

Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. Part XXXI.¹ Intramolecular Interactions in Arylacetylenes¹

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Integrated i.r. intensities of both the ν_8 ring-stretching and $\nu(\text{C}\equiv\text{C})$ bands of a series of *m*- and *p*-substituted phenylacetylenes indicate that the ethynyl group is a weak resonance donor when attached to a benzene ring. The group can become a strong resonance donor or acceptor in situations of high electron demand or excess, respectively.

We have shown that the i.r. intensities of ring-stretching bands in benzenes² and $\nu(\text{C}=\text{C})$ in ethylenes³ are directly related to the intramolecular electronic interactions in these compounds, as measured by the empirical sigma parameter $\sigma^{\circ}_{\text{R}}$. This work is being extended to acetylenes, and we now report work on monoarylacetylenes $\text{ArC}\equiv\text{CH}$. Apart from phenylacetylene, ring vibrations in such compounds have not been studied previously: earlier work on the frequency⁴ and intensity⁵ of $\nu(\text{C}\equiv\text{C})$ is discussed later.

The ethynyl group is of particular interest as the direction as well as the magnitude of its interaction can vary.^{6,7} We have previously shown that NCO, NCS, and other groups⁸ are strongly polarised according to electron demand; and literature work^{9,10} indicates the same for the 2-furyl and 2-thienyl groups as substituents. The results disclosed in this paper confirm that ethynyl is also strongly polarisable in both directions.

¹ Part XXX, N. C. Cutress, T. B. Grindley, A. R. Katritzky, C. Eaborn, D. R. M. Walton, and R. D. Topsom, *J. Organometallic Chem.*, in the press.

² For summaries see (a) A. R. Katritzky and R. D. Topsom, *Angew. Chem. Internat. Edn.*, 1970, **9**, 87; (b) A. R. Katritzky and R. D. Topsom, 'Linear Free Energy Relationships and Optical Spectroscopy,' in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, p. 119.

³ J. M. Angelelli, A. R. Katritzky, R. Pinzelli, M. V. Sinnott, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1969, **91**, 4013.

⁴ A. D. Allen and C. D. Cook, *Canad. J. Chem.*, 1963, **41**, 1084.

EXPERIMENTAL

Compounds.—Physical properties and methods of preparation are summarised in Table 1. The structures were confirmed by n.m.r. and i.r. methods, and the purities were further established by g.l.c.

Spectroscopy.—The spectra (Tables 2 and 3) were recorded on a Perkin-Elmer 125 i.r. spectrometer (sodium chloride cells). The solvent used was CCl_4 -benzene (90:10 v/v), spectroscopic grade. 4-Nitrophenylacetylene was measured in CHCl_3 , which was purified before use by passing down an alumina column. The spectroscopic technique and the integration procedure for the bands were as previously described.^{11,12} The reproducibility in $A^{1/2}$ values is ± 1 .

The concentration dependence of the intensities of both the acetylene and benzene ν_8 bands (ν_{16} in Herzberg's notation) of phenylacetylene was investigated over as large a concentration range as was practicable (0.22—3.00M for the acetylene band and 0.68—3.81M for the benzene ν_8

⁵ T. L. Brown, *J. Chem. Phys.*, 1963, **38**, 1049.

⁶ J. A. Landgrebe and R. H. Rynbrandt, *J. Org. Chem.*, 1966, **31**, 2585.

⁷ C. Eaborn, A. R. Thompson, and D. R. M. Walton, *J. Chem. Soc. (B)*, 1969, 859.

⁸ A. R. Katritzky, H. J. Keogh, S. Ohlenrott, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1970, **92**, 6855.

⁹ F. Fringuelli, G. Marino, and A. Taticchi, *J. Chem. Soc. (B)*, 1971, 2302.

¹⁰ F. Fringuelli, G. Marino, and A. Taticchi, *J. Chem. Soc. (B)*, 1971, 2304.

¹¹ R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1966, **88**, 1413.

¹² P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1968, **90**, 1767.

bands). The variation with concentration was found to be insignificant.

TABLE 1
Substituted phenylacetylenes

Substituent on ring	B.p. or m.p. ^a (°C) [mmHg]	Lit. b.p. or m.p. ^a (°C) [mmHg]	Ref. for prep.
3-MeO	110—114 [35]	80 [12] ^b	<i>b</i>
3-Br	82—83 [12]	89 [15] ^c	<i>c</i>
3-Cl	36—38 [25]	71 [15] ^c	<i>c</i>
3-Me	106—108 [105]	58—59 [14] ^b	<i>b</i>
3-NO ₂	110—113 [18]	118—120 [20] ^b	<i>b, f</i>
4-MeO	40—42 [0.5]	86 [9] ^b	<i>b, g</i>
4-F	54—56 [17]	34—35 [10] ^b	<i>b</i>
4-Br	62 ‡	64—65 ‡ ^d	<i>d</i>
	78—80 [13]	88—90 [16] ^b	
4-Cl	43.5—44 †	43 † ^b	<i>h</i>
	66—69 [15]	62—63 [13] ^b	
4-Bu ^t	70 [2]	67 [1.7] ^e	<i>i</i>
4-Me	66—69 [20]	59—60 [16] ^b	<i>d</i>
4-NO ₂	148—149 †	149—150 ^b †	<i>b, f, j</i>

^a M.p.s denoted by †. ^b Ref. 4. ^c R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.*, 1965, 384. ^d T. L. Jacobs, *Org. Reactions*, 1949, **5**, 50. ^e The method of ref. 4 for the preparation of 3-methylphenylacetylene was adapted. ^f A. T. Dann, A. Howard, and W. Davies, *J. Chem. Soc.*, 1928, 605. ^g J. R. Johnson, *Org. Reactions*, 1942, **1**, 249. ^h The method given in footnote *d* for the preparation of 4-bromophenylacetylene was adapted. ⁱ The method of footnote *d* for the preparation of 4-methylphenylacetylene was adapted. ^j S. Dutt, *Quart. J. Chem. Soc.*, 1925, **1**, 297 (*Chem. Abs.*, 1925, **19**, 2475).

RESULTS AND DISCUSSION

1600 *cm*⁻¹ Band for *meta*-Substituted Phenylacetylenes.—The σ°_R value of ± 0.07 determined¹³ for phenylacetylene itself appeared to be in good agreement with the ¹⁹F n.m.r.-derived value¹⁴ of $+0.08$. However, the

the use of which is also preferable for determination of the magnitude of small values.

$$A_{meta} = 19,000\{[\sigma^{\circ}_R(1)]^2 + [\sigma^{\circ}_R(2)]^2 + \sigma^{\circ}_R(1)\sigma^{\circ}_R(2)\} + 340 \quad (1)$$

Intensities calculated for *meta*-substituted phenylacetylenes with σ°_R (C≡CH) $+0.07$ are in poor agreement with the theoretical values obtained using equation (1)¹⁵ (see Figure 1). Use of σ°_R (C≡CH) -0.07 is a considerable improvement, and we consider that the ¹⁹F n.m.r. value of $+0.08$ is distorted by substituent-substituent interaction, as previously noted¹² (see later). A value of σ°_R (C≡CH) -0.09 gives the most satisfactory correlation for the *meta*-compounds (Figure 1) and we henceforth adopt this value.

1600 *cm*⁻¹ Band for *para*-Substituted Phenylacetylenes.—The intensities of *para*-derivatives are correlated¹⁶ by equation (2) (which replaces the equation previously¹²

$$A_{para} = 15,000[\sigma^{\circ}_R(1) - \sigma^{\circ}_R(2) + \lambda]^2 + 170 \quad (2)$$

used). In this equation λ represents the mutual interaction between the substituents. That such interaction exists is shown clearly by Figure 2, for when λ is equated to zero wide deviations occur.

These interactions were treated by methods previously developed for through-conjugation in *para*-disubstituted benzenes.¹² Thus for one donor and one acceptor substituent, $\lambda = K_A(\sigma^+ - \sigma^{\circ})$, where σ^+ and σ° refer to the donor substituent, and K_A is a constant characteristic of the acceptor.¹² We find that K_A (C≡CH) = 0.21

TABLE 2
I.r. spectral data for *meta*-substituted phenylacetylenes

Substituent	σ°_R	σ^+	1600 <i>cm</i> ⁻¹ band			2100 <i>cm</i> ⁻¹ band			$\left(\frac{A - 340}{19,000}\right)^{1/2}$	$f_m\sigma^{\circ}_R$ ^c
			ν/cm^{-1}	ϵ_A ^a	A ^b	ν/cm^{-1}	ϵ_A ^a	A ^b		
NMe ₂	-0.53	-0.21	1596	483	9938	2107	21	299	0.71	0.58
			1572	164						
			1598	128						
MeO	-0.43	+0.05	1582	152	5523	2110	10	178	0.52	0.47—0.49
			1574	167						
			1609	58	3331					
F ^d	-0.34	+0.35	1581	276		2112	2	36	0.40	0.38
			1589	80	2006					
			1557	117						
Br	-0.23	+0.40	1594	85	1104	2112	3	53	0.30	0.26
			1563	105						
			1597	27	289					
Cl	-0.22	+0.40	1580	23		2113	3	48	0.20	0.25
			1615	12						
			1605	8	530					
Me	-0.10	-0.07	1574	12		2106	10	165	0.10	0.13
			1605	8	530					
			1574	12						
NO ₂	+0.17	+0.67	1605	8	530	2120	4	88	0.10	0.16
			1574	12						
			2102	2						

^a Peak extinction coefficient $\epsilon_A = a_{max}/cl$ in $l \text{ mol}^{-1} \text{ cm}^{-2}$ where a_{max} is the peak maximum, c is the concentration in mol l^{-1} and l is the cell path length in cm. ^b The integrated intensity for the band in $l \text{ mol}^{-1} \text{ cm}^{-2}$. ^c $f_m\sigma^{\circ}_R = \{[\sigma^{\circ}_R(1)]^2 + [\sigma^{\circ}_R(2)]^2 - \sigma^{\circ}_R(1)\sigma^{\circ}_R(2)\}^{1/2}$. ^d Donated by Dr. D. R. M. Walton.

use of monosubstituted benzenes does not give the sign of σ°_R , and for values <0.1 is subject to error.¹³ The sign of σ°_R is given by *meta*-substituted compounds¹⁵

¹³ R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1968, **90**, 1757.

¹⁴ R. W. Taft, personal communication.

¹⁵ A. R. Katritzky, M. V. Sinnott, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1969, **91**, 628.

well correlates the points for Me, Bu^t, Cl, Br, F, OMe, and NMe₂ (Figure 2); the ethynyl group is thus shown to be, in situations of electron excess, readily polarisable as an acceptor, *cf.* K_A (COMe) 0.16,¹⁶ K_A (NCO) 0.30.¹⁷

¹⁶ R. T. C. Brownlee, D. G. Cameron, R. D. Topsom, A. R. Katritzky, and A. F. Pozharsky, *J.C.S. Perkin II*, 1974, 247.

¹⁷ G. Butt, M. Davis, Y. T. Pang, R. D. Topsom, and A. R. Katritzky, *J.C.S. Perkin II*, 1974, 260.

For π -acceptor substituents, again $\lambda = K_A(\sigma^+ - \sigma^\circ)$, as above. Although a $K_A(\text{NO}_2)$ of 0.55 has been quoted,¹² based on this, the literature⁶ values of $\sigma_p^+(\text{C}\equiv\text{CH}) = 0.179$ and $\sigma_p(\text{C}\equiv\text{CH}) = 0.233$ give a λ value that appears to be far too small. However, in this compound there is intensity sharing of the ν_8 vibrations with the NO_2 asymmetric stretch at 1521 cm^{-1} . Fermi

the $\nu(\text{C}\equiv\text{C})$ intensity are correlated well by σ^+ , and poorly by other sigma parameters as shown:

Parameter	σ^+	σ	σ°
Correlation coefft.	0.995	0.970	0.905
Standard deviation	1.02	2.88	4.78

A similar conclusion was reached by T. L. Brown,⁵ however his intensities were measured in I.U.P.A.C.

TABLE 3

I.r. spectral data for *para*-substituted phenylacetylenes

Substituent			1600 cm^{-1} region			2110 cm^{-1} region			$(\frac{A-170}{15,000})^{1/2}$	[-0.09 - $\sigma_{\text{R}}^\circ(2)$]	λ^e	f_p^d
	σ_{R}	σ^+	ν/cm^{-1}	ϵ_A^a	A^b	ν/cm^{-1}	ϵ_A^a	A^b				
NMe ₂ ^e	-0.53	-1.70	1609	626	7285	2102	152	1923	0.69	0.44	0.26	0.70
MeO	-0.43	-0.78	1607	335	4064	2107	48	668	0.51	0.34	0.14	0.48
			1572	74								
F	-0.34	-0.07	1602	174	1636	2113	11	150	0.31	0.25	0.05	0.30
Br	-0.23	+0.15	1615	5	389	2108	9	118	0.12	0.14	-0.01 ^f	0.13
			1585	48								
Cl	-0.22	+0.11	1608	4	378	2113	9	117	0.12	0.13	0.01 ^f	0.14
			1592	48								
Bu ^t	-0.13	-0.25	1606	15	224	2109	27	306	0.06	0.04	0.01 ^g	0.05
	-0.125		1575	3								
Me	0.10	-0.31	1616	7	220	2107	23	317	0.06	0.01	0.03	0.04
			1604	9								
NO ₂	+0.17	+0.79	1610	84	3216				0.45	0.26		
			1594	333								

^a Peak extinction coefficient, $\epsilon_A = a_{\text{max}}/cl$ in $l \text{ mol}^{-1} \text{ cm}^{-2}$ where a_{max} is the peak maximum, c is the concentration in mol l^{-1} , and l is the cell path length in cm. ^b The integrated intensity in $l \text{ mol}^{-1} \text{ cm}^{-2}$. ^c $K_A(\sigma^+ - \sigma^\circ)$. ^d $f_p = |[\sigma_{\text{R}}^\circ(1) - \sigma_{\text{R}}^\circ(2) + K_A(\sigma^+ - \sigma^\circ)]|$. ^e Donated by Dr. D. R. M. Walton. ^f Also corrected for d -orbital interaction, $K_X = 0.22$ for Cl, 0.32 for Br. ^g Value of $(\sigma^+ - \sigma)$ from T. J. Broxton, G. Capper, L. W. Deady, A. Lenko, and R. D. Topsom, *J.C.S. Perkin II*, 1972, 1237.

resonance between these vibrations which led to increased ν_8 vibration intensity has been observed to be

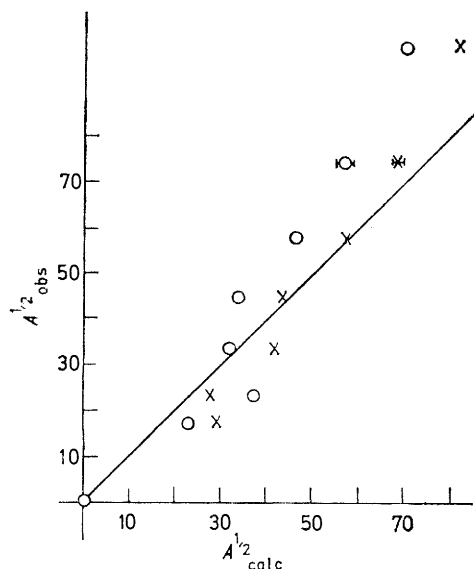


FIGURE 1 Plot of the square root of the observed intensity for the ν_8 mode of *meta*-substituted phenylacetylenes against the square root of the intensity calculated from equation (1) using (a) +0.09 as σ_{R}° value for ethynyl (O) and (b) -0.09 as σ_{R}° value for ethynyl (X) (see text); the line shown is of unit slope. (The range of values shown for the OMe substituent arises from the asymmetry factor; see ref. 15)

important previously for *p*-nitrobenzenes where the *para*-substituent is electron withdrawing.¹⁶

Intensity of the $\nu(\text{C}\equiv\text{C})$ Vibration.—The $A^{1/2}$ values for

standard units, which are related to the I.U.P.A.C. practical units used in this paper by the factor 2.303. The intensities measured by both Brown⁵ and ourselves are correlated by equation (3), with $r = 0.997$. All the

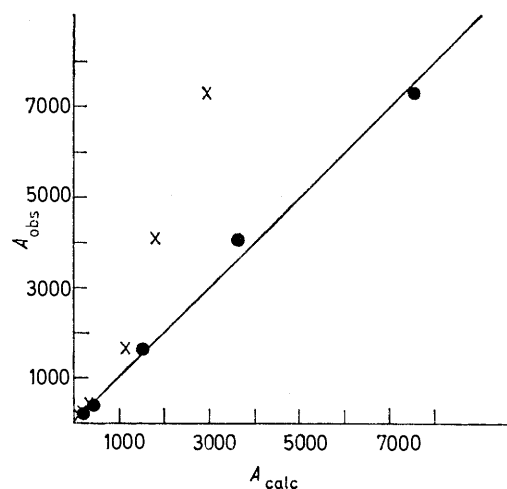


FIGURE 2 Plot of observed intensity for the ν_8 mode of *para*-substituted phenylacetylenes against the intensity calculated from equation (2) using (a) $\lambda = 0$ (X) and (b) λ values (●) for individual substituents as detailed in the text; the line shown is of unit slope

results of Brown and ourselves are shown in Figure 3, where the scales are related by equation (3). They fit

$$A_{(\text{Brown})} = 2.69A_{\text{obs}} \quad (3)$$

equation (4) with $r = 0.989$.

$$A^{1/2}_{\text{C}\equiv\text{C}} = -17.6\sigma^+ + 12.9 \quad (4)$$

Correlations with σ^+ have been recently observed for the intensities of the $\nu(\text{C}\equiv\text{N})$ band of substituted benzonitriles¹⁸ and of the SO_2 symmetric and asymmetric stretches of substituted phenyl sulphones.¹⁹

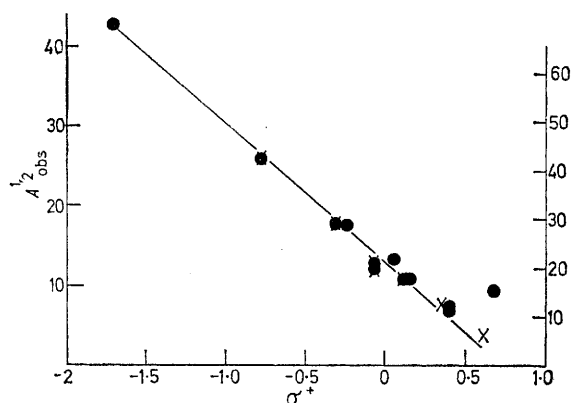


FIGURE 3 Plot against σ^+ values of the substituents of the square root of the integrated intensity of $\nu(\text{C}\equiv\text{C})$ of arylacetylenes (a) as determined in present work (left-hand scale) (●); (b) as reported by T. L. Brown⁵ (right-hand scale) (×); the right- and left-hand scales have been adjusted as described in the text, and the line is that of equation (4)

Frequency of the $\nu(\text{C}\equiv\text{C})$ Mode.—Allen and Cook⁴ found little variation of this frequency in a variety of mono-substituted phenylacetylenes, and no correlation of such small variations as were found. The $\nu(\text{C}\equiv\text{C})$ bands for the present compounds were all within the range 2106—2120 cm^{-1} . Although electron-donor substituents tend to give frequencies at the lower end of this range, there is no precise relationship.

Electronic Nature of the $\text{C}\equiv\text{CH}$ Group: Comparison with Previous Work.—In general agreement with the above results, Cook and Danyluk²⁰ have related the chemical shift of the ethynyl proton in *para*-substituted phenylacetylenes to $-0.330\sigma_{\text{I}} - 0.408\sigma_{\text{R}}$. Otto and

¹⁸ L. W. Deady, A. R. Katritzky, R. A. Shanks, and R. D. Topsom, *Spectrochim. Acta*, 1973, **29A**, 115.

¹⁹ N. C. Cutress, T. B. Grindley, A. R. Katritzky, M. Shome, and R. D. Topsom, preceding paper.

Wenzke,²¹ on the basis of a comparison of the dipole moments of substituted benzenes and some *para*-substituted phenylacetylenes showed that through-resonance in the latter compounds was negligible. For the derivatives studied²¹ (Cl, Br, Me, NO_2), the through-resonance effect as observed in this publication is also small (see Figure 2).

Work by Landgrebe and Rynbrandt⁶ and by Eaborn, Thompson, and Walton⁷ has established the following sigma constants for ethynyl: $\sigma_{\text{p}}^+ 0.18$, $\sigma_{\text{p}} 0.23$, $\sigma_{\text{p}}^- 0.52$, $\sigma_{\text{m}}^+ 0.33$, $\sigma_{\text{m}} 0.21$. These workers have pointed out that these figures indicate that the ethynyl group is strongly electron withdrawing by the inductive effect, but that its resonance effect is variable in that it can act as a strong donor (*cf.* $\sigma_{\text{p}}^+ - \sigma_{\text{p}}$ and especially $\sigma_{\text{p}}^+ - \sigma_{\text{m}}^+$ both negative) or as a strong acceptor (*cf.* $\sigma_{\text{p}}^- - \sigma_{\text{p}}$ positive). (Both groups comment on the unusual positive value for $\sigma_{\text{m}}^+ - \sigma_{\text{m}}$: we believe this to result from the greater sensitivity of the solvolysis reaction to inductive effects as well as resonance effects.)

Our results support strongly the above conclusions: in particular the large λ values for *para*-substituted phenylacetylenes with both electron donor and acceptor substituents confirms the variable resonance effects of ethynyl depending on the electron demand of the system to which the $\text{C}\equiv\text{CH}$ group is attached. However, for phenylacetylene itself the present results indicate that the ethynyl group is a resonance donor: a similar conclusion was recently reached²² from n.m.r. chemical shifts.

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²⁰ C. D. Cook and S. S. Danyluk, *Tetrahedron*, 1963, **19**, 177.

²¹ M. M. Otto and H. H. Wenzke, *J. Amer. Chem. Soc.*, 1934, **56**, 1314.

²² D. Rosenberg and W. Drenth, *Tetrahedron*, 1971, **27**, 3893.