Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. Part XXXVII.[1] 1,1-Disubstituted Ethylenes

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Infrared intensities of the ν(C=C) vibration of 1,1-disubstituted ethylenes are proportional to the sum of the squares of the σ^0_R constants of the substituents. This result is rationalised in terms of the contributions of the substituents to the rate of change of dipole moment with normal co-ordinate. CNDO/2 MO calculations of charge densities and intensities are also reported.

WE have shown previously [2] that the integrated intensities of the ν(C=C) band for monosubstituted ethylenes are correlated by the σ^0_R values of the substituents according to equation (1). In the monosubstituted benzene series the analogous relationship between A_{ν_6} (ν_{16} in Herzberg's notation) and the substituent constant σ^0_R led, on application to disubstituted benzenes, to a significant elucidation of the electronic interactions in these compounds.[3-5] In the expectation of similar progress we are now investigating disubstituted ethylenes; the present paper records our results for the 1,1-disubstituted compounds.

$$A = 27{,}100(\sigma^0_R)^2 + 80 \qquad (1)$$

EXPERIMENTAL

Compounds available commercially were checked by g.l.c. and purified as necessary. Table 1 lists the physical properties of compounds prepared by literature methods. The purities of all compounds were checked by g.l.c. and/or m.p. and by n.m.r. and i.r. spectroscopy.

Spectroscopic grade carbon tetrachloride was stored over molecular sieves (4A). Chloroform was passed through alumina immediately prior to use. Dimethyl sulphoxide was distilled from calcium hydride and stored over molecular sieves.

Most of the spectral measurements were made in carbon tetrachloride as described previously.[6] In a few cases the compounds were insufficiently soluble in this solvent and were measured in chloroform or in dimethyl sulphoxide in calcium fluoride cells.[7] Integration of absorption bands was carried out as previously [3] and the error in the integrated intensities, A (the mean of four determinations), is estimated to be ±1 in units of $A^{\frac{1}{2}}$.

1,1-Diethoxyethylene and 1-chloro-1-ethoxyethylene underwent ready hydrolysis to give ethyl acetate. In these cases the amount of impurity was estimated at the time of measurement from the integrated intensity of the carbonyl band of the contaminating ethyl acetate and the necessary correction made. The weight percentage of ethyl acetate observed was 2·5% in the former and 3·0% in the latter case.

Calculation of Intensities.—The observed intensity of an i.r. absorption band in I.U.P.A.C. units (A in l mol^{-1} cm^{-2}) is given by equation (2), where b is the concentration in mol l^{-1} and l is the path length in cm. The intensity is related to the rate of change of dipole moment with normal co-ordinate [8] ($\partial\mu/\partial Q$ in e.s.u.) by equation (3) where N_0 is Avogadro's number and c is the velocity of light in cm s^{-1}. The calculation of $\partial\mu/\partial Q$ has been described previously [9-12] and essentially follows ref. 9. The geometries of the equilibrium and

TABLE 1

Physical properties of 1,1-disubstituted ethylenes prepared in this work

Substituents		M.p.[a] or b.p. (°C) [mmHg]	Lit. m.p.[a] or b.p. (°C) [mmHg]	Ref.
OEt	OEt	126—128	83—85 [200]	*b*
OEt	Cl	89·5—90	89·5—92·5	*c*
OEt	Bu^n	30 [10]	113—113·5	*d*
OEt	Me	63—64	61·2—61·8	*e*
OEt	CN	68 [60]	63 [60]	*f*
Cl	Bu^t	97—98	97—99	*g*
Cl	Bu^n	115—116	109·6 [680]	*h*
Cl	$CH_2N^+Me_3Cl^-$	174 ‡		*i*
Cl	CO_2H	64—65 ‡	64—65 ‡	*j*
Me	$CH_2N^+Me_3Cl^-$	196 ‡		*i*
CN	$CH_2N^+Me_3I^-$	189—190 ‡	110 ‡	*k*
Cl	CO_2Me	40 [15]	57—59 [55]	*l*

[a] M.p. indicated by ‡. [b] P. R. Johnson, H. M. Barnes, and S. M. McElvain, *J. Amer. Chem. Soc.*, 1940, **62**, 964. [c] L. Heslinga and J. F. Arens, *Rec. Trav. Chim.*, 1957, **76**, 982. [d] M. F. Shostakovskiĭ and M. Mamedov, *Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk*, 1959, 1636 (*Chem. Abs.*, 1960, **54**, 8595*f*). [e] M. L. Sherrill and G. F. Walter, *J. Amer. Chem. Soc.*, 1936, **58**, 742. [f] C. C. Price, E. C. Coyner, and D. DeTar, *J. Amer. Chem. Soc.*, 1941, **63**, 2796. [g] P. D. Bartlett and L. J. Rosen, *J. Amer. Chem. Soc.*, 1942, **64**, 543. [h] G. A. Chukhadzhyan, E. O. Azhandzhyan, and L. G. Melkonyan, *Armyan. khim. Zhur.*, 1966, **19**, 597 (*Chem. Abs.*, 1967, **66**, 29,265*p*). [i] Prepared according to the procedure given by E. Grovenstein, jun., S. Chandra, C. E. Collum, and W. E. Davis, jun., *J. Amer. Chem. Soc.*, 1966, **88**, 1275. [j] C. S. Marvel, J. Deck, H. G. Cooke, jun., and J. C. Cowan, *J. Amer. Chem. Soc.*, 1940, **62**, 3495. [k] J. Stevens, Ph.D. Thesis, University of East Anglia, 1972. [l] C. S. Marvel and J. C. Cowan, *J. Amer. Chem. Soc.*, 1939, **61**, 3156.

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several vibrationally distorted configurations corresponding to the mode under discussion are calculated. The dipole moment in each of these configurations is then calculated using the CNDO/2 technique; the rate of change of dipole moment with normal co-ordinate can then be deduced for each of its cartesian components.

$$A = (bl)^{-1} \int \log_{10} (I_0/I) d\nu \tag{2}$$

$$A = N_0\pi(2{\cdot}303 \times 3000c^2)^{-1}(\partial\mu/\partial Q)^2 \tag{3}$$

$$\left[\sum_{\mu}^{n}\sum_{\nu}^{n} (P_{\mu,\nu} - P_{\mu,\nu}')^2\right]^{\frac{1}{2}} \leqslant \delta \tag{4}$$

The standard CNDO/2 program [13] was modified [14] to converge on the bond order matrix according to equation (4) where $P_{\mu,\nu}$ are the elements of the bond order matrix and $P_{\mu,\nu}'$ are the same quantities saved from the previous iteration.

TABLE 2

L Matrix elements for mono- and 1,1-di-substituted ethylenes [a]

	L_1	L_2	L_3	L_4	L_5	L_6	L_7	L_8	L_9
$H_2C{=}CHCl$	0·396	−0·129	0·015	0·026	0·019	−0·0602	−0·265	−0·380	−0·313
$H_2C{=}CCl_2$	0·406	−0·174		0·034		−0·0657		−0·321	

[a] Linear co-ordinates in Å; angular co-ordinates in rad. The angular co-ordinates given by Sverdlov [16] have been divided by the C–Cl (1·73 Å) or the C–H (1·08 Å) bond lengths where appropriate. The internal co-ordinates corresponding to L_1—L_9 are given in Figure 1.

The equilibrium geometries were calculated from standard bond lengths and angles compiled by Pople and Gordon.[15] The geometries of the vibrationally distorted configurations were determined from the form of the vibration for vinylidene chloride as described by the matrix elements, L_i [16] given in Table 2. We therefore assume that the form of the vibration is essentially insensitive to the nature of the substitution; an assumption which we have found to hold well in both the benzene [10-12] and monosubstituted ethylene [9] series.

It has recently been pointed [17] out that for ethylene and other small molecules containing the methylene group that more than one solution for the molecular force field exists. In the case of ethylene itself, the solution chosen originally by Crawford, Lancaster, and Inskeep [18] has been shown [17,19] to be the incorrect one. Although Sverdlov makes no mention of this problem in the case of the chloroethylenes, in view of these recent results the reliability of Sverdlov's data may not be beyond doubt. However, our intensity calculations based on Sverdlov's data reported in this paper and previously [9] are in satisfactory agreement with the experimental values. The incremental changes in the internal co-ordinates, R_i are specified through the transformation of equation (5) where Q is the normal co-ordinate for the vibration. The factors given in Table 2 referring to bond lengths (Å) and bond angles (rad) correspond to the internal co-ordinates of Figure 1. ΔQ is in units of $u^{\frac{1}{2}}$ Å where u is the unified atomic mass unit. Dipoles were calculated at five points along the normal co-ordinate; $\Delta Q = 0, \pm 0{\cdot}04, \pm 0{\cdot}14$, corresponding to 20 and 70% of the maximum amplitude of the vibration found by equating $hc\nu$ to the increase in potential energy caused by making one of the normal co-ordinates different from zero: $E = \frac{1}{2}\lambda\Delta Q^2$ where $\lambda = 4\pi^2c^2\nu$.[20] The calculated dipole moment for each geometry is plotted against the corresponding value of ΔQ and the gradient $\Delta\mu/\Delta Q$ at $Q = 0$ determined by a least-squares procedure then converted into the required units; e.s.u. through equation (6) for each of the in-plane cartesian components.

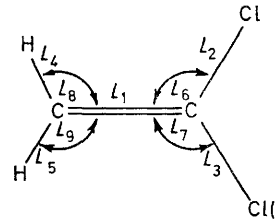

FIGURE 1 Key to L matrix elements for mono- and 1,1-di-substituted ethylenes

$$\Delta R_i = L_i \Delta Q \tag{5}$$

$$\partial\mu/\partial Q \simeq 77{\cdot}60\Delta\mu/\Delta Q \tag{6}$$

RESULTS AND DISCUSSION

The dipole transition moments, like those in monosubstituted ethylenes seem to follow π electron properties as described by $\sigma^0{}_R$ values (see below) which can be understood in terms of the previously [3] developed vector model.

$$\partial\mu/\partial Q = \sum_{i}^{n} (\partial\mu/\partial Q)_i \tag{7}$$

$$A = a\sum_{i}^{n}\sum_{j}^{n} (\partial\mu/\partial Q)_i \,.\, (\partial\mu/\partial Q)_j + w \tag{8}$$

$$A = a'[\sigma^0{}_R(1)^2 + \sigma^0{}_R(2)^2 + 2\sigma^0{}_R(1)\sigma^0{}_R(2)\cos(\theta_1 - \theta_2)] + (w) \tag{9}$$

In this approach we assume that the total dipole derivative, $\partial\mu/\partial Q$ can be represented as the sum of n vectors, $(\partial\mu/\partial Q)_i$ characteristic of the separate interaction of each of the n substituents with the double bond [equation (7)]. Using equation (3) and adding a constant w to allow for any background spectral activity included in the practical intensities, equation (8) results. a is a constant of proportionality and the term to the right of the summation signs is the scalar product of the

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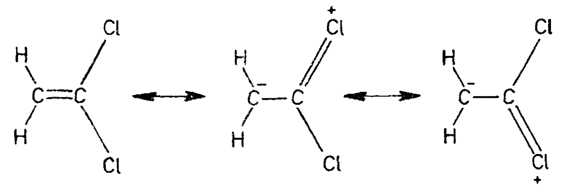
two vectors $(\partial\mu/\partial Q)_i$ and $(\partial\mu/\partial Q)_j$ (*i.e.* the product of their scalar magnitudes multiplied by the cosine of the angle between them). Comparison of equations (1) and (8) suggests that $\sigma^0{}_R(i) \propto |(\partial\mu/\partial Q)_i|$ which in turn suggests the form of the empirical equation relating to the observed intensities in disubstituted ethylenes ($n = 2$); equation (9). The qualitative significance of the vectors in equation (8) and hence the angles θ_1 and θ_2 can be envisaged from a consideration of the changes in weight of the valence bond canonical structures during the vibration. It can be seen from a comparison of the corresponding matrix elements (Table 2) that the form of the vibration of 1,1-disubstituted ethylenes is very little changed with respect to that of the monosubstituted compounds. This form for vinylidene chloride is shown in Figure 2 for a five-fold change in the normal coordinate. During the positive phase of the vibration the length of the C=C bond increases while the C–Cl bonds become shorter. Thus, the contributions to the resonance hybrid of structures (2) and (3) relative to (1) increase during this distortion, resulting in an oscillating dipole moment. This dipole moment is essentially a superposition of two vectors, one resulting from the interaction of each of the substituents with the double bond. As a result of the high symmetry of monosubstituted benzenes this type of valence bond approach made possible an unambiguous assignment of the angular parts of the constituent dipole changes associated with the substituents in disubstituted benzenes.[3,4] Unfortunately such a simplification cannot be made in this case and we must admit additional empirical parameters. However, to avoid a proliferation of such parameters, we are forced to seek a solution of equation (9) in terms of the ' best ' value of $\theta_1 - \theta_2$ appropriate to the entire series.* With this assumption we have fitted the measured intensity data (Table 3) to equation (8) using a dual parameter regression analysis which leads to equation (10). Thus the dipole derivative vectors of the two substituent contributions add at almost 90°; however, the cosine term is so small that we consider it to be hardly statistically significant and have analysed the data for the best fit to the line A *vs.* $[\sigma^0{}_R(1)^2 + \sigma^0{}_R(2)^2]$ with equation (11) as the result. The standard deviation of the intensities calculated from equation (10) from the observed intensities was 9·8% of the r.m.s. of the data which only rises to 10·0% when equation (11) is used. Thus adoption of the simpler equation seems entirely desirable. The correlation is presented graphically in Figure 3 where we have plotted $[(A - 60)/24{,}100]^{\frac{1}{2}}$ against $[\sigma^0{}_R(1)^2 + \sigma^0{}_R(2)^2]^{\frac{1}{2}}$ for comparison with the line of unit slope. These quantities are also collected in Table 3. The overall linearity of the plot demonstrates that the electronic effects of the substituents monitored in this way and correlated with their $\sigma^0{}_R$ parameters are rather accurately additive.



(1) (2) (3)

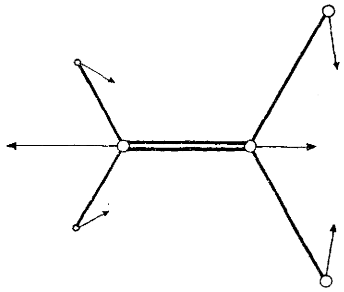


FIGURE 2 Form of the ν(C=C) vibration for vinylidene chloride described by the L matrix elements of Table 2 [16]

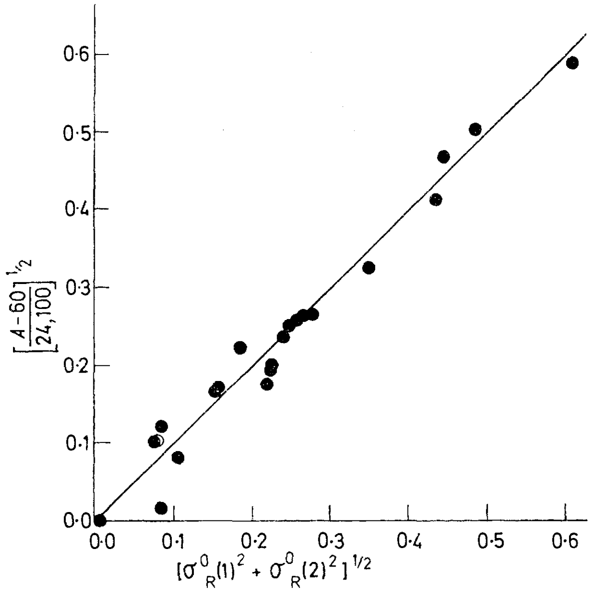


FIGURE 3 $[(A - 60)/24{,}100]^{\frac{1}{2}}$ *vs.* $[\sigma^0{}_R(1)^2 + \sigma^0{}_R(2)^2]^{\frac{1}{2}}$ for 23 1,1-disubstituted ethylenes

To investigate further the precise nature of this additivity we have calculated the charge distribution in a

$$A = 23{,}500[\sigma^0{}_R(1)^2 + \sigma^0{}_R(2)^2 + 2\sigma^0{}_R(1)\sigma^0{}_R(2)\cos 88°] + 80 \qquad (10)$$

$$A = 24{,}100[\sigma^0{}_R(1)^2 + \sigma^0{}_R(2)^2] + 60 \qquad (11)$$

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* We have also fitted the measured intensity data to equation (9) assuming a separate angle, characteristic of each group, by using a multiple parameter, function minimisation program; VA02A, available from the Numerical Analysis Group of the Theoretical Physics Division, Atomic Energy Research Establishment, Harwell, Didcot, Berks. (M. J. D. Powell, *Computer J.*, 1965, **7**, 155). The values found for the slope and intercept were 27,600 and 50 respectively and the angles (deg.) characteristic of each substituent were OEt, 50·0; Cl, 44·7; Bu^t, 51·5; Bu^n, 45·3; Me, 46·8; CH_2Cl, 87·1; $CH_2\overset{+}{N}Me_3$, 123·5; CN, –66·5; CHO, 45·8; CO_2Me, 42·0; and CO_2H, 30·1. With the angles defined in this way the angle between two $\sigma^0{}_R$ vectors is $\theta_1 + \theta_2$. The resulting standard deviation of the calculated intensities from the observed is only 4·4% (that expected on the basis of an uncertainty of ±1 in units of $A^{\frac{1}{2}}$ in the measured intensities is $\leqslant$3%): however, since a relatively large number of disposable parameters have been introduced, the physical significance of these results is uncertain and we will not pursue this type of analysis further in this paper.

TABLE 3

Infrared data [a] for 1,1-disubstituted ethylenes

Substituents				1640 cm^{-1} band				
1	2	$\sigma^0_R(1)$ [b]	$\sigma^0_R(2)$ [b]	ν(C=C)	ε_A [c]	A [d]	R_g [e]	f_g [f]
OEt	OEt	−0·43	−0·43	1642	330	8434	0·589	0·608
OEt	Cl	−0·43	−0·22	1638	222	6138	0·502	0·483
				1576	37			
OEt	Me	−0·43	−0·10	1666	213	5340	0·468	0·441
				1600	46			
OEt	CN	−0·43	0·04	1614	342	4188	0·414	0·432
Cl	Cl	−0·22	−0·22	1614	164	2708	0·331	0·311
				1552	16			
Cl	Me	−0·22	−0·10	1641	83	1438	0·239	0·242
Cl	CN	−0·22	0·04	1603	96	1032	0·201	0·224
				1576	4			
Me	Bu^n	−0·10	−0·12	1644	42	791	0·174	0·156
Me	CN	−0·10	0·04	1624	22	339	0·108	0·108
				1650	3			
Cl	CH_2Cl	−0·22	−0·04	1647	66	1064	0·204	0·224
				1631	56			
Cl	Bu^n	−0·22	−0·12	1633	101	1625	0·255	0·251
Cl	Bu^t	−0·22	−0·13	1617	94	1680	0·259	0·256
				1644	24			
Cl	CO_2H	−0·22	0·29	1614	90	2656	0·328	0·356
				1598	62			
Bu^n	OEt	−0·12	−0·43	1652	155	5349	0·468	0·446
				1596	59			
Me	CH_2Cl	−0·10	−0·04	1654	15	313	0·102	0·108
				1638	6			
Me	CHO [g]	−0·10	0·06	1636	20	440	0·126	0·117
Me	CO_2Me	−0·10	0·15	1638	71	1300	0·227	0·180
CF_3	CN	0·11	0·04	1650	3	100	0·041	0·117
Cl	CO_2Me	−0·22	0·15	1604	74	1740	0·264	0·266
				1627	37			
Cl	$CH_2N^+Me_3Cl^-$ [g]	−0·22	−0·03 [i]	1624	57	844	0·180	0·222
Me	$CH_2N^+Me_3Cl^-$ [g]	−0·10	−0·03 [i]	1643	23	260	0·091	0·104
CN	$CH_2N^+Me_3I^-$ [g]	0·04	−0·03 [i]	[j]	[j]	[j]	[j]	0·050
CO_2Me	$CH_2N^+Me_3I^-$ [g]	0·15	−0·03 [i]	1626	34	755	0·170	0·153

[a] Measured in CCl_4 solution unless otherwise specified. [b] From ref. 2 if available, otherwise from ref. 3. [c] ε_A, the peak extinction coefficient $= a_{max.}/cl$, where $a_{max.}$ is the absorbance at the peak maximum, c is the concentration (mol l^{-1}) and l is the path length (cm). [d] A is the integrated absorption intensity of the main and subsidiary bands taken together, in l mol^{-1} cm^{-2}. [e] $R_g = \{[(A - 60)/24,100]\}^{\frac{1}{2}}$. [f] $f_g = \{\sigma^0_R(1)^2 + \sigma_R^0(2)^2\}^{\frac{1}{2}}$. [g] Measured in $CHCl_3$ solution. [h] Measured in Me_2SO solution. [i] Ref. 22. [j] No band found in the 1640 cm^{-1} region.

series of 1,1-disubstituted ethylenes using the CNDO/2 technique and give the σ and π charges transferred to the ethylenic nucleus in Table 4 together with the calculated static dipole moments for comparison with available experimental values. The same charge density data for vinyl compounds are given in Table 5. In Figure 4 the sum of the π charges calculated in the corresponding vinyl compounds are plotted against those calculated directly for the 1,1-disubstituted compounds. These data are compared in three different ways; at the α-position, the β-position, and as the total charge transferred (α + β) to the ethylenic double bond. In each case the correspondence between the directly calculated data and those summed in the vinyl compounds is very close, although the *total* π charge transfer is noticeably the most closely additive. Thus it is clear that, at least within the CNDO/2 approximation, the π charges transferred to the double bond are additive properties of the substituents. This however, may be less true than Figure 4 implies as we have used standard rather than accurate experimental geometries in the calculations and have thus not taken account of small geometric changes that may take place on disubstitution. The σ charges are not additive and considerable saturation effects are observed. The calculated values of $\partial\mu/\partial Q$ reported in Table 4 are in good agreement with the observed values; the relationship is shown graphically in Figure 5 and

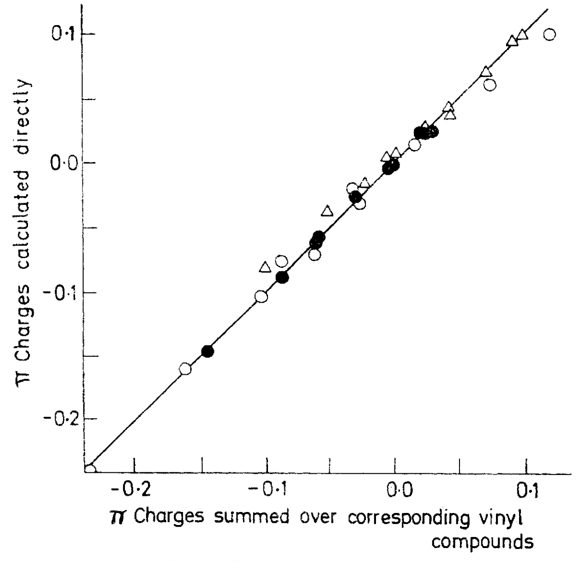

FIGURE 4 Comparison of excess π charges calculated directly with those summed over the values calculated in the corresponding vinyl compounds for 1,1-disubstituted ethylenes $H_2C=CXY$, where X,Y = OMe, Me, CN, CF_3: ● = Σq^π; ○ = $q^\pi{}_\alpha$; △ = $q_{\pi\beta}$

TABLE 4

Calculated charge densities and dipole transition moments from CNDO/2 theory for 1,1-disubstituted ethylenes

Substituents [a]		μ_{CNDO}	Σq^{σ} [b]	Σq^{π} [c]	$q^{\pi}{}_{\alpha}$ [d]	$q^{\pi}{}_{\beta}$ [e]	$\left\{\frac{\partial\mu}{\partial Q}\right\}_{\text{CNDO}}$ [f]	$\left\{\frac{\partial\mu}{\partial Q}\right\}_{\text{Obs}}$ [g]	
OMe	OMe	2·49	0·3065	−0·1447	0·0944	−0·2391	186·7 (214·4)	165·7	166·3 [h]
OMe	Me	0·94	0·1628	−0·0872	0·0715	−0·1785	127·3 (151·2)	131·6	132·3 [h]
OMe	CN	3·60	0·1932	−0·0585	0·0435	−0·1020	109·8	116·3	117·2 [h]
OMe	CF_3	3·22	0·1564	−0·0625	0·0069	−0·0694	105·0		
Me	Me	0·62 [i]	0·0153	−0·0263	0·0482	−0·0745	50·3 (58·8)	49·0	50·9 [j]
Me	CN	2·95 [k]	0·0443	−0·0024	0·0266	−0·0290	33·4	30·2	33·3
Me	CF_3	2·20	0·0049	−0·0029	−0·0165	0·0136	20·7		
CN	CN	3·02	0·0775	0·0243	0·0049	0·0199	2·4		
CN	CF_3	2·90	0·0381	0·0242	−0·0382	0·0624	23·2	11·5	18·1
CF_3	CF_3	2·62	0·0075	0·0220	−0·0814	0·1034	44·6 (46·8)		

[a] The *s-cis* conformation has been assumed for all methyl vinyl ethers. [b] The net σ charge summed over all the atoms of the ethylene skeleton. [c] The net π charge summed over both carbon atoms of the ethylene skeleton. [d] The net π charge at the α carbon. [e] The net π charge at the β carbon. [f] Calculated according to the form of the vibration derived from vinyl chloride, or in parentheses, from vinylidene chloride. [g] The first column has been corrected for an overtone of 60 [from equation (11)]. [h] Data for the ethoxy-compound. [i] Experimental value, 0·503 (V. W. Laurie, *J. Chem. Phys.*, 1961, **34**, 1516). [j] Data for $H_2C{=}C(Me)Bu^n$. [k] Experimental value, 3·69 (A. L. McClellan, ' Tables of Experimental Dipole Moments,' W. H. Freeman, San Francisco, 1963).

TABLE 5

Charge densities calculated from CNDO/2 theory for monosubstituted ethylenes

Substituents	μ_{CNDO}	$\mu_{\text{Obs.}}$ [b]	Σq^{σ} [c]	Σq^{π} [d]	$q^{\pi}{}_{\alpha}$ [e]	$q^{\pi}{}_{\beta}$ [f]
OMe [a]	1·23	1·27 [g]	0·1493	−0·0718	0·0459	−0·1177
Me	0·34	0·36	0·0021	−0·0151	0·0274	−0·0425
CN	2·98	3·89	0·0523	0·0131	−0·0017	0·0148
CF_3	2·33	2·45	0·0371	0·0118	−0·0487	0·0605

[a] The *s-cis* conformation is assumed. [b] From A. L. McClellan, ' Tables of Experimental Dipole Moments,' W. H. Freeman, San Francisco, 1963. [c] The net σ charge summed over all atoms of the ethylene skeleton $H_2C{=}CH{-}$. [d] The net π charge summed over both atoms of the ethylene skeleton. [e] The net π charge at the α carbon atom. [f] The net π charge at the β carbon atom. [g] Data for OEt.

gives some confidence in the deductions based on the calculated charge distribution. Surprisingly we find that the calculations based on the form of the vibration derived from a normal co-ordinate analysis of vinyl chloride to be in better agreement with experimental values than those based on the form of the vibration derived from vinylidene chloride which emphasises the difficulties inherent in using the same form of the vibration for different compounds.

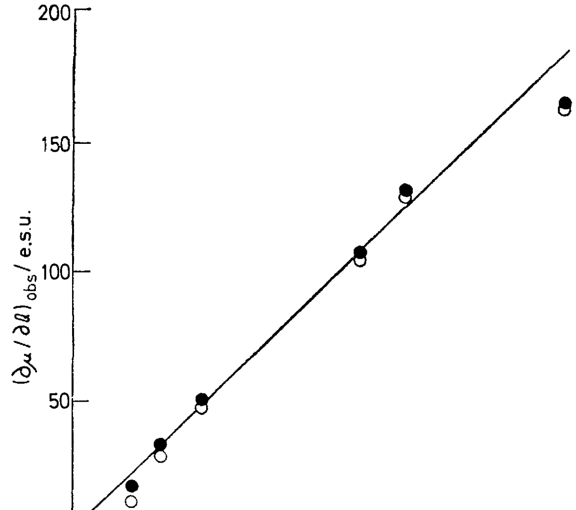

FIGURE 5 Comparison of observed and calculated values of $(\partial\mu/\partial Q)$ for 1,1-disubstituted ethylenes, $H_2C = CXY$, where X,Y = OMe, Me, CN, CF_3: (●) uncorrected and (○) corrected for an overtone contribution of 60. Calculated values are based on the form of the vibration for vinylidene chloride

TABLE 6

Comparison of intensity data with literature values

	ν(C=C)		A [a]		
Compound	Lit.	This work	Lit.	This work	Ref.
$H_2C{=}C(Me)CHO$	1638	1636	600	440	*b*
$H_2C{=}C(Me)Pr^n$	1645		760		*c*
$H_2C{=}C(Me)Bu^n$		1644		791	

[a] In l mol⁻¹ cm⁻². [b] R. Mecke and K. Noack, *Chem. Ber.*, 1960, **93**, 210. [c] A. X. Wexler, *Spectrochim. Acta*, 1965, **21**, 1725.

Literature intensity data for comparison with the present work are available in only two cases, and these are given in Table 6. It is difficult to interpret the intensity data directly in a rigorous way. However, some rationalisation for the above results can be given if $\partial\mu/\partial Q$ is assumed to be dominated by terms arising in the π electron system alone. On the surface this seems a reasonable assumption in view of the existence of equation (1) and the small intensities observed in ethylenic compounds carrying highly polar but weakly conjugating substituents.[2] On approximating the molecular dipole moment as the sum of contributions from (a) the net atomic charges and (b) the one-centre atomic polarisation terms[21] (as in the standard CNDO/2 program), the dipole moment arising from the displacement of the π electrons alone is given by contribution (a) where the charges are due to movement of π electrons only. The atomic polarisation terms make no contribution to the π dipole moment for reasons of symmetry. With these approximations the additivity of dipole vectors [equation (7)] follows simply as a consequence of the additivity of π charges. Thus if the contribution to the π charge at atom i due to the presence of substituent j is $q_{i,j}$, so that the total π charge at atom i is $\sum_j q_{i,j}$, then the π dipole moment is given by equation (12) where r is the position vector of the ith atom. Differentiating equation (12) with respect to the normal co-ordinate, Q, gives equation (13). The jth contribution to $\partial\mu^{\pi}/\partial Q$ is given by equation (14), which, with equation (12), leads to an expression for the additivity of dipole vectors; equation (15). Thus additivity of contributing dipole vectors is expected in as far as they are dominated by π electron terms which are themselves additive. To what extent this condition is met is a current topic of research in this laboratory. Preliminary CNDO/2 calculations indicate[22] that $\partial\mu/\partial Q$ for methyl vinyl ether is almost wholly dominated (96%) by π electron terms although this dominance becomes less complete as the electron donating power of the substituent decreases (*e.g.* CF_3, 86%, CO_2Me, 75%).

$$\mu^{\pi} = e\sum_i\sum_j r_i q_{i,j} \qquad (12)$$

$$\frac{\partial\mu^{\pi}}{\partial Q} = \frac{\partial}{\partial Q}\left[e\sum_i\sum_j r_i q_i\right] \qquad (13)$$

$$\left\{\frac{\partial\mu^{\pi}}{\partial Q}\right\}_j = \frac{\partial}{\partial Q}\left[e\sum_i r_i q_{i,j}\right] \qquad (14)$$

$$\frac{\partial\mu^{\pi}}{\partial Q} = \sum_j\left[\frac{\partial\mu^{\pi}}{\partial Q}\right]_j \qquad (15)$$

Although the additivity of substituent effects in limited classes of 1,1-disubstituted ethylenes has occasionally been noted there appears to have been no systematic investigation into the nature of this additivity. For example, some degree of additivity has been found in work concerning the pK_a values of *trans*-3-substituted acrylic acids relative to the 3-substituted isocrotonic acids,[23] the radical copolymerisation[24] of 2-substituted acrylonitriles and acrylate esters with styrene, and some nucleophilic displacement reactions of the halogen atom in 1,1-diaryl-2-halogenoethylenes.[25] However, these studies are necessarily restricted to a rather limited range of substituent types. Additivity rules for the calculation of n.m.r. chemical shifts[26] embrace a rather wider range of substituents although here interpretation of results in terms of electron distribution is particularly difficult. Thus although it is known that some chemical and physical properties of 1,1-disubstituted ethylenes are dependent in an additive fashion on the substituents present little has been known about the electron distribution in these compounds.

Conclusions.—The integrated intensities of the ν(C=C) band in the i.r. spectra of a wide range of 1,1-disubstituted ethylenes have been shown to depend additively on the π electron parameters, σ^0_R, of the substituents. CNDO/2 calculations which rather accurately reproduce these intensities predict a precise additivity of the total π electron density transferred to the ethylenic double bond; an additivity which extends to individual positions only slightly less well. Some rationalisation has been given for this additivity of intensities in as far as they are well represented by π electron terms.

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