Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. Part XXXIII.[1] Conjugation of Substituents with the Triple Bond in Disubstituted Acetylenes

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The integrated intensities of the C≡C stretching vibrations are recorded for series of 2-substituted t-butyl- and phenyl-acetylenes. These intensities are related to the resonance effects of the substituents; such resonance interaction is shown to involve both the acetylene π-orbitals.

In the preceding paper[1] we examined the intensities of the C≡C stretching bands of monosubstituted acetylenes. We now report the extension of this work to disubstituted acetylenes of the t-butyl and phenyl series.

Electronic effects in disubstituted acetylenes have been previously examined using a variety of techniques. Acetylenic bond lengths, obtained from *X*-ray[2] and electron diffraction studies,[3,4] have been shown to be insensitive to substitution. The numerous dipole moment studies on disubstituted acetylenes[5,6] can be interpreted in terms of the inductive resonance contributions of the individual substituents. Changes in nuclear quadrupole coupling constants[4,7] for a series of compounds $R_3X\cdot C\equiv CCl$ (X = C, Si, or Ge) have been used to demonstrate p_π–d_π interactions. ^{13}C N.m.r. spectroscopy has been used to demonstrate[8,9] mesomeric charge transfer from oxygen in alkyl ethynyl ethers and to sulphur in alkyl ethynyl thioethers as well as charge polarisation. For alkylethynyl-phosphines and -phosphine oxides,[9] both ^{13}C and ^{31}P n.m.r. studies indicate charge transfer to the phosphorus atom. However, except for oxygen these conclusions are not certain because of the complications of variable acetylenic

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[1] Part XXXII, T. B. Grindley, K. F. Johnson, A. R. Katritzky, H. J. Keogh, C. Thirkettle, R. T. C. Brownlee, J. A. Munday, and R. D. Topsom, preceding paper.

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shielding and of sulphur and phosphorus magnetic anisotropy.

Chemical reactions have also been used to investigate disubstituted acetylenes. The rates of hydrolysis of alkyl-substituted propiolic acids and the rates of decarboxylation of their sodium salts may be related to the inductive and hyperconjugative effects of the alkyl groups.[10,11] The rates of addition of hydrogen bromide to a series of acetylenic [12] ketones, $MeCO{\cdot}C{\equiv}CR$ ($R =$ alkyl or phenyl) correlate with σ^*, as do basicities of alkynylphosphines [13] $R'_2PC{\equiv}CR$, and the dipole moments of tertiary acetylenic phosphine sulphides.[14] Veschambre *et al.*,[15] from studies of acid and base strengths and u.v. spectra of *p*-hydroxy-, *p*-amino-, and *p*-nitrodiphenylacetylenes, and the corresponding *p*-substituted 1,2-diphenylethylenes, concluded that the $C{\equiv}C$ bond transmits electronic effects less effectively than does the $C{=}C$ bond. This is supported by the work of Charton,[6] Fuchs,[16] and Bowden [17] and their co-workers on acetylene reactions. However the transmission of electronic effects has been shown to be significant over a series of acetylenic bonds.[18]

Previous Infrared Results.—The form of the vibration [19,20] in disubstituted acetylenes (I) is different from that in monosubstituted acetylenes. As discussed [1] for monosubstituted acetylenes, mass effects are negligible. Fermi resonance does not in general affect observed intensities significantly although it does affect band shapes (see later).

$$\overset{\leftarrow}{R^2}-\vec{C}\equiv\overset{\leftarrow}{C}-\overset{\rightarrow}{R^1} \qquad \text{(I)}$$

As for monosubstituted acetylenes, numerous studies have appeared on the frequencies and intensities of $C{\equiv}C$ stretching vibrations. Queignec and Wojtkowiak [21] have related the $\nu(C{\equiv}C)$ frequency to differences in electronegativity for six different series of acetylenes although no overall correlation was obtained. A number of authors [22]* have suggested that increased conjugation lowers the frequency. In an early investigation, Wotiz and Miller [23] explained the low intensity for some dialkyl and substituted dialkylacetylenes on the basis of a 'pseudo-centre of symmetry.' The intensities of the $C{\equiv}C$ stretching bands of some germanium, phosphorus, and arsenic compounds have been related [24,25] to σ^*, as have the intensities of the same bands for alkyl and prop-2-ynyl derivatives.[26] Various authors have compared the effect on intensities of individual pairs of groups. Thus an α-carbonyl group enhanced intensities more than an α-cyano-group; [27] phenyl groups enhanced intensities more than alkyl groups.[28] A number of metal and metalloid derivatives have been studied. In these compounds, $Me_3SiC{\equiv}C{-}CH{=}CHX$ ($X = SBu^n$, OBu^n, or NEt_2), the change in intensity was related [29] to the dipole moment of X. In compounds $R_3SiC{\equiv}C{\cdot}COR$, the intensity decreases [30] with increasingly electronegative substituents. The intensity of the $C{\equiv}C$ stretching band for the compounds $Et_3SnC{\equiv}CR$ increased [31] as R was changed from methyl to vinyl to phenyl. Most of this evidence is compatible with the relationships developed in the previous paper [1] between intensities and resonance effects.

EXPERIMENTAL

With one exception, all compounds were prepared by literature methods and their physical properties are listed in Table 1. Their purities were examined by g.l.c. and/or m.p. determination and by spectroscopic methods.

Spectroscopic grade CCl_4 was stored over molecular sieves (4A). Benzene was dried over sodium wire. Chloroform was purified by passing it through alumina immediately prior to use.

The spectroscopic techniques for solutions in CCl_4 [32] and $CHCl_3$ [33] were as previously described. The solvent absorptions in spectra of compounds measured in CCl_4–benzene (9 : 1) were balanced [32] with a variable path length cell using the 1811 cm^{-1} band of benzene. Integration procedures for all compounds were as previously described, and reproducibilities of $A^{1/2}$ were ± 1 for all compounds.

Ethyl 3,3-*Dimethylbut*-1-*ynyl Sulphone.*—Ethyl 3,3-dimethylbut-1-ynyl sulphide [34] (2·5 g), glacial acetic acid

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* See preceding paper (ref. 1) for an outline.

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TABLE 1

Infrared spectra of disubstituted acetylenes ($XC{\equiv}CY$)

Substituents		M.p. or b.p. [a] (°C)[mmHg]	Lit. m.p. or b.p. [a] (°C)[mmHg]	Lit. ref.	Source	ν(C≡C)			
X	Y					ν/cm^{-1}	ε_A	A [b]	$A^{1/2}$
Bu^t	NMe_2	120—123	122—124	*c*	*d*	2220 2231sh	140	5050	71·0
	NMePh				*e*	2240	142	4950	70·3
	SEt	48—50[5·8—6·0]	52[8]	*f*	*f*	2262 2284sh 2245sh	2	96	9·8
	Br	58[118]	54—58[110]	*g*	*g*	2178	2	63	7·9
	I	50—51[22]	54—58[30]	*g*	*g*	2191	2	56	7·5
	Cl	40[150]	35—39[150]	*g*	*g*	2207 2243sh	2	58	7·7
	Me	81—83	82	*h*	*h*	2186 2241sh	<1	27	5·2
	Ph	57—58[2·1]	84[10]	*i*	*j*	2235 2283sh 2189sh	12	266	16·3
	CH_2OH	28[0·4]	71·6[18]	*k*	*k*	2232	19	527	23·0
	CH_2Br	27[3·5]	50—52·5[18—20]	*k*	*k*	2237	49	966	31·1
	CH_2NMe_2	39[33]	55[25]	*l*	*l*	2221 2239sh 2284sh	9	218	14·8
	$CH_2NMe_3{}^+I^-$	180—181‡	183‡	*m*	*m*	2245	66	1240	35·2
	$SiMe_3$	36—39[58]	57[60]	*n*	*o*	2152	71	1590	39·8
	SO_2Et	108[2·2]		*p*	*p*	2209 2173	151 160	6340	79·6
	$CONH_2$	93‡	92·5—93‡	*q*	*r*	2212 2239	100	4870	69·8
	CO_2Me	50[5·2]	66[13]	*q*	*r*	2238	242	6290	79·3
	COCl	34—35[7·5—8]	52[20]	*q*	*s*	2221 2150sh	441	8690	93·2
	CO_2H	80[1·4]	112·5—113[14]	*t*	*t*	2218	266	8990	94·8
Ph	NMe_2	60[0·8]	52[0·2]	*u*	*u*	2231 2202	382 303	15,240	123·5
	SMe	88—89[1·8]	113—114[8]	*v*	*w*	2167	39	818	28·6
	Br	61—62[3·5]	40—41[0·1]	*x*	*x*	2203	21	397	19·9
	I	82—83[1·7]	117[15]	*y*	*z*	2173	3	66	8·1
	Cl	64—65[9]	71[16]	*aa*	*aa*	2223	51	961	31·0
	Me	61[7]	90[20]	*bb*	*bb*	2246 2215	8 5	262	16·2
	CH(Me)OH	129—130[8]	121—122[9]	*cc*	*cc*	2228 2201	9 5	293	17·2
	CH_2OH	89—90[0·2]	97[0·3]	*dd*	*dd*	2236 2195	10 3	291	17·1
	CH_2Br	82—83[0·8]	135[15]	*ee*	*ee*	2260 2221	26 8	766	27·7
	CH_2NMe_2	80—81[1·8]	128[18]	*ff*	*ff*	2331 2313	1 1	28	5·3
	$CH(OEt)_2$	129—131[6]	153—156[19]	*gg*	*gg*	2236	30	982	31·3
	$SiMe_3$	88—90[9·5]	67[5]	*hh*	*hh*	2157	122	2700	52·0
	SO_2Me	60‡	61—62‡	*ii*	*ii*	2184	87	1990	44·6
	CO_2Et	88—90[0·5]	144[13]	*jj*	*jj*	2235 2210	118 97	7690	87·7
	COMe	75[0·9]	122—128[12]	*kk*	*kk*	2202	369	6778	82·3
	CHO	77—78[1·5]	114—117[17]	*gg*	*gg*	2236 2189	75 439	9970	99·8
	CO_2H	136‡	136—137‡	*ll*	*mm*	2224	366	13,710	117·1

[a] Melting points are marked ‡. [b] Measured in CCl$_4$-benzene (9 : 1 v/v). [c] Neth. P. Appl. 6,415,095/1965 (*Chem. Abs.*, 1966, **64**, 1957*d*). [d] H. G. Viehe and M. Reinstein, *Angew. Chem. Internat. Edn.*, 1964, **3**, 506. [e] Donated by Professor H. G. Viehe and used without further purification. [f] Ref. 34. [g] Heel and W. Zeil, *Z. Elektrochem.*, 1960, **64**, 962. [h] L. Brandsma, ' Preparative Acetylenic Chemistry,' Elsevier, Amsterdam, 1971, p. 34. [i] B. S. Kupin and A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), 1961, **31**, 2958 (*Chem. Abs.*, 1962, **57**, 2125*h*). [j] J. A. Taylor, Ph.D. Thesis, University College of Swansea, 1968, [k] P. D. Bartlett and L. J. Rosen, *J. Amer. Chem. Soc.*, 1942, **64**, 543. [l] I. Marszak, J. P. Guermont, and R. Epsztein, *Mém. services chim. état* (*Paris*). 1951, **36**, 301 (*Chem. Abs*, 1954, **48**, 8725*d*). [m] I. Marszak, J.-P. Guermont, R. Epsztein, and J. Jacob, *Compt. rend.*, 1951, **233**, 531. [n] R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *J. Amer. Chem. Soc.*, 1961, **83**, 4385. [o] C. S. Kraihanzel and J. E. Poist, *J. Organometallic Chem.*, 1967, **8**, 239. [p] New compound, see Experimental section for preparation. [q] ' Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965, vol. 2, p. 1206. [r] Synthesised from the acid chloride by standard methods. [s] Prepared from the acid like the acetyl chloride in A. I. Vogel, ' Textbook of Practical Organic Chemistry including Qualitative Organic Analysis,' Longmans, London, 1956, 3rd edn., p. 367. [t] Ref. 10. [u] ' Chemistry of Acetylenes,' ed. H. G. Viehe, Marcel Dekker, New York, 1969, p. 906. [v] Yu. A. Boiko, B. S. Kupin, and A. A. Petrov, *Zhur. org. Khim.*, 1966 **2**, 1923 (*Chem. Abs.*, 1957, **66**, 75,473*c*). [w] M. Schmidt and V. Potschka, *Naturwiss.*, 1963, **50**, 302. [x] S. I. Miller, G. R. Ziegler, and R. Wieleseck, *Org. Synth.*, 1965, **45**, 86. [y] ' Beilsteins Handbuch der Organischen Chemie,' eds. B. Prager and P. Jacobson, vol. V, Springer-Verlag, Berlin, 1922, p. 513. [z] T. H. Vaughn and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1933, **55**, 2150. [aa] R. Truchet, *Ann. Chim.* (*Italy*), 1931, **16**, 309. [bb] C. D. Hurd and A. Tockman, *J. Org. Chem.*, 1958, **23**, 1087. [cc] See footnote *z*, vol. VI, 1923, p. 588. [dd] R. E. Atkinson, R. F. Curtis, D. M. Jones, and J. A. Taylor, *J. Chem. Soc.* (*C*), 1969, 2173. [ee] J. von Braun and L. Tauber, *Annalen*, 1927, **458**, 105. [ff] C. Mannich and Fu Tsong Chang, *Ber.*, 1933, **66***B*, 418. [gg] *Org. Synth.*, Coll. Vol. III, 1955, p. 731. [hh] R. A. Benkeser and R. A. Hickner, *J. Amer. Chem. Soc.*, 1958, **80**, 5298. [ii] G. A. Russel and L. A. Ochrymowycz, *J. Org. Chem.*, 1970, **35**, 2106. [jj] C. Moureu, *Ann. Chim. Phys.*, Series 8, 1906, VII, 560. [kk] U. Nef, *Annalen*, 1899, **308**, 278. [ll] C. Glaser, *Annalen*, 1870, **154**, 141. [mm] M. Tiffeneau, *Compt. rend.*, 1902, **135**, 1346.

acid (10 ml), and hydrogen peroxide (14 ml; 30%), were heated under reflux for 0·5 h, then water (25 ml) was added and the mixture was extracted with ether (3 × 20 ml). The combined extracts were washed with saturated sodium hydrogen carbonate solution (2 × 30 ml) and water (2 × 20 ml), and dried ($MgSO_4$). The ether was distilled off leaving a yellow liquid which was distilled to yield the *sulphone* (0·9 g, 29%) as an oil, b.p. 108° at 2·2 mmHg (Found: C, 54·9; H, 8·1. $C_9H_{14}O_2S$ requires C, 55·1; H, 8·1%); $\nu_{max.}$ (film) 3000—2820, 2220—2110, 1350—1290, 1170—1090, and 810—750 cm^{-1}; $\tau(CCl_4)$ 6·8—7·2 (2H, m), 8·5—8·7 (3H, m), and 8·7 (9H, s).

Band Shapes.—Most of the C≡C stretching bands in the t-butyl series do not occur as a single symmetrical peak. The band shapes vary from a single peak with a slight shoulder to two peaks of comparable intensity with additional shoulders. This phenomenon has been previously observed in disubstituted alkynes and attributed to Fermi resonance with various bands.[28,35] Hüttner and Zeil[36] have recently shown for some t-butylacetylenic halides that the combination band arising from the CH_3 rocking vibration at 1230—1270 cm^{-1} and the C–C≡C skeletal vibration at 880—1030 cm^{-1} is involved in Fermi resonance with the C≡C stretch. Because the intensities of the combination bands are low, the measured intensity is not significantly affected: Table 1 indeed includes acetylenes with intensities of <30 in support of this.

RESULTS AND DISCUSSION

It has been previously shown[37] that $A^{1/2}$ (the square root of the intensity of the band under consideration) is related to σ°_R treated as a vector quantity. The form of the normal co-ordinate for the C≡C stretching vibration of disubstituted acetylenes[19,20] suggested the relationship (1) if the substituents each interact with only one of the acetylene π-orbitals, but (2) if interaction occurs with both acetylene π-orbitals. The experimental results will now be discussed in terms both of equations (1) and (2).

TABLE 2

Disubstituted acetylenes from the literature

Substituent X	Substituent Y	Ref.	Solvent	A_{obs} (original units)	Units	A_{obs}(I.U.P.A.C. practical units)	$A^{1/2}$ [a]
n-C_6H_{13}^{n}	$CONH_2$	*b*	*g*	1·35	*i*	5860	76·6
n-C_6H_{13}^{n}	CHO	*b*	*g*	1·32	*i*	5730	75·7
n-C_6H_{13}^{n}	CO_2H	*b*	*g*	2·38	*i*	10,300	102
n-C_5H_{11}^{n}	CO_2Pr	*b*	*g*	1·3	*i*	5600	75·1
n-C_5H_{11}^{n}	COCl	*b*	*g*	2·09	*i*	9080	95·3
n-C_5H_{11}^{n}	CHO	*b*	*g*	1·34	*i*	5820	76·3
Bu^n	$CH(OH)C_6H_{13}$	*b*	*g*	0·16	*i*	700	26
Bu^n	$Ge(Bu^n)_3$	*c*	*g*	0·479	*i*	2080	45·6
Bu^n	C≡N	*b*	*g*	0·58	*i*	2500	50
Bu^n	CO_2Pr	*b*	*g*	1·49	*i*	6470	80·4
Bu^n	COC_7H_{15}	*b*	*g*	1·27	*i*	5520	74·3
Bu^n	COEt	*b*	*g*	1·18	*i*	5120	71·6
Bu^n	COCl	*b*	*g*	2·25	*i*	9770	98·8
Bu^n	CHO	*b*	*g*	1·35	*i*	5860	76·8
Bu^n	CO_2H	*b*	*g*	2·35	*i*	10,200	101
Pr^n	$Ge(Bu^n)_3$	*c*	*g*	0·437	*i*	1900	43·5
Me	Ph_2P	*d*	*g*	0·31—0·34	*i*	1300—1500	38
Me	Ph_2As	*d*	*g*	0·26—0·37	*i*	1100—1600	37
Me	$Ph_2P(O)$	*d*	*g*	1·25—1·48	*i*	5430—6430	77·0
Me	COPh	*e*	*g*	4·22, 3·35 × 10^{-7}	*j*	3680, 2930	60·6, 54·1
Me	COMe	*e*	*g*	4·36, 0·90 × 10^{-7}	*j*	3810, 786	61·7, 28·0
$CH_2{\cdot}CH{:}CH_2$	$GeEt_3$	*c*	*g*	0·339	*i*	1470	38·4
Ph	Ph_2P	*d*	*g*	0·21—0·31	*i*	910—1300	34
Ph	$Ph_2P(O)$	*d*	*g*	1·73—2·00	*i*	7510—8690	90·0
Ph	C≡N	*f*	*g*	1·77	*i*	7430 [k]	86·1
Ph	$CONH_2$	*f*	*g*	1·49	*i*	6470	80·4
Ph	CO_2Me	*f*	*g*	2·0	*i*	8700	93·2
Ph	COPh	*e*	*g*	11·3 × 10^{-7}	*j*	9870	99·3
Ph	COCl	*f*	*g*	3·92	*i*	7430	86·2
Ph	COMe	*f*	*g*	1·9	*i*	8300	91
Ph	COMe	*e*	*g*	9·51 × 10^{-7}	*j*	8300	83·0
Ph	CO_2H	*f*	*g*	3·65	*i*	15,800	126
CMe_2OH	Ph_2P	*d*	*g*	0·13—0·16	*i*	560—690	25
CMe_2OH	$Ph_2P(O)$	*d*	*h*	0·94—1·18	*i*	4080—5120	67·8
CH(OH)Pr	Et_3Ge	*c*	*g*	0·113	*i*	491	22·1
$Ph_2P(O)$	$[CH_2]_3{\cdot}CH{:}CH$	*d*	*h*	2·21—2·69	*i*	9600—11,700	103·1

[a] Where intensity ranges are given, the $A^{1/2}$ value was obtained from the median of the range. [b] Ref. 27. [c] Ref. 25. [d] Ref. 24. [e] Ref. 28. [f] R. Mathis, L. Lopez, and J. Barrans, *Compt. rend.*, 1964, **258**, 4944. [g] CCl_4. [h] $CHCl_3$. [i] 10^7 mol^{-1} cm. [j] cm^2 mol^{-1} s^{-1}. Converted into I.U.P.A.C. practical units by multiplying by $N_0/(2{\cdot}303 \times 10^3c)$. [k] Omitted from graphs because of potential C≡C, C≡N mixing.

$$A^{1/2} = K_1[\sigma^\circ_R(1) - \sigma^\circ_R(2)] \qquad (1)$$

$$A^{1/2} = K_1\{\sigma^\circ_R(1) + [\sigma^\circ_R(1)]_{tw} - \sigma^\circ_R(2) - [\sigma^\circ_R(2)]_{tw}\} \qquad (2)$$

Alkylacetylenes.—A series of substituted t-butylacetylenes, $Me_3C{\cdot}C{\equiv}CX$, was synthesised; their physical and i.r. spectral properties are listed in Table 1. The

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[35] R. Queignec and B. Wojtowiak, *Compt. rend.*, 1966, **262***B*, 486; R. M. Badger, *J. Chem. Phys.*, 1937, **5**, 178.

[36] W. Hüttner and W. Zeil, *Z. Naturforsch.*, 1970, **25***A*, 1281.

[37] A. R. Katritzky, M. V. Sinnott, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1969, **91**, 628.

t-butyl series was chosen because electronic interaction between the two substituents should be small and because of the low volatility of t-butyl- compared to other alkyl-acetylenes. When $A^{1/2}$ is taken to be negative when $\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(\mathrm{Bu^t})$ is negative, plotting $A^{1/2}$ for the C≡C stretching vibration *vs.* $\sigma^{\circ}_{R}(1) - \sigma_{R}(\mathrm{Bu^t})$ gave a good straight line (Figure 1), represented by equation (3). The σ°_{R} values used in this treatment are listed in Table 3 of the preceding paper. The intensities of the C≡C stretching bands for numerous alkylacetylenes of type RC≡CX are recorded in the literature, and those for which σ°_{R} values are available are compiled in Table 2. Plotting $A^{1/2}$ *vs.* σ°_{R} for the compounds of both Tables 1 and 2 yields equation (4) (see Figure 1). This correlation is less satisfactory than that of equation (3); however, there exist discrepancies in intensities reported for identical or similar compounds by different workers. The treatment just described is based on the implicit assumption that substituent–acetylene interaction takes place only with one of the acetylene π-orbitals. Interaction with both the (orthogonal) π-orbitals should be related to the *sum* of the interactions found in substituted benzenes in the fully conjugated planar position and in the twisted orthogonal position. We have denoted [38] the σ°_{R} values relevant to the latter position as $(\sigma^{\circ}_{R})_{\mathrm{tw}}$.

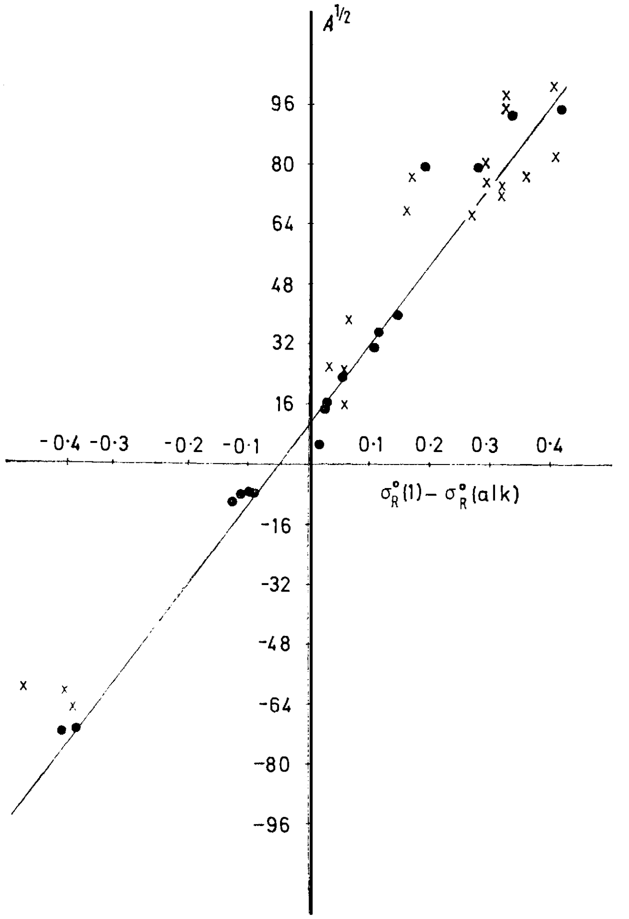

FIGURE 1 The square root of the intensity of the C≡C stretch ($A^{1/2}$) for substituted alkylacetylenes, plotted against $[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(\mathrm{alk})]$; (●) present study, (×) literature results; The line shown was derived from present measurements

$$A^{1/2} = 213[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(\mathrm{Bu^t}) + 0{\cdot}05] \quad (3)$$
$$(r = 0{\cdot}995,\ 17\ \text{points})$$
$$A^{1/2} = 198[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(\mathrm{alk}) + 0{\cdot}09] \quad (4)$$
$$(r = 0{\cdot}980,\ 41\ \text{points})$$

The alternative treatment is to plot $A^{1/2}$ against the right hand side of equation (2) where substituent (2) is t-butyl. The $(\sigma^{\circ}_{R})_{\mathrm{tw}}$ terms are defined as previously [1] as the ability of the substituent to interact by resonance orthogonal to the normal geometry and are listed in Table 4 of the preceding paper. $[\sigma^{\circ}_{R}(\mathrm{Bu^t})]_{\mathrm{tw}}$ is equal to $\sigma^{\circ}_{R}(\mathrm{Bu^t})$ $(-0{\cdot}125)$, since the $\mathrm{Bu^t}$ group has C_3 symmetry. We take $-0{\cdot}06$ for $[\sigma^{\circ}_{R}(\mathrm{Ph})]_{\mathrm{tw}}$; this value is derived from the phenylacetylenes discussed later in this paper. The heavy halogens represent a special case which, for reasons explained later in this paper, is omitted from this treatment. Again, treatment of the present results alone gives the good correlation of equation (5) whereas treatment including literature results gives the similar but less precise relation of equation (6). Figure 2 demonstrates the satisfactory

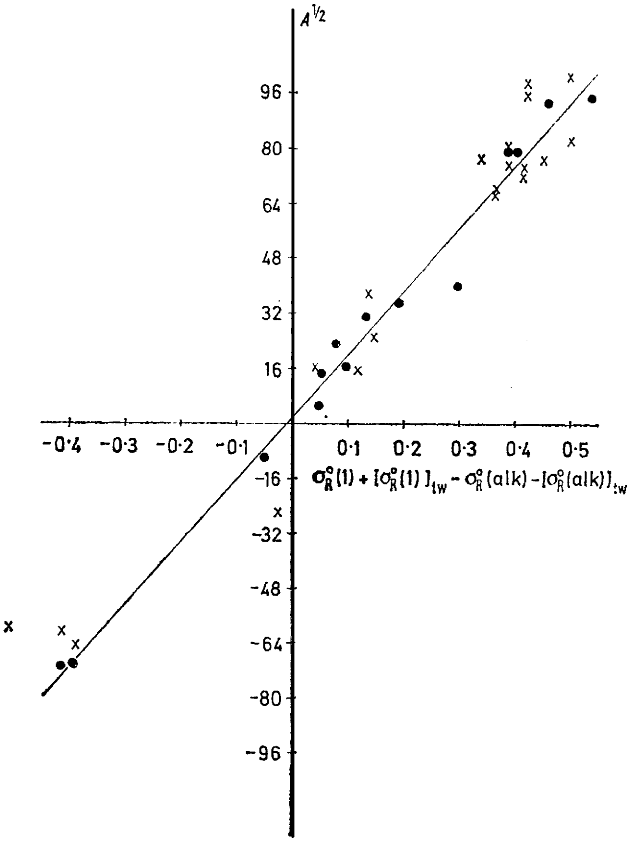

FIGURE 2 The square root of the intensity of the C≡C stretch ($A^{1/2}$) for substituted alkylacetylenes, plotted against $\{\sigma^{\circ}_{R}(1) + [\sigma^{\circ}_{R}(1)]_{\mathrm{tw}} - \sigma^{\circ}_{R}(\mathrm{alk}) - [\sigma^{\circ}_{R}(\mathrm{alk})]_{\mathrm{tw}}\}$; (●) present study, (×) literature results; the line shown was derived from present measurements

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[38] T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *Tetrahedron Letters*, 1972, 2643.

linear relation, which also, in contrast with Figure 1, passes close to the origin.

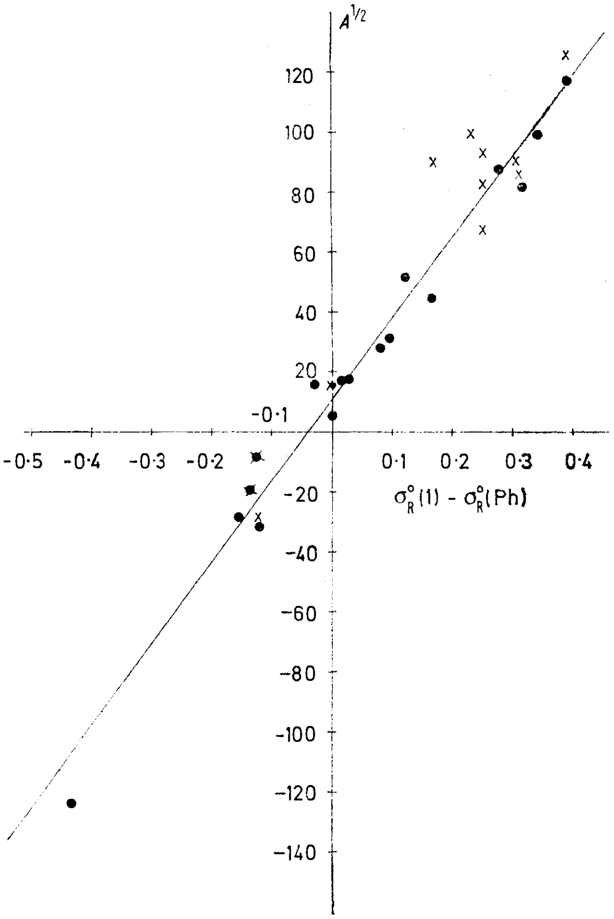

FIGURE 3 The square root of the intensity of the C≡C stretch ($A^{1/2}$) for substituted phenylacetylenes, plotted against [σ°_{R} (1) − σ°_{R}(Ph)]; (●) present study, (×) literature results; the line shown was derived from present measurements

Equation (5) gives $\sigma^{\circ}_{R}(CONH_2)$ as +0·13. No value could be obtained previously because ν(C=O) obscures ν_8 for benzenes and ν(C=C) for ethylenes. The result compares well with σ°_{R} values for CHO of 0·24 and CO_2Me of 0·16.

Phenylacetylenes.—The same treatments as above for (*a*) the series of phenylacetylenes synthesised for this work (Table 1) and (*b*) as (*a*) but including also the literature values (Table 2) yielded equations (7)—(10)

$$A^{1/2} = 181\{\sigma^{\circ}_{R}(1) + [\sigma^{\circ}_{R}(1)]_{tw} - \sigma^{\circ}_{R}(Bu^{t}) - [\sigma^{\circ}_{R}(Bu^{t})]_{tw} + 0{\cdot}01\}\ (r = 0{\cdot}992,\ 15\ \text{points}) \qquad (5)$$

$$A^{1/2} = 174\{\sigma^{\circ}_{R}(1) + [\sigma^{\circ}_{R}(1)]_{tw} - \sigma^{\circ}_{R}(Bu^{t}) - [\sigma^{\circ}_{R}(Bu^{t})]_{tw} + 0{\cdot}03\}\ (r = 0{\cdot}982,\ 36\ \text{points}) \qquad (6)$$

$$A^{1/2} = 270[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(Ph) + 0{\cdot}04]\ (r = 0{\cdot}988,\ 18\ \text{points}) \qquad (7)$$

$$A^{1/2} = 277[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(Ph) + 0{\cdot}04]\ (r = 0{\cdot}976,\ 30\ \text{points}) \qquad (8)$$

$$A^{1/2} = 233\{\sigma^{\circ}_{R}(1) + [\sigma^{\circ}_{R}(1)]_{tw} - [\sigma^{\circ}_{R}(Ph) - 0{\cdot}06]\}\ (r = 0{\cdot}983,\ 15\ \text{points}) \qquad (9)$$

$$A^{1/2} = 249\{\sigma^{\circ}_{R}(1) + [\sigma^{\circ}_{R}(1)]_{tw} - [\sigma^{\circ}_{R}(Ph) - 0{\cdot}06]\}\ (r = 0{\cdot}980,\ 24\ \text{points}) \qquad (10)$$

and Figures 3 and 4. Equation (9) defines $(\sigma^{\circ}_{R})_{tw}$ for the phenyl group as −0·06. It is expected to be intermediate between zero, the $(\sigma^{\circ}_{R})_{tw}$ value for COR groups, and −0·1, the σ°_{R} value for Me.

Comparison of Alternative Treatments.—Equations (3), (4), (7), and (8) predict that the intensities of ν(C≡C) for symmetrically disubstituted acetylenes are non-zero, which is not valid on theoretical[19] and experimental grounds.* Equations (5), (6), (9), and (10), involving $(\sigma^{\circ}_{R})_{tw}$ terms, predict that symmetrically disubstituted acetylenes will have zero intensity. In other words equations (3), (4), (7), and (8) predict that the $[(d\mu/dQ)(1) - (d\mu/dQ)(2)]$ term will be proportional to $[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(2) + \text{constant}]$. Such a constant would be inconsistent with the results in other systems where the intensities of multiple bond stretching vibrations[39] are involved, and would be of uncertain physical meaning. Brownlee and Taft,[40] from CNDO/2 calculations on

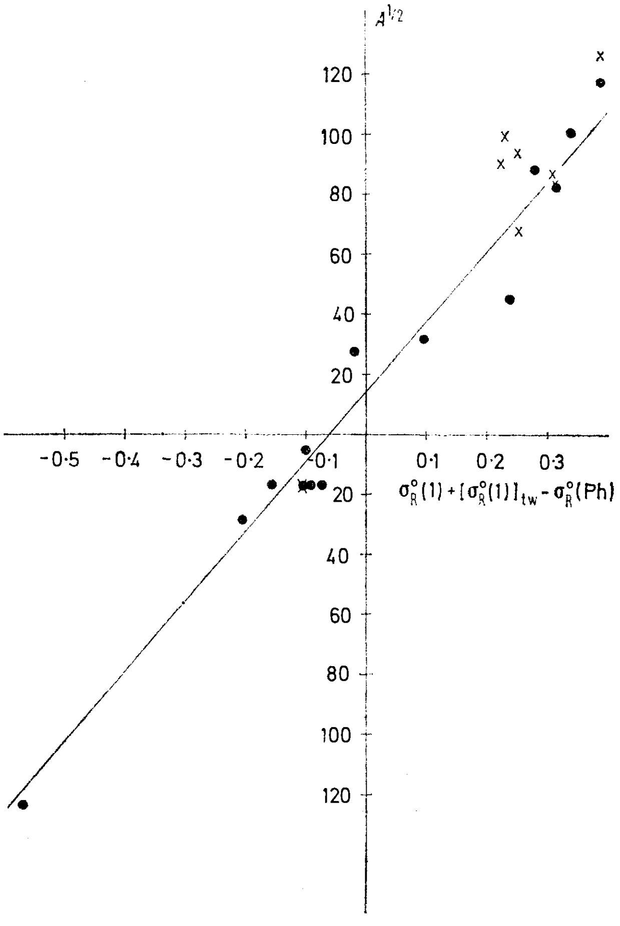

FIGURE 4 The square root of the intensity of the C≡C stretch ($A^{1/2}$) for substituted phenylacetylenes, plotted against {σ°_{R} (1) + [σ°_{R} (1)]$_{tw}$ − σ°_{R}(Ph)}; (●) present study, (×) literature results; the line shown was derived from present measurements

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* All symmetrically disubstituted compounds measured for this study had A values of <30.

[39] A. R. Katritzky and R. D. Topsom, *Angew. Chem. Internat. Edn.*, 1970, **9**, 87.

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

fluoroacetylenes, found (Table VI in ref. 40) that the fluorine $2px$- and $2pz$-orbitals (the lone pair orbitals which can interact with the π-system) have identical charge densities for those substituents for which we take $\sigma°_R = (\sigma°)_{tw}$ and different charge densities for those in which $\sigma°_R \neq (\sigma°_R)_{tw}$. The same is not true for ethylenes or benzenes. For those reasons, for the remainder of our consideration of acetylene intensities we apply equations (5) and (9), involving the appropriate $(\sigma°_R)_{tw}$ terms. Although equations (6) and (10) are in reasonable agreement with (5) and (9), the variety of sources for which the data for (6) and (10) were obtained makes these less precise.

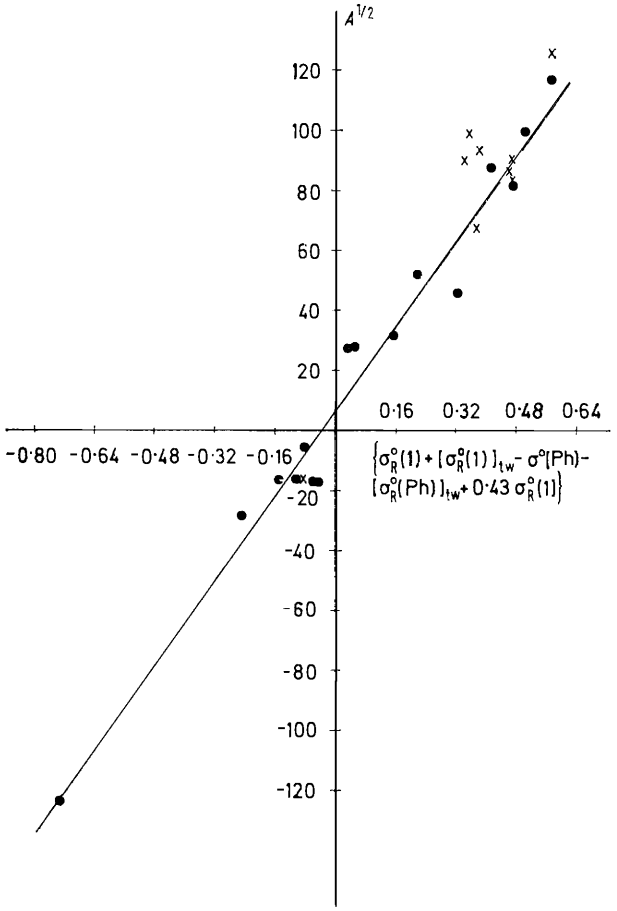

FIGURE 5 The square root of the intensity of the C≡C stretch ($A^{1/2}$) for substituted phenylacetylenes, plotted against $\{\sigma°_R\ (1) + [\sigma°_R\ (1)]_{tw} - \sigma°_R(Ph) - [\sigma°_R(Ph)]_{tw} + 0{\cdot}43\,\sigma°_R\ (1)\}$; (●) present study, (×) literature results; the line shown was derived from present measurements

Substituent–Substituted Interactions in Disubstituted Acetylenes.—Equations (5) and (9) are to be compared with equation (11) for monosubstituted acetylenes. We interpret the small difference between the constants of 164 for equation (11) and 181 for equation (5) as indicating little interaction between the substituents in the t-butylacetylenes. In the phenylacetylene series, we believe that a direct resonance interaction between the substituent and the phenyl ring causes the constant 233 of equation (9) to be larger than that in the monosubstituted or t-butyl series. Such direct resonance interaction is indeed proved by the variable intensities of the ν_8 vibrations (ν_{16} in Herzberg's notation) of the phenyl ring. A direct interaction term, λ, defined in equation (12), can be used to convert equation (9) into equation (13). The term λ is a product as previously,[41] of $\sigma°_R$ for the substituent, and 0·43 for the phenyl group. The use of $\sigma°_R$ is appropriate for the substituent as direct interaction with the π-orbitals of the phenyl ring occurs *via* one only of the acetylene π-orbitals. The phenyl constant of 0·43 was obtained empirically from a plot of the difference between $A^{1/2}/181$ and $\{\sigma°_R(1) + [\sigma°_R(1)]_{tw} - \sigma°_R(Ph) - [\sigma°_R(Ph)]_{tw}\}$ against $\sigma°_R$. Figure 5 shows a plot of equation (13).

These considerations allow definition of equation (14), which describes the intensities of C≡C stretching vibrations of all the disubstituted acetylenes measured. Figure 6 shows a plot of equation (14), including all available data.

$$A^{1/2} = 164[\sigma°_R + (\sigma°_R)_{tw} + 0{\cdot}15] \tag{11}$$

$$\lambda = 0{\cdot}43\sigma°_R \tag{12}$$

$$A^{1/2} = 181\{\sigma°_R(1) + [\sigma°_R(1)]_{tw} - \sigma°_R(Ph) - [\sigma°_R(Ph)]_{tw} + \lambda\} \tag{13}$$

$$A = 30{,}100\{\sigma°_R(1) + [\sigma°_R(1)]_{tw} - \sigma°_R(2) - [\sigma°_R(2)]_{tw} + \lambda\}^2\ [r = 0{\cdot}963,\ 29\ \text{points}\ (\text{int. } 0{\cdot}0002)] \tag{14}$$

$(\sigma°_R)_{tw}$ *for Halogens.*—The heavy halogens, Cl, Br, and I, possess negative $\sigma°_R$ values of considerable magnitude, but they are also capable of electron acceptor

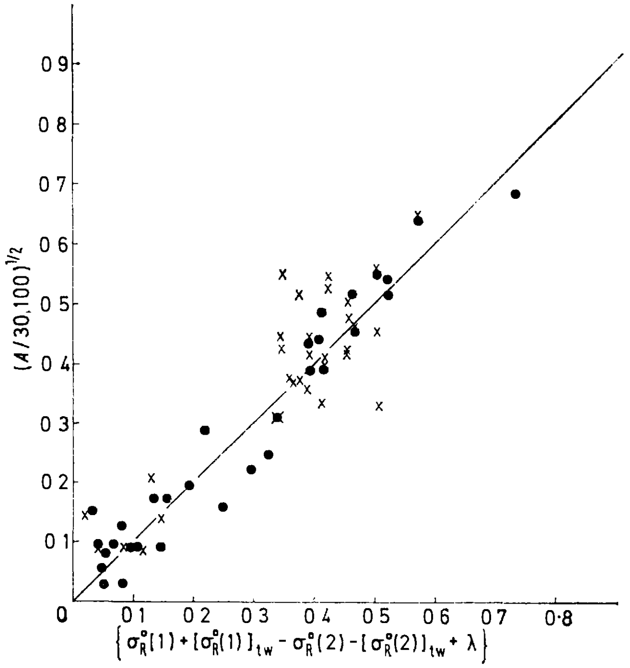

FIGURE 6 $(A/30{,}000)^{1/2}$ for all disubstituted acetylenes plotted against $\{\sigma°_R\ (1) + [\sigma°_R\ (1)]_{tw} - \sigma°_R\ (2) - [\sigma°_R\ (2)]_{tw} + \lambda]$; (●) present study, (×) literature results; the line shown was derived from present measurements properties involving delocalisation into their *d*-orbitals.[41] It would be expected that their effective $(\sigma^\circ_R)_{tw}$ values, for simultaneous interaction with a second π-system, should be less in magnitude. Empirically, we find from equation (5) values of —0·07, —0·06, and —0·07, respectively. Our physical interpretation is that σ°_R is reduced from —0·22, —0·23, and —0·22 respectively to *ca.* —0·15 in each case for simultaneous interaction with two π-systems.

We thank the 3M Company for studentships (to K. F. J. and H. J. K.).

[3/1201 *Received, 8th June,* 1973]

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[41] P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1968, **90**, 1767.