Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. Part XLII.[1] 1,2-Disubstituted Ethylenes

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Infrared intensities of *cis*- and *trans*-1,2-disubstituted ethylenes indicate that interactions between substituents are qualitatively similar to but quantitatively 1.5 times those in the corresponding *para*-disubstituted benzenes. Successful calculations of the dipole transition moments from CNDO/2 molecular orbital theory are presented.

WE have recently shown that the integrated intensities of the ν(C=C) vibration in a series of 1,1-disubstituted ethylenes may be interpreted in terms of additive contributions to the π-electron perturbation from each substituent,[2] in good accord with results of CNDO/2 molecular orbital calculations. The absolute intensities of this vibration were calculated with excellent precision by the CNDO/2 molecular orbital technique assuming a constant form of the normal vibration based on published normal co-ordinate analyses of either vinyl or vinylidene chloride. In the present paper we consider the analogous 1,2-disubstituted ethylenes; here the additional factor of ' through conjugation ' can occur, as in *p*-disubstituted benzenes.[3,4]

EXPERIMENTAL

Some of the compounds were available commercially as *cis–trans* mixtures and were separated by preparative scale g.l.c. on a Perkin-Elmer F21 gas chromatograph. Table 1 lists the details of these separations and the physical properties of those compounds prepared by literature procedures. 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 and cyclohexane were stored over molecular sieves (4 Å). Chloroform was passed down a column of alumina immediately prior to use to remove both water and the small quantity of ethanol present as stabiliser. Most of the spectral measurements were made in carbon tetrachloride as described in earlier parts of this series. In a few cases the compounds were insufficiently soluble in this solvent and data were measured in chloroform. One compound, *NN*-diethylbut-1-enylamine, reacts with carbon tetrachloride and was studied in cyclohexane. Integration of the absorption bands was carried out as previously and the errors in the integrated intensities, A (the mean of four determinations), are estimated to be ± 1 in units of $A^{1/2}$.

Calculation of Intensities.—These calculations were performed exactly as described previously [2,5,6] using a standard

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[1] Part XLI, C. Pouchan, A. Dargelos, M. Chaillet, G. Ford, R. D. Topsom, and A. R. Katritzky, *J. chim. Phys.*, 1974, 934.

[2] G. P. Ford, T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *J.C.S. Perkin II*, 1974, 1569.

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

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

[5] 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.

[6] R. T. C. Brownlee, J. Munday, R. D. Topsom, and A. R. Katritzky, *J.C.S. Faraday II*, 1973, 349.

CNDO/2 program [7] modified to a bond order matrix criterion as described in ref. 8 (with $\delta = 1 \times 10^{-5}$).

TABLE 1

Physical properties of compounds prepared in this work

Compound	M.p.[a] or b.p. (°C [mmHg]) Found	Lit.	Ref.
trans-Et_2N–CH=CH–Et	54 [15]	39 [11]	*b*
trans-Et_2N–CH=CH–CN	80 [0.1]	85—87 [0.5]	*c*
trans-Et_2N–CH=CH–CO_2Me	76 [0.08]	80 [0.01]	*d*
trans-EtO–CH=CH–Me	75.4 [e]	74.5	*f, g*
trans-EtO–CH=CH–CN	72 [8]	76—78 [15]	*c*
trans-MeO–CH=CH–CO_2Me	60 [12]	80 [16]	*d*
trans-Cl–CH=CH–CN	41—42	45—46	*h*
trans-Cl–CH=CH–CO_2Me	122—124	128	*i*
trans-Me–CH=CH–CN	122.4 [e]	122.1 [757]	*j, k*
trans-CN–CH=CH–CN	96—97 ‡	96 ‡	*l*
trans-Cl–CH=CH–CO_2H	82—83 ‡	84.7—85.1	*m*
cis-EtO–CH=CH–Me	69.7 [e]	68.5	*f, g*
cis-Me–CH=CH–CN	105.4 [e]	107.4 [757]	*j, k*
cis-Cl–CH=CH–CO_2H	60.5—61 ‡	60.8—61.4 ‡	*m*
cis-Cl–CH=CH–CO_2Me	141	79—83 [78]	*m*
cis-MeO_2C–CH=CH–CO_2Me	102—102.5 [17]	99—101 [18]	*n*

[a] M.p. indicated by ‡. [b] P. Wittig and R. Mayer, *Z. Chem.*, 1967, **7**, 57. [c] F. Scotti and E. J. Frazza, *J. Org. Chem.*, 1964, **29**, 1800. [d] E. Winterfeldt and H. Preuss, *Chem. Ber.*, 1966, **99**, 450. [e] Measured on a Mettler automatic b.p. apparatus. [f] T. Okuyama, T. Fueno, H. Nakatsuji, and J. Furukawa, *J. Amer. Chem. Soc.*, 1967, **89**, 5826. [g] Prepared as a *cis–trans* mixture (H. Adkins and B. H. Nissen, *J. Amer. Chem. Soc.*, 1922, **44**, 2749) and separated by g.l.c. [1 m × 2.5 mm polypropylene glycol column; carrier gas N_2, 20 ml min^{-1}; oven temperature, ambient; retention times 9.4 (*cis*), 11.6 min (*trans*)]. [h] E. Gryszkiewicz-Trochimowski, W. Schmidt, and O. Gryszkiewicz-Trochimowski, *Bull. Soc. chim. France*, 1948, 593. [i] G. Pattenden and B. J. Walker, *J. Chem. Soc.* (*C*), 1969, 531. [j] G. Heim, *Bull. Soc. chim. belges*, 1933, **42**, 461 (*Chem. Abs.*, 1934, **28**, 2328[6]). [k] Available commercially and separated by g.l.c. [2 m × 2.5 mm polypropylene glycol column; carrier gas N_2, 20 ml min^{-1}; oven temperature 65 °C; retention times 12.0 (*cis*), 17.0 min (*trans*)]. [l] D. T. Mowry and J. M. Butler, *Org. Synth.*, Coll. Vol. 4, 1963, p. 486. [m] A. N. Kurtz, W. E. Billups, R. B. Greenlee, H. F. Hamil, and W. T. Pace, *J. Org. Chem.*, 1965, **30**, 3141. [n] R. P. Linstead and M. Whalley, *J. Chem. Soc.*, 1952, 4839.

The equilibrium geometries were calculated from standard bond lengths and angles compiled by Pople and Gordon.[9] The geometries of the vibrationally distorted configurations were determined from the L matrix elements given in Table 2 for *cis*- or *trans*-1,2-difluoroethylene [10,11] as appropriate, and equation (1), where Q is the normal co-ordinate for the vibration. Thus we assume that a single set of atomic displacements applies within each series. Our previous work indicates that this holds well for mono- [6] and 1,1-di-substituted ethylenes. The factors given in Table 2 referring to bond lengths and bond angles are expressed in Å and radians, respectively, and correspond to the internal co-ordinates of Figure 1. ΔQ is in units of $u^{1/2}$ Å where u is the unified atomic mass unit. Dipoles were calculated at five points along the normal co-ordinate; $\Delta Q = 0, \pm 0.04, \pm 0.14$ corresponding to 20 and 70% of the maximum amplitude of the vibration. 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 to the required units, e.s.u. $g^{-1/2}$, through equation (2) for each of the in-plane cartesian components. The intensity in SI units (A in l mol^{-1} cm^{-2}) is then related [12] to $\partial\mu/\partial Q$ by equation (3).

$$R_i = L_i Q \qquad (1)$$

$$\partial\mu/\partial Q \approx 77.6\ \Delta\mu/\Delta Q \qquad (2)$$

$$A = \frac{N_0 \pi}{3 \times 10^3 c^2\, 2.303}\left(\frac{\partial\mu}{\partial Q}\right)^2$$

$$\left|\frac{\partial\mu}{\partial Q}\right| = \left[\sum\left(\frac{\partial\mu\xi}{\partial Q}\right)^2\right]^{\frac{1}{2}} \qquad (3)$$

$$\xi = x, y, z$$

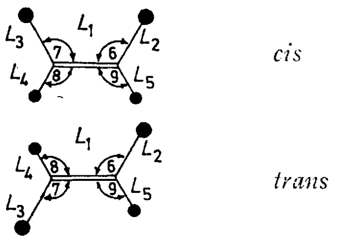

FIGURE 1 Internal co-ordinates corresponding to the L matrix elements in Table 2

RESULTS AND DISCUSSION

The principal intramolecular interactions characteristic of 1,2-disubstituted ethylenes are represented in resonance theory in terms of the canonical forms (I)—(IV) where the extent of π-electron displacement is

$$\underset{\text{(I)}}{\text{X-CH=CH-Y}} \longleftrightarrow \underset{\text{(II)}}{\overset{\pm}{\text{X}}\text{=CH-}\overset{\mp}{\text{C}}\text{H-Y}} \longleftrightarrow$$

$$\underset{\text{(III)}}{\text{X-}\overset{\mp}{\text{C}}\text{H-CH=}\overset{\pm}{\text{Y}}} \longleftrightarrow \underset{\text{(IV)}}{\overset{\pm}{\text{X}}\text{=CH-CH=}\overset{\mp}{\text{Y}}}$$

determined by the weight of each structure in the resonance hybrid. During the ν(C=C) vibration the changing molecular geometry, in particular the changing length of the central double bond, leads to a parallel fluctuation of the relative contributions of the charged structures.

TABLE 2

L-Matrix elements [a,b] for the ν(C=C) vibration in 1,2-difluoroethylenes

	L_1	L_2	L_3	L_4	L_5	L_6	L_7	L_8	L_9
trans-FHC=CHF	0.3804	−0.1474	−0.1474	−0.0055	−0.0055	−0.0395	−0.0395	−0.4081	−0.4081
cis-FHC=CHF	0.3924	−0.1310	−0.1310	−0.0019	−0.0019	−0.1189	−0.1189	−0.2971	−0.2971

[a] Linear co-ordinates are in Å and angular co-ordinates in radians. [b] Data from refs. 10 and 11.

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[7] P. A Dobosh, Quantum Chemical Program Exchange, Program 141, Indiana University, Bloomington, Indiana, U.S.A.

[8] J. A. Pople and D. L. Beveridge, ' Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970, p. 72.

[9] J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, 1967, **89**, 4253.

[10] N. C. Craig and J. Overend, *J. Chem. Phys.*, 1969, **51**, 1127.

[11] N. C. Craig and J. Overend, personal communication.

[12] J. Overend in ' Infrared Spectroscopy and Molecular Structure. An Outline of the Principles,' ed. M. Davies, Elsevier, Amsterdam, 1963, p. 353.

This generally causes an oscillating dipole moment $\partial\mu/\partial Q$, and hence an i.r. absorption band.

According to the theory developed earlier [2] the total dipole derivative $\partial\mu/\partial Q$, should be expressed as a vector sum of contributions characteristic of the intramolecular interactions [equation (4)]. The intensity, which is proportional to the square of the dipole derivative, is then given by the sum over the scalar products of these vector contributions [equation (5)]. An empirical constant w is included to allow for any overtone and/or combination bands integrated with the band under consideration. In monosubstituted ethylenes the dipole transition moment is proportional to the σ°_{R} constant.[6,13] The contribution to the dipole transition moment due to the interaction between each substituent and the double bond is therefore described by an equation of the type (6) where e_i is the unit vector which describes the directional part of $(\partial\mu/\partial Q)_i$, and depends on the molecular geometry and the form of the vibration.

$$\partial\mu/\partial Q = \sum_{i} (\partial\mu/\partial Q)_i \qquad (4)$$

$$A = a' \sum_{i}\sum_{j} (\partial\mu/\partial Q)_i \,.\, (\partial\mu/\partial Q)_j + w \qquad (5)$$

$$(\partial\mu/\partial Q)_i = a_i\sigma^{0}_{R}(i)e_i \qquad (6)$$

trans-1,2-*Disubstituted Ethylenes*.—The form of the ν(C=C) vibration in these compounds based on the L matrix elements in Table 2 for a unitary change in the normal co-ordinate is illustrated in Figure 2. When the substituents are identical and symmetrical the molecule has C_{2h} symmetry and the vectors describing the interaction of each substituent with the double bond necessarily add at 180°. In the general case where the substituents are different, the vector contributions to the overall dipole derivative do not necessarily add at 180° although the deviations are expected to be small except perhaps for a highly unsymmetrical substituent such as methoxycarbonyl.

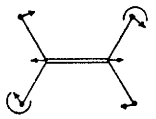

FIGURE 2 Atomic displacements in *trans*-1,2-difluoroethylene for unitary change in the normal co-ordinate

In the absence of through conjugation equation (7), relating to the intensities in these compounds, is deduced from equations (5) and (6) where the scalar product of the vectors (*i.e.* the cosine of the angle between them) has been expressed in terms of the angles ϕ_1 and ϕ_2 associated with the vectors individually (see Figure 3). The second term within the main brackets is a correction term relative to the case where the contributions to $\partial\mu/\partial Q$ add at exactly 180° and is analogous to the ' asymmetry correction ' introduced previously [3,4] in the treatment of p-disubstituted benzenes.

When direct mutual substituent interaction is possible an additional contribution λ must be included. Figure 3 shows this contribution at an angle ϕ_{λ} approximately equal to ϕ_1, *i.e.* the sign of λ is chosen to represent electron donation in the direction ① $\longrightarrow$ ②.* The expansion of equation (5) in terms of $\sigma^{\circ}_{R}(1)\sigma^{\circ}_{R}(2)$ and λ leads [14] to an equation analogous to (7) which, with the simplifying assumption that the vector contributions are parallel, reduces to equation (8) which is of exactly the same form as that found [3,4] to correlate the intensities of p-disubstituted benzenes. The determination of the various λ constants would then provide a measure of the extent of intersubstituent interaction in these compounds in the units of σ°_{R}.

$$A = a\{[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(2)]^2 + 2\sigma^{\circ}_{R}(1)\sigma^{\circ}_{R}(2)[1 - \cos(\phi_1 - \phi_2)]\} + w \qquad (7)$$

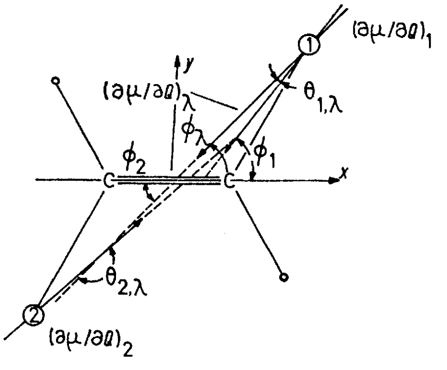

FIGURE 3 Vectors contributing to $\partial\mu/\partial Q$ in *trans*-1,2-difluoroethylene

$$A = a[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(2) + \lambda]^2 + w \qquad (8)$$

λ represents electron donation in the direction ① $\longrightarrow$ ②

We have previously [3] derived such a series of λ values appropriate to p-disubstituted benzenes where we found that the additional interaction could be distributed in terms of the resonance effects of the two substituents. Equation (9) applied for π-acceptor groups, where K_A was a constant characteristic of the π-acceptor and $[\sigma^{+}(D) - \sigma^{\circ}(D)]$ represents the ability of the donor group to respond to further electron demand. However, we found a different relation for d-orbital acceptors [equation (10)] in which K_X is characteristic of the d-orbital acceptor, but the additional interaction here appeared to be proportional to σ°_{R} for the donor group.

$$\lambda = K_A[\sigma^{+}(D) - \sigma^{\circ}(D)] \qquad (9)$$

$$\lambda = K_X\sigma^{\circ}_{R} \qquad (10)$$

While we do not necessarily expect the same values of λ to be appropriate to 1,2-disubstituted ethylenes we do expect them to be proportional. The data in Table 3 were fitted to equation (8) using an iterative least-squares

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* This angle is deduced here and below for two substituents of the same type. If in an actual example the substituents are of different types, *i.e.* one donor and one acceptor, the necessary rotation of one of the vectors through 180° is taken care of by the different signs of their σ°_{R} values.

[13] A. R. Katritzky, R. F. Pinzelli, M. V. Sinnott, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1970, **92**, 6861.

[14] G. P. Ford, Ph.D. Thesis, University of East Anglia, 1974. (*a*) p. 72; (*b*) p. 31.

TABLE 3

I.r. spectral data [a] for *trans*-1,2-disubstituted ethylenes

Substituents 1	Substituents 2	$\sigma^\circ_R(1)$	$\sigma^\circ_R(2)$ [b]	$\nu(C{=}C)$	ε_A [c]	$A_{obs.}$ [d]	$A_{\nu(C=C)}$ [e] calc.
NEt_2	Et	−0.57	−0.10	1 654	383	5 560 [f]	5 871
NEt_2	CN	−0.57	0.04	1 628	1 702	18 564	19 501
NEt_2	CO_2Me	−0.57	0.15	1 613	1 418	28 156	26 432
OEt	CN	−0.43	0.04	1 622	631	8 840	9 853
				1 643	352		
OMe	CO_2Me	−0.43	0.15	1 630	965	12 214	13 724
				1 650	234		
OEt	Cl	−0.43	−0.22	1 631	43	2 090 [g]	3 250
				1 620	135		
OEt	Me	−0.43	−0.10	1 676	172	3 821	2 904
				1 658	117		
Cl	Cl	−0.22	−0.22	1 650	20	484	
Cl	Me	−0.22	−0.10	1 640	36	545	229
Cl	CN	−0.22	0.04	1 593	289	2 273	2 029
Cl	CO_2Me	−0.22	0.15	1 611	356	5 600	4 278
				1 606			
Cl	CO_2H	−0.22	0.29	1 608	421	7 056	
Me	Me	−0.10	−0.10		0	0 [h]	19
Me	CN	−0.10	0.04	1 638	71	842	793
Me	CO_2Me	−0.10	0.15	1 650	193	2 300 [g]	2 100
CN	CN	0.04	0.04	1 610	1.5	29 [i]	19
CO_2Me	CO_2Me	0.15	0.15	1 644	53	626	
Me	CO_2H	−0.10	0.29	1 654	398	5 780 [g]	

[a] Measured in CCl_4 unless otherwise noted. [b] σ°_R Values from i.r. intensities of monosubstituted ethylenes (ref. 13) or, where these were not available, from i.r. intensity studies of monosubstituted benzenes (R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1965, **81**, 3260). [c] Peak extinction coefficient, $\varepsilon_A = a_{max.}/cl$. [d] Integrated absorption of the main and subsidiary bands in units of l mol^{-1} cm^{-2}. [e] Calculated from equation (11). [f] Measured in cyclohexane solution. [g] R. F. Pinzelli, Ph.D. Thesis, University of East Anglia, 1971. [h] A. X. Wexler, *Spectrochim. Acta*, 1965, **21**, 1725. [i] Measured in $CHCl_3$ solution.

procedure [15,16] and values of K_A, K_X, and $(\sigma^+ - \sigma^\circ)$ from our recent compilation,[4] treating the proportionality constant for λ as an additional empirical parameter. This procedure leads to equation (11) which holds with a multiple correlation coefficient of 0.9934.* The calculated intensities are compared with the observed in Table 3 and the comparison is presented graphically in Figure 4. The data for *trans*-1,2-dichloroethylene were not included since there are unusually strong combination bands in the 1 600 cm^{-1} region for this compound.[17] The data for dimethyl fumarate were also rejected since there are problems of rotational isomerism.

$$A = 26\,500[\sigma^\circ_R(1) - \sigma^\circ_R(2) + 1.5\lambda]^2 - 7 \qquad (11)$$

The constant 26 500 obtained from this treatment is very close to the 27 100 found for monosubstituted ethylenes, which, according to the reasoning presented earlier,[2] suggests an almost completely additive perturbation to the electron density in the ethylenic double bond but with an additional interaction between the substituents

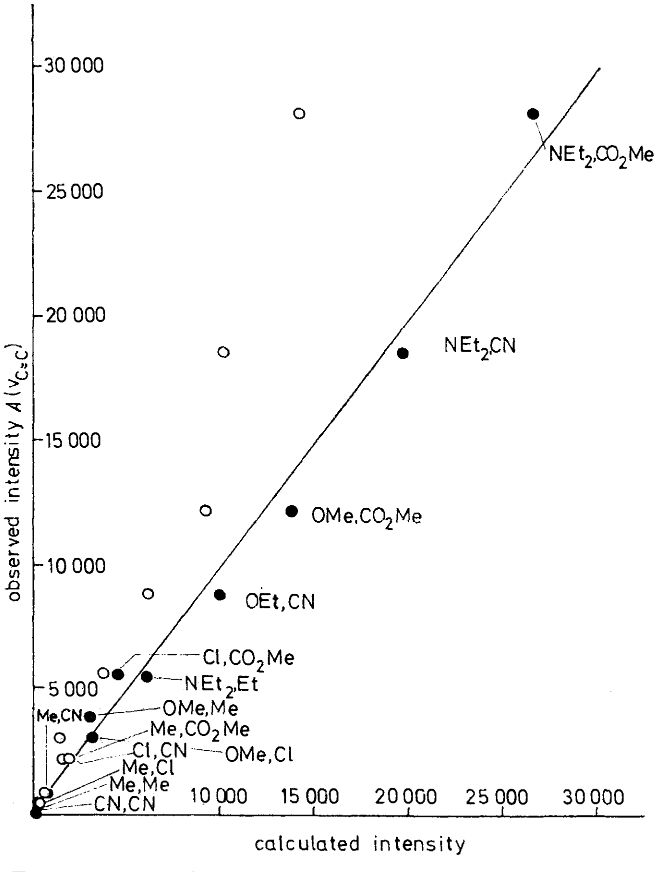

FIGURE 4 Plot of observed intensities in *trans*-1,2-disubstituted ethylenes against those calculated from equation (11) with λ deduced from *p*-disubstituted benzenes (●) and λ = 0 (○). The line is that of unit slope

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* The near zero intercept in equation (11) is very poorly defined (−7 ± 893) and the data give no evidence for assuming it to be other than zero. Removing the intercept as a fitted parameter then gives at the 95% confidence limit the following equation:

$$A = 26.5 \pm 6.4 \times 10^3[\sigma^\circ_R(1) - \sigma^\circ_R(2) + 1.5 \pm 0.7\lambda]^2$$

Although it could appear that the equation (11) is *less* well defined than (12), this is a consequence of the much larger absolute magnitudes of the i.r. intensities in the *trans*- series.

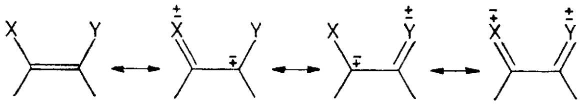
[15] M. J. D. Powell, *Computer J.*, 1965, **7**, 155.

[16] Fortran programs VA02A, VD01A, and SV01A available from the Numerical Analysis Group of the Theoretical Physics Division, Atomic Energy Research Establishment, Harwell, Didcot, Berks.

[17] H. J. Bernstein and D. A. Ramsay, *J. Chem. Phys.*, 1949, **17**, 556.

parallel to, but somewhat more extensive than, that operating in *p*-disubstituted benzenes.

cis-1,2-Disubstituted Ethylenes.—The form of the vibration in this series is shown in Figure 5. The oscillating dipole moment induced by the changing weight of the canonical form describing the through-resonance interaction will be approximately in a direction parallel to the double bond, although the angles associated with the oscillating dipole induced by the substituent–double bond interaction are less easy to determine but will presumably be at approximately 45° to the central bond as in the case of the 1,1-disubstituted compounds.[2] This situation is shown in Figure 6. Expansion of equation (5) in terms of $\sigma^\circ_R(1)$, $\sigma^\circ_R(2)$, and λ and assuming that $\phi_\lambda = 0$ and a single value $\theta = \theta_{12}$ applicable to the entire series can be found, equation (12) results.



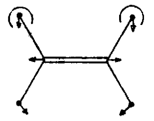


FIGURE 5 Atomic displacements in *cis*-1,2-difluoroethylene for a unitary change in the normal co-ordinate

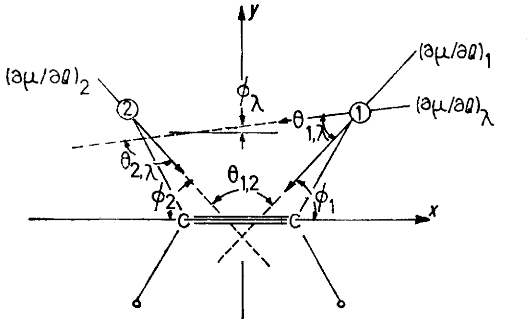


FIGURE 6 Vectors contributing to $\partial\mu/\partial Q$ in *cis*-1,2-disubstituted ethylenes

$$A = a\Big[\sigma^\circ{}_R{}^2(1) + \sigma^\circ{}_R{}^2(2) + 2\sigma^\circ_R(1)\sigma^\circ_R(2)\cos\theta + \lambda\{\lambda + 2\sin\frac{\theta}{2}[\sigma^\circ_R(1) - \sigma^\circ_R(2)]\}\Big] + w \quad (12)$$

Since there were relatively few data in this series it was necessary to assume that the same λ values as operated in the *trans*-series applied here. With this assumption the data in Table 4, with the exception of those for *cis*-3-chloroacrylic acid, for which there was no λ value, were fitted to equation (12) using an iterative least-squares procedure[15,16] treating *a*, θ, and *w* as empirical parameters. The quality of the least-squares fit was improved by rejecting the data for dimethyl maleate; even so the final precision was not high. The numerical values deduced in this treatment were $a = 20.1 \pm 5.5 \times 10^3$; $w = 220 \pm 880$; $\theta = 145.4 \pm 28.6$, where the uncertainties were deduced from the covariance matrix[15,16] for the 95% confidence level. The intensities calculated with these parameters are given in Table 4 and compared graphically with those observed in Figure 7. The out-of-plane component is smaller in these compounds than was found for 1,1-disubstituted ethylenes and the assumption of a constant angle θ holds less well.

TABLE 4

I.r. spectral data[a] for *cis*-1,2-disubstituted ethylenes

Substituents							
1	2	$\sigma^\circ_R(1)$	$\sigma^\circ_R(2)$[b]	ν(C=C)	ε_A[c]	$A_{obs.}$[d]	$A_{calc.}$[e]
OEt	Cl	−0.43	−0.22	1 645	174	2 840[f]	3 429
OEt	Me	−0.43	−0.10	1 667	240	3 345	2 908
Cl	Cl	−0.22	−0.22	1 587 1 562	74 21	1 387	784
Cl	Me	−0.22	−0.10	1 635	44	897	620
Me	Me	−0.10	−0.10	1 657		260[g]	339
Me	CN	−0.10	0.04	1 627	37	522	683
Cl	CO_2Me	−0.22	0.15	1 620	355	3 882	3 654
Cl	CO_2H	−0.22	0.29	1 608	426	5 698	5 446
CO_2Me	CO_2Me	0.15	0.15	1 646	66	1 700	585

[a] Measured in CCl_4. [b] σ°_R Values from i.r. intensities of monosubstituted ethylenes (ref. 13), or, where these were not available, from i.r. intensity studies of monosubstituted benzenes (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). [c] Peak extinction coefficient, $\varepsilon_A = a_{max.}/cl$. [d] Integrated absorption of the main and subsidiary bands in units of $l\ mol^{-1}\ cm^{-2}$. [e] Calculated from equation (12). [f] R. F. Pinzelli, Ph.D. Thesis, University of East Anglia, 1971. [g] A. X. Wexler, *Spectrochim. Acta*, 1965, **21**, 1725.

Molecular Orbital Calculations.—The results of these calculations are reported in Table 5 and compared graphically with the observed values in Figure 8, where the calculated $\partial\mu/\partial Q$ values for the two conformers of the acrylate esters have been averaged. A planar *s-cis*-conformation for the methyl vinyl ethers in the *trans*-series was adopted in accord with the known[18-20] preference for this conformation. For *cis*-1-methoxypropene the *s-trans*-conformer was adopted in agreement with recent findings.[18,19] It has been suggested that the *s-trans*-form of this compound[18] and other alkyl vinyl

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[18] S. W. Charles, F. C. Cullen, and N. L. Owen, *J. Mol. Structure*, 1973, **18**, 183.

[19] E. Taskinen and P. Liukas *Acta Chem. Scand.*, 1974, **B28**, 114.

[20] R.-M. Lequan and M.-P. Simonnin, *Bull. Soc. chim. France*, 1970, 4419.

ethers[21,22] is non-planar. However this view has not been universally accepted[19,23] and in the absence of more specific evidence relating to their geometry we have adopted a planar *s-trans*-conformation in these calculations. On the other hand, calculations were performed on both conformations of the *trans*-3-substituted methyl acrylates as these are known[24] to be approximately equally populated although again these conformers may not be planar. In the absence of more specific information we carried out calculations on the planar conformations. The agreement shown in Figure 8 is pleasing. Discrepancies are noted for *cis*-but-2-ene and the two *trans*-3-substituted methyl acrylates. The CNDO/2 method predicts almost zero intensity for *cis*-but-2-ene, *i.e.* the component of $\partial\mu/\partial Q$ perpendicular to the double bond is underestimated.

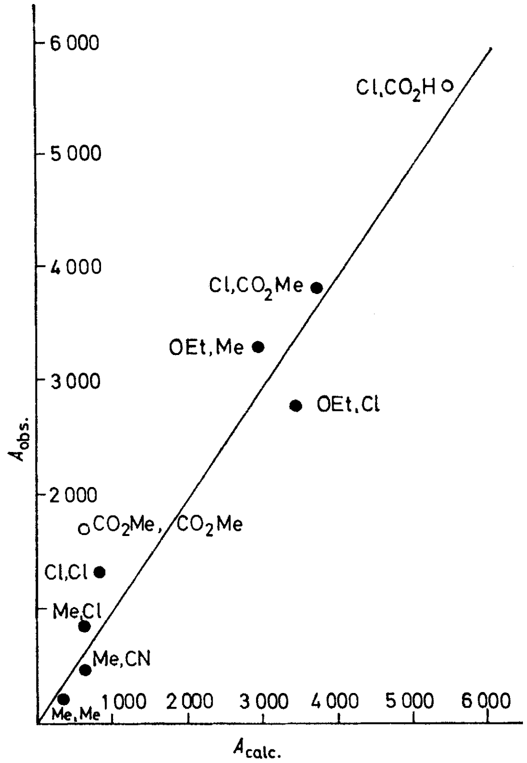

FIGURE 7 Plot of observed intensities in *cis*-1,2-disubstituted ethylenes against those calculated from equation (12). Points indicated as open circles (○) not included in least squares treatment. The line is that of unit slope

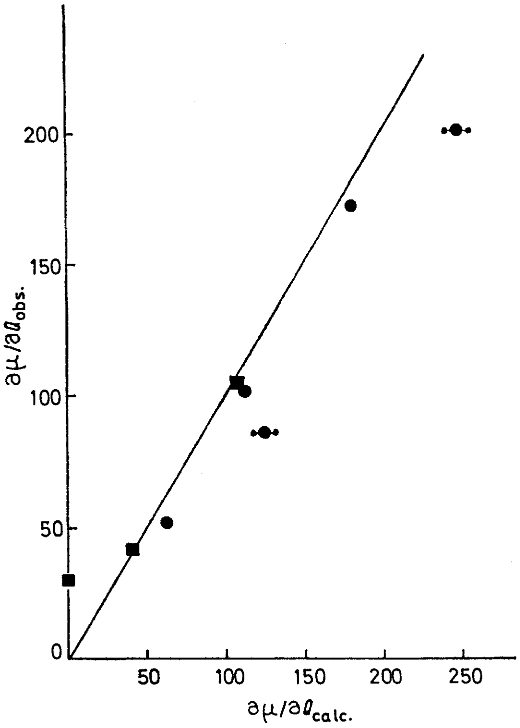

FIGURE 8 Plot of observed dipole transition moments against those calculated from CNDO/2 theory for *cis*- (■) and *trans*- (●) disubstituted ethylenes. The line is that of unit slope

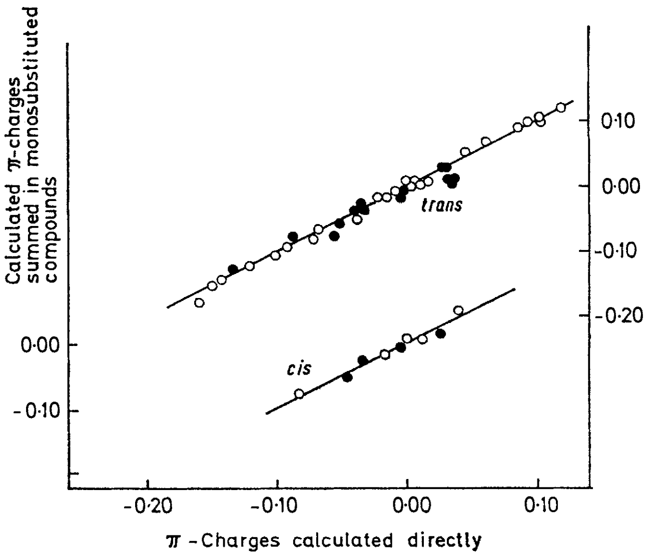

FIGURE 9 Comparison of calculated π-charges at the vinyl carbon atoms in *cis*- and *trans*-1,2-disubstituted ethylenes. $q_{\alpha}{}^{\pi}$, $q_{\beta}{}^{\pi} = 0$, $\Sigma q^{\pi} = 0$. The lines are those of unit slope with zero intercept

The dipole transition moments for the acrylate esters were overestimated. This may be due to the assumption of planar conformations although it is possible that the form of the vibration based on *trans*-1,2-difluoroethylene may not be a good model for the form of the vibration in the esters in which coupling between the C=C and C=O motions can occur. Calculations on compounds containing chlorine (not reported) were unsuccessful. The CNDO/2 method with the parameters suggested by Santry and Segal[25] assigns too important a role to the *d* orbitals so that the known electron-releasing effect of the chloro-substituent is essentially cancelled by back donation in the chlorine 3*d* orbitals, leading to a

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[21] N. L. Owen and N. Sheppard, *Spectrochim. Acta*, 1966, **22**, 1101.

[22] K. Hatada, M. Takeshita, and H. Yuki, *Tetrahedron Letters*, 1968, 4621.

[23] A. R. Katritzky, R. F. Pinzelli, and R. D. Topsom, *Tetrahedron*, 1972, **28**, 3441.

[24] W. O. George, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II*, 1972, 400.

[25] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 1967, **47**, 158.

TABLE 5

Calculated values of $\partial\mu/\partial Q$[a] for the ν(C=C) vibration in 1,2-disubstituted ethylenes

Substituents		$\mu_{calc.}$	$\frac{\partial\mu^x}{\partial Q}$	$\frac{\partial\mu^y}{\partial Q}$	$\left\|\frac{\partial\mu}{\partial Q}\right\|$	$\left(\frac{\partial\mu}{\partial Q}\right)_{exp.}$
trans[b]						
OMe	Me	1.39	94.0	61.9	112.6	111.9[c]
OMe	CN	2.89	148.1	105.5	181.8	170.2[c]
OMe	CO_2Me (*trans*)	0.88	217.8	132.3	254.8	200.1
OMe	CO_2Me (*cis*)	1.90	194.6	140.3	239.7	
Me	CN	3.40[d]	49.3	37.3	61.8	52.5
Me	CO_2Me (*trans*)	2.06	113.0	60.3	128.1	86.8
Me	CO_2Me (*cis*)	1.61	100.3	63.2	118.6	
cis[e]						
OMe	Me	2.16	94.3	52.9	108.1	104.7[c]
Me	Me	0.14[f]	0.0	−0.9	0.9	29.2
Me	CN	3.11[g]	−29.7	−30.3	42.4	41.4
CN	CN	4.88	0.0	−52.6	52.6	

[a] Units e.s.u. $g^{-\frac{1}{2}}$ cm^{-1}. [b] Based on the L matrix elements for *trans*-1,2-difluoroethylene in Table 2. Orientation as in Figure 3 with the left hand substituent in the first quadrant. [c] Data for OEt compound. [d] Experimental value, 4.53 (M. Podzinková and M. Procházka, *Coll. Czech. Chem. Comm.*, 1970, **35**, 1708). [e] Based on L matrix elements for *cis*-1,2-difluoroethylene in Table 2. Orientation as in Figure 6; left hand substituent is in the first quadrant. [f] Experimental value, 0.25 (S. Kondo, Y. Sakurai, E. Hirota, and Y. Morino, *J. Mol. Spectroscopy*, 1970, **34**, 231). [g] Experimental value, 4.08; see footnote *d*.

TABLE 6

Charge densities from CNDO/2 theory for 1,2-disubstituted ethylenes

$X-\overset{\alpha}{C}H=\overset{\beta}{C}H-Y$		Calculated directly				Summed in monosubstituted compounds			
		Σq^{σ}[a]	Σq^{π}[b]	q_{α}^{π}[c]	q_{β}^{π}[d]	Σq^{σ}[a]	Σq^{π}[b]	q_{α}^{π}[c]	q_{β}^{π}[d]
trans									
OMe[e]	OMe[e]	0.3009	−0.1264	−0.0632	−0.0632	0.3010	−0.1310	−0.0655	−0.0655
OMe[e]	Me	0.1610	−0.0784	0.0087	−0.0871	0.1538	−0.0869	0.0034	−0.0903
OMe[e]	CN	0.1958	−0.0528	0.0654	−0.1182	0.2040	−0.0487	0.0607	−0.1194
OMe[e]	CF_3	0.1783	−0.0683	0.1062	−0.1745	0.1888	−0.0537	0.1041	−0.1578
OMe[e]	CO_2Me[e]	0.1386	−0.0304	0.1131	−0.1435	0.1428	−0.0321	0.1121	−0.1442
OMe[e]	CO_2Me[f]	0.1381	−0.0327	0.1071	−0.1398	0.1410	−0.0342	0.1065	−0.1407
Me	Me	0.0194	−0.0244	−0.0122	−0.0122	0.0042	−0.0302	−0.0151	−0.1051
Me	CN	0.5536	0.0013	0.0479	−0.0466	0.0544	−0.0020	0.0422	−0.0442
Me	CO_2Me[e]	−0.0060	0.0252	0.0987	−0.0735	−0.0068	0.0246	0.0936	−0.0690
Me	CO_2Me[f]	−0.0065	0.0231	0.0926	−0.0695	−0.0086	0.0225	0.0880	−0.0655
CN	CN	0.0980	0.0178	0.0089	0.0089	0.1046	0.0262	0.0131	0.0131
Me	CF_3	0.0322	−0.0076	0.0934	−0.1010	0.0392	−0.0033	0.0879	−0.0912
CN	CF_3	0.0716	0.0137	0.0562	−0.0425	0.0894	0.0249	0.0588	−0.0339
CF_3	CF_3	0.0374	0.0166	0.0083	0.0083	0.0742	0.0236	0.0118	0.0118
cis									
OMe[f]	Me	0.1472	−0.0740	0.0029	−0.0769	0.1533	−0.0806	0.0011	−0.0817
Me	Me	0.0136	−0.0278	−0.0139	−0.0139	0.0042	−0.0302	−0.0151	−0.0151
Me	CN	0.0443	−0.0017	0.0481	−0.0498	0.0544	−0.0020	0.0422	−0.0442
CN	CN	0.0834	0.0190	0.0095	0.0095	0.0146	0.0262	0.0131	0.0131

[a] The net σ-charge summed over all atoms at the ethylene skeleton. [b] The net π-charge summed over both carbon atoms of the ethylene skeleton. [c] Net π-charge at the α-carbon atom. [d] Net π-charge at the β-carbon atom. [e] *s-cis*-Conformation. [f] *s-trans*-Conformation.

grossly underestimated net π-electron effect for the Cl substituent.

The π-electron charges at the ethylenic carbon atoms of *trans*- and *cis*-1,2-disubstituted ethylenes are listed in Table 6 and compared with the analogous quantities deduced by assuming additivity of the previously reported [2] π-electron charges in the corresponding monosubstituted compounds. The correspondence is very close and is shown graphically in Figure 9.

Reasoning analogous to that presented for 1,1-disubstituted ethylenes suggests that this can be anticipated from the existence of the correlation embodied in equation (11). Interestingly, this precise additivity seems to hold even in the presence of a substantial through-conjugation contribution, and for example presumably explains why the ^{13}C chemical shifts of the ethylenic nuclei in *cis*- and *trans*-disubstituted ethylenes are rather precisely additive functions of the individual substituent perturbations.* The σ-charge transfer also shows a

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* A number of workers [26–31] have presented additivity rules which illustrate this point in limited series of 1,2-disubstituted ethylenes. We have collected ^{13}C shift data [14b] from diverse sources [28–33] and find that the observed chemical shift for 42 *trans*-1,2-disubstituted ethylenes are calculated additively from the chemical shifts of the monosubstituted compounds with a standard deviation of 4.1 p.p.m. The standard deviation for 44 *cis*-compounds was 3.9 p.p.m.

[26] C. Rappe, E. Lippmaa, T. Pehk, and K. Andersson, *Acta Chem. Scand.*, 1969, **23**, 1447.

[27] E. Lippmaa, T. Pehk, K. Andersson, and C. Rappe, *Org. Magnetic Resonance*, 1970, **2**, 109.

[28] D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, 1971, **36**, 2757.

[29] G. B. Savitsky, P. D. Ellis, K. Namikawa, and G. E. Maciel, *J. Chem. Phys.*, 1968, **49**, 2395.

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[32] G. E. Maciel, P. D. Ellis, J. J. Natterstad, and G. B. Savitsky, *J. Magnetic Resonance*, 1969, **1**, 589.

[33] R. A. Friedel and H. L. Retcofsky, *J. Amer. Chem. Soc.*, 1963, **85**, 1300.

degree of additivity although saturation effects are predicted here.

Conclusions.—The i.r. intensity of the ν(C=C) band in *trans*-1,2-disubstituted ethylenes can be correlated with π-delocalisation parameters if allowance is made for the through-resonance effect which is shown to be approximately parallel to, but *ca.* 1.5 times larger than that operating in *p*-disubstituted benzenes. Conclusions regarding the electron effect in the *cis*-compounds are less certain. CNDO/2 Calculations predict the dipole transition moments well and give confidence in the interpretation of the empirical results in terms of additive substituent π-electron perturbations.

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