955, **74**, 271. [z] Measured in $CHCl_3$–MeOH (9 : 1). [aa] Measured in $Me_2N{\cdot}CHO$.

density units. The normal co-ordinates were available[40] for fluoro- and chloro-acetylene as follows, where R^1 indicates the C–X, R^2 the C≡C, and R^3 the C–H bond.

	R^1	R^2	R^3
Fluoroacetylene	–0·273	0·374	0·124
Chloroacetylene	–0·232	0·354	0·130

The geometry adopted was that used by Brownlee and Taft.[41] Calculations were made corresponding to both sets of normal co-ordinates and the results are listed in Table 3.

TABLE 3

Calculated dμ/dQ values for monosubstituted acetylenes

Substituent	dμ/dQ[a]	dμ/dQ[b]	dμ/dQ[c]	dμ/dQ[d]
F	112	135	121	
CHO	115[e]	49·1	44·6	82·3[e]
CN	55	56·5	55·4	
NH_2[f]	162	173	161	
NH_2[g]	162	146	134	
OH	135	132	121	158[h]
NO_2	86	37·2	37·1	
BF_2[i]	158	188	177	
CF_3	63	49·9	46·4	
OMe	147	150	137	158[h]
CH_2CN	55	59·4	56·2	
Me	19	52·0	49·0	26·1[j]
NMe_2	189	195	180·0	
COMe	108[e]	40·9	36·6	82·3[e]
Ph	19	37·2	37·1	21·2

[a] Derived from equation (7). [b] Derived from FCCH L matrix. [c] Derived from ClCCH L matrix. [d] Derived from experimental data. [e] COEt value. [f] Planar. [g] Non-planar. [h] OEt value. [i] $\sigma^\circ_R = 0{\cdot}35$ (ref. 41). [j] Bu^n value.

The frequency of ν(C≡C) for fluoroacetylene is considerably higher than for other halogenoacetylenes; this probably[25] arises from interaction between ν(C≡C) and ν(CF). The normal co-ordinates also differ between chloro- and fluoro-acetylene. In addition to the calculations reported in Table 3 we have carried out some using the set of normal co-ordinates for 3-chloropropyne,[34] but the results were not substantially different from those obtained from the other sets. These results indicate that the intensities are insensitive to minor changes in the normal co-ordinates.

RESULTS AND DISCUSSION

As in the procedure used previously,[3] the $A^{1/2}$ values for the C≡C stretching bands for the monosubstituted acetylenes measured in this work (Table 2) were plotted against σ°_R. This plot requires that $A^{1/2}$ values be negative if $\sigma^\circ_R < -0{\cdot}05$: $A^{1/2}$ is proportional to dμ/dQ, a vector, and the different signs for $A^{1/2}$ represent the different directions for the dμ/dQ vector in compounds with donor and acceptor substituents. The resulting correlation is represented by equation (7).

$$A^{1/2} = 217(\sigma^\circ_R + 0{\cdot}05) \quad (r = 0{\cdot}992,\ 18 \text{ points}) \qquad (7)$$

Compounds $HC{\equiv}C{\cdot}CH_2{\cdot}NH_3^+Cl^-$ and $HC{\equiv}C{\cdot}CH_2{\cdot}NMe_3^+Br^-$, for solubility reasons, had to be studied in polar solvents; their intensities are larger than those predicted by the subsequent correlations (4)—(7)

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[40] J. L. Duncan, personal communication to H. J. Keogh, December 1969.

[41] R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, 1970, **92**, 7007.

probably because of hydrogen bonding with the solvent [see (II)]. Gastilovich *et al.*[30a,31] have observed that the

$$\underset{\text{(II)}}{\text{R–C}\equiv\text{C–H}\cdots\text{B–R}}$$

intensity of the C≡C stretching band in monosubstituted acetylenes is larger in solvents where hydrogen bonds can form.

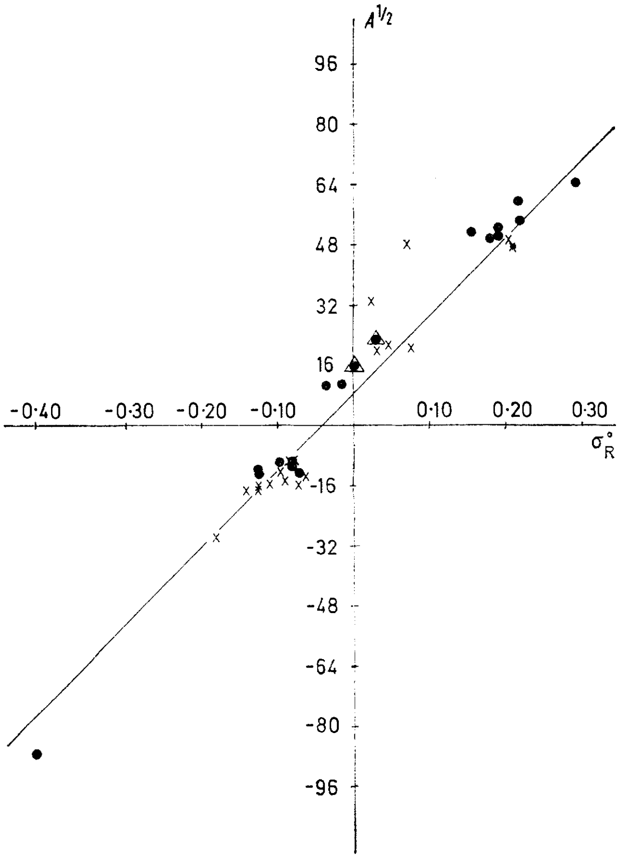

FIGURE 1 Square root of the observed intensity for ν(C≡C) of monosubstituted acetylenes plotted against $\sigma^{\circ}_{\mathrm{R}}$; (●) present results in CCl_4, (△) present results in polar solvents, (×) literature results; the line shown is defined by the present results

Because the C≡C stretching vibration is well separated from other vibrations, the intensities of this vibration for a large number of compounds have been previously recorded. The plot in Figure 1 includes, with the data of Table 2, literature $A^{1/2}$ values for the monosubstituted acetylenes for which the substituent $\sigma^{\circ}_{\mathrm{R}}$ values are available. The line obtained is represented by equation (8). Correlations (7) and (8) clearly show that the square root of the intensity of a monosubstituted acetylene is directly related to the electronic properties of the substituent.

$$A^{1/2} = 218(\sigma^{\circ}_{\mathrm{R}} + 0{\cdot}05)\ (r = 0{\cdot}980,\ 37\ \text{points}) \qquad (8)$$

Since the acetylene bond has two π-orbitals, both should interact with substituents simultaneously. Recently a measure of the ability of a substituent to interact with a π-system at 90° to its normal geometry, $(\sigma^{\circ}_{\mathrm{R}})_{\mathrm{tw}}$, has been developed.[42] As an example, for the NR_2 substituent $\sigma^{\circ}_{\mathrm{R}}$ applies to the normal geometry in aniline and $(\sigma^{\circ}_{\mathrm{R}})_{\mathrm{tw}}$ to the orthogonal arrangement in benzoquinuclidine. Such $(\sigma^{\circ}_{\mathrm{R}})_{\mathrm{tw}}$ values have been obtained experimentally or estimated for all the substituents considered and are compiled along with the normal $\sigma^{\circ}_{\mathrm{R}}$ values in Table 4.

Equations (9) and (10) (and Figure 2) represent the

$$A^{1/2} = 162[\sigma^{\circ}_{\mathrm{R}} + (\sigma^{\circ}_{\mathrm{R}})_{\mathrm{tw}} + 0{\cdot}14] \qquad (9)$$
$$(r = 0{\cdot}989,\ 18\ \text{points})$$

$$A^{1/2} = 153[\sigma^{\circ}_{\mathrm{R}} + (\sigma^{\circ}_{\mathrm{R}})_{\mathrm{tw}} + 0{\cdot}14] \qquad (10)$$
$$(r = 0{\cdot}969,\ 37\ \text{points})$$

correlation obtained by the assumption of simultaneous interaction of the substituent with both acetylene π-orbitals, measured by $[\sigma^{\circ}_{\mathrm{R}} + (\sigma_{\mathrm{R}}^{\circ})_{\mathrm{tw}}]$. Comparison of these correlations with (7) and (8) does not allow a choice between the alternative treatments, although the

TABLE 4

σ Constants

Substituent	$\sigma^{\circ}_{\mathrm{R}}$	Ref.	$(\sigma^{\circ}_{\mathrm{R}})_{\mathrm{tw}}$	Ref.
NEt_2	−0·57	*b*	−0·13	*w*
NMe_2	−0·53	*b*	−0·13	*w*
NMePh	−0·50	*c*	−0·13	*w*
OEt	−0·44	*b*	−0·23	*x*
SMe	−0·25	*b*	−0·05	*y*
Br	−0·23	*b*	−0·23	*z*
SEt	−0·25	*d*	−0·05	*y*
I	−0·22	*b*	−0·22	*z*
Cl	−0·22	*b*	−0·21	*z*
CH_2GeEt_3	−0·18	*e*	−0·10	*aa*
$C_6H_{13}{}^{n}$	−0·11	*f*	−0·10	*aa*
$C_5H_{11}{}^{n}$	−0·11	*f*	−0·10	*aa*
$SnEt_3$	+0·07	*g*	+0·07	*z*
Bu^{t}	−0·13	*b*	−0·13	*z*
Bu^{n}	−0·11	*f*	−1·10	*aa*
Pr^{n}	−0·11	*b*	−0·10	*aa*
Et	−0·10	*b*	−0·10	*z*
Me	−0·10	*b*	−0·10	*z*
CH_2NMe_2	−0·10	*h*	−0·10	*aa*
$Ge(Bu^{n})_3$	+0·041	*i*	+0·031	*z*
$GeEt_3$	+0·051	*i*	+0·051	*z*
Ph	−0·10	*b*	−0·06	*bb*
CMe_2OH	−0·08	*j*	−0·12	*aa*
Me_2EtSi	+0·02	*k*	+0·02	*z*
CH(OH)Ph	−0·08	*l*	−0·10	*aa*
CH(OH)Me	−0·08	*j*	−0·11	*aa*
CH(OH)Et	−0·08	*j*	−0·11	*aa*
$CH(OH)C_6H_{13}$	−0·08	*j*	−0·12	*aa*
Ph_2As	−0·07	*m*	−0·05	*cc*
CH_2OH	−0·06	*h*	−0·10	*aa*
Ph_2P	−0·06	*m*	0·02	*cc*
CMe_2Cl	−0·06	*n*	−0·10	*aa*
Cyclopent-1-enyl	−0·05	*o*	0·0	*dd*
$CH(OEt)_2$	0·0	*p*	0·0	*z*
CH_2Cl	−0·04	*h*	−0·10	*aa*
CH_2Br	−0·02	*h*	−0·10	*aa*
$SiMe_3$	+0·03	*q*	+0·03	*z*
SO_2Me	0·07 [a]	*b*	0·07	*z*
CN	+0·10	*b*	+0·10	*z*
CO_2Me	+0·16	*b*	0·0	*dd*
CO_2Et	+0·18	*b*	0·0	*dd*
CO_2Pr^{n}	+0·18	*r*	0·0	*dd*
COPh	0·19	*b*	0·0	*dd*
COCl	+0·21	*b*	0·0	*dd*
COEt	+0·21	*s*	0·0	*dd*
COMe	0·22	*b*	0·0	*dd*

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[42] T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *Tetrahedron Letters*, 1972, 2643; T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *J.C.S. Perkin II*, 1974, 289.

TABLE 4 *Continued.*

Substituent	σ°_R	Ref.	$(\sigma^\circ_R)_{tw}$	Ref.
COC_7H_{15}	+0·22	*t*	0·0	*dd*
CHO	0·24	*b*	0·0	*dd*
CO_2H	0·29	*b*	0·0	*dd*
$CH_2N^+Me_3Br^-$	+0·03	*u*	−0·10	*aa*
$CH_2N^+D_3Cl^-$	0·00	*b*	−0·10	*aa*
Ph_2PO	+0·07	*v*	+0·07	*z*

[a] SO_2Et taken equivalent to SO_2Me. [b] Ref. 2. [c] By analogy with NHPh ($\sigma^\circ_R = 0{\cdot}504$) (ref. 2). [d] Assumed equivalent to SMe since steric interactions are small here; see A. R. Katritzky, R. F. Pinzelli, and R. D. Topsom, *Tetrahedron*, 1972, **28**, 3441. [e] Equivalent to CH_2SiMe_3 (ref. 5). Taken to be equal to Pr^n value (ref. 2). [g] Value for $SnMe_3$ (footnote *q*). [h] Ref. 5. [i] Taken for $GeEt_3$ to be equal to or for $Ge(Bu^n)_3$ to be slightly smaller than σ°_R for $GeMe_3$ (footnote *q*). [j] By modification of CH_2OH value (0·06) (ref. 5). [k] As for $SiMe_3$ (footnote *q*). [l] Estimated from CH_2OH, by considering $\sigma_I(Ph)$. [m] J. M. Angelelli, R. T. C. Brownlee, A. R. Katritzky, R. D. Topsom, and L. Yakhontov, *J. Amer. Chem. Soc.*, 1969, **91**, 4500. [n] Estimated from CH_2Cl in same way as for CHROH (*j*). [o] Taken to be the same as $CH=CH_2$ (ref. 2). [p] By analogy with $CH(O{\cdot}CH_2)_2$ group (ref. 2). [q] N. C. Cutress, A. R. Katritzky, C. Eaborn, D. R. M. Walton, and R. D. Topsom, *J. Organometallic Chem.*, 1972, **43**, 131. [r] As for CO_2Et. [s] A. R. Katritzky, R. F. Pinzelli, and R. D. Topsom, *Tetrahedron*, 1972, **28**, 3449. [t] As for COMe. [u] G. P. Ford and A. R. Katritzky, unpublished results. [v] K. F. Johnson and A. R. Katritzky, unpublished results. [w] By analogy with benzoquinuclidine; see N. C. Cutress, T. B. Grindley, A. R. Katritzky, M. V. Sinnott, and R. D. Topsom, *J.C.S. Perkin II*, 1972, 2255. [x] Taken as the same as for OMe (ref. 42). [y] Estimated to be $> -0{\cdot}075$ observed for SBu^t; A. R. Katritzky, R. F. Pinzelli, and R. D. Topsom, *Tetrahedron*, 1972, **28**, 3441. [z] Substituent taken to have cylindrical symmetry. [aa] For α-substituted alkyl groups, $(\sigma^\circ_R)_{tw}$ is taken to be equal to σ°_R for the corresponding alkyl group in which the substituent has been replaced by a hydrogen atom. [bb] Ref. 43. [cc] Estimated from relationship between σ°_R and $(\sigma^\circ_R)_{tw}$ for NR_2, where $(\sigma^\circ_R)_{tw} = (\sigma^\circ_R)$Alk (footnote *w*), to be equal to the value for the element in Group IV in the same row of the Periodic Table (footnote *q*). [dd] Ref. 42.

second is theoretically preferable, and is supported by consideration of disubstituted acetylenes.[43]

The above correlations may also be formulated as relationships between *A* and σ°_R terms as previously.[2-4] For example equation (11) correlates intensity values

$$A = 26{,}250[\sigma^\circ_R + (\sigma^\circ_R)_{tw} + 0{\cdot}15]^2 + 100 \quad (11)$$
$$(r = 0{\cdot}987,\ 18 \text{ points})$$

from the present results with $[\sigma^\circ_R + (\sigma^\circ_R)_{tw} + 0{\cdot}15]^2$, and is used as a working equation.

Bock and Seidl,[44] on the basis of photoelectron spectra, have concluded that the SiR_3 group interacts with both the orthogonal orbitals of the acetylene bond, However their basic assumption[44] that the $CH_2{\cdot}SiMe_3$ group has no mesomeric effect is incorrect;[45] CH_2SiMe_3 has σ°_R −0·20.

Bogatkin *et al.*[46] have recently observed that the i.r. intensities for the C≡C stretch for compounds $R^1R^2R^3SiC{\equiv}C{-}H$, where R^1, R^2, and R^3 are various alkyl or aryl groups decreased as the electron donating ability of the groups R increased. They concluded that, whatever the substituents on silicon, the organosilicon group accepts electrons from the triple bond. This conclusion is compatible with the relationship developed here.

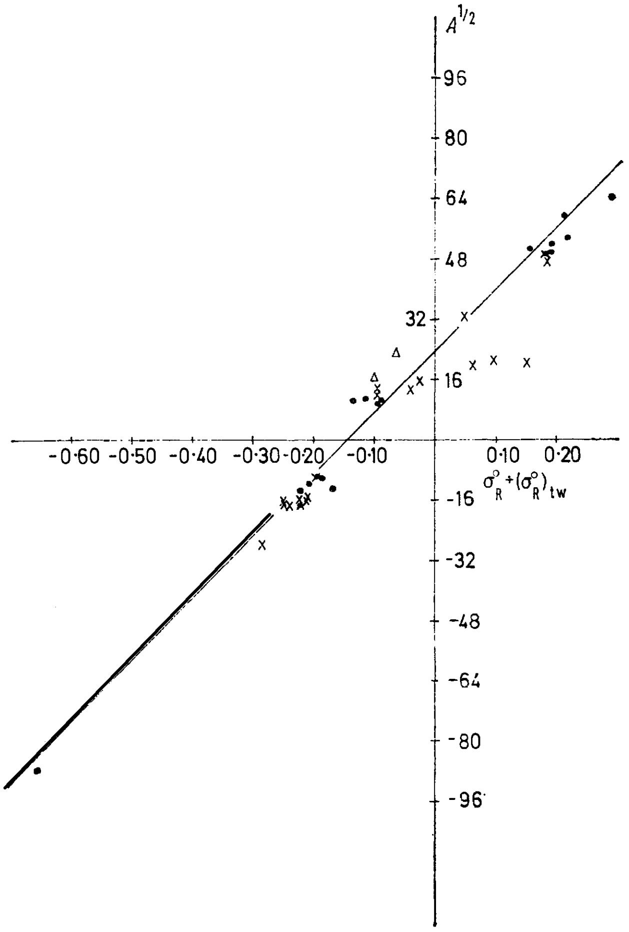

FIGURE 2 Square root of the observed intensity for ν(C≡C) of monosubstituted acetylenes plotted against $\sigma^\circ_R + (\sigma^\circ_R)_{tw}$; (●) present results in CCl_4, (△) present results in polar solvents, (×) literature results; the line shown is defined by the present results

Calculations.—The use of molecular orbital methods to calculate the changing dipole moment during vibration permits the direct calculation[4,38,47,48] of the absolute intensity provided that the form of the normal coordinate is known. The CNDO/2 molecular orbital method[39] has been used most widely and while the approximations in the scheme have been criticised, the charge densities and dipole moments appear to be calculated accurately.[49] We have previously reported

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[43] T. B. Grindley, K. F. Johnson, A. R. Katritzky, H. J. Keogh, C. Thirkettle, and R. D. Topsom, following paper.

[44] H. Bock and H. Seidl, *J. Chem. Soc.* (*B*), 1968, 1158.

[45] For a summary, see N. C. Cutress, A. R. Katritzky, C. Eaborn, D. R. M. Walton, and R. D. Topsom, *J. Organometallic Chem.*, 1972, **43**, 131.

[46] R. A. Bogatkin, O. V. Sverdlova, and V. A. Gindin, *J. Gen. Chem.* (*U.S.S.R.*), 1971, **41**, 2245.

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

[48] See also for example, G. A. Segal and M. L. Klein, *J. Chem. Phys.*, 1967, **47**, 4236; G. A. Segal, R. Bruns, and W. B. Person, *ibid.*, 1969, **50**, 3811; T. P. Lewis and I. W. Levin, *Theor. Chim. Acta*, 1970, **19**, 55; N. B. Colthup and M. K. Orloff, *Spectrochim. Acta*, 1971, **27***A*, 1299; I. W. Levin, *J. Chem. Phys.*, 1971, **55**, 5393; R. Bruns and W. B. Person, *ibid.*, p. 5401.

[49] R. G. Jesaitis, *J. Amer. Chem. Soc.*, 1971, **93**, 3849.

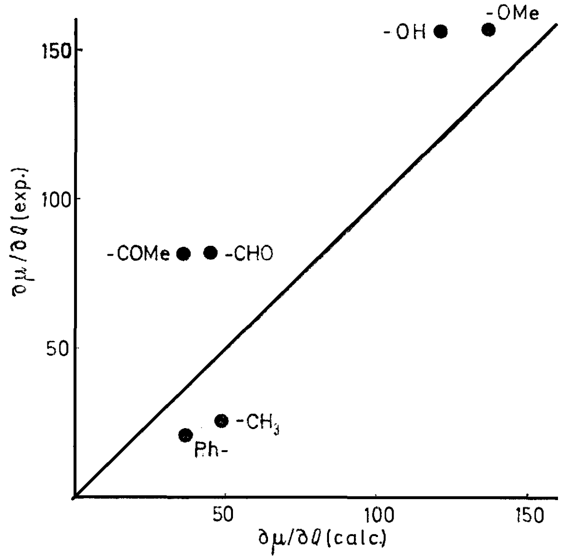

FIGURE 3 Plot of experimental *vs.* calculated $\partial\mu/\partial Q$ values for monosubstituted acetylenes; the line shown has unit slope

good agreement between measured intensities and calculations of the absolute values for the ν_8 and ν_{19} ring vibrations of a series of mono- and di-substituted benzenes[47] and for the ν(C=C) vibration of a series of monosubstituted ethylenes.[4] Using available normal co-ordinates we have calculated the rate of change of dipole moment with normal co-ordinate ($\partial\mu/\partial Q$) for the C≡C stretching vibration for a series of monosubstituted acetylenes by the CNDO method as described above.

The results of these calculations are presented in Table 3 and plotted against the experimental values in Figure 3. The calculated values depend to some extent on the set of normal co-ordinates chosen, as expected; Figure 3 shows a plot of the values calculated by using the co-ordinates for chloroacetylene. The strong anisotropy of the matrix elements in the CNDO/2 calculations on substituted acetylenes may present a problem here,[50] but the electron density and dipole moment values have been shown [9b] to be reasonable. Certainly, the general agreement of calculated and measured intensities provides further support both for the CNDO/2 approach and for the method adopted.

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[50] S. Ehrenson, personal communications.