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The Influence of Polar Substituents at Carbon-Carbon Multiple Bonds on the Properties of Linear Unsaturated Compounds

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Data on the influence of polar substituents at multiple bonds on the physicochemical properties of unsaturated molecules are discussed and reviewed primarily in the light of quantitative estimates of the transmission of influence via multiple bonds. The bibliography includes 202 references.

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I. INTRODUCTION

The problem of the influence of polar substituents at multiple carbon–carbon bonds on the properties of linear unsaturated compounds is part of the general problem of the mutual influence of atoms and atomic groups in an organic molecule and is of considerable theoretical and practical interest in connection with the great importance of unsaturated compounds in nature and technology. During recent years, there has been an appreciable growth of interest in the study of the characteristics and mechanism of the influence of substituents at multiple bonds, because the principle of linear free energies (LFE) has been extended to unsaturated compounds and thus a basis has been created for a quantitative estimation of the influence of substituents in terms of correlation equations of the type of the Hammett equation[1-3]. Fairly extensive data have now accumulated on the influence of polar substituents at multiple bonds on the properties of unsaturated molecules and in many cases quantitative estimates of this influence have been made and certain characteristics of the transmission of the influence via multiple bonds have been discovered. Some advances have been achieved also in the elucidation of the nature and mechanism of the transmission of the influence of substituents via multiple carbon–carbon bonds. Although the individual aspects of the problem have been considered in several reviews[4-8], the data as a whole have not been surveyed.

In the present paper an attempt is made to review the information obtained in the last 10–15 years concerning the influence of polar substituents in compounds of the type $X(CH=CH)_nY$ and $X(C\equiv C)_nY$, primarily in the light of quantitative estimates of the transmission of influences via multiple bonds.

II. GENERAL POSTULATES

The Hammett equation, which is widely used nowadays to estimate the influence of polar substituents in different classes of organic compounds, has the following general form:

$$Q=\rho\sigma, \qquad (1)$$

where Q is the molecular property to be correlated, ρ the reaction constant (a measure of the sensitivity of the property Q to the polar effect of the substituent), and σ the substituent constant (a measure of the polar effect of the substituent relative to the hydrogen atom).

The applicability of Eqn. (I) to unsaturated compounds was demonstrated by Jaffe[8] as early as 1953 and has been proved convincingly by Charton and Meislich[9] in 1958 in relation to unsaturated aliphatic compounds.

A quantitative estimate of the influence of polar substituents on the properties of unsaturated compounds obeying the Hammett equation can be achieved in two ways: (1) by comparing the constants ρ obtained in the correlation analysis of identical properties Q determined under identical conditions using the same method for similar series of saturated, ethylenic, or acetylenic compounds, which makes it possible to determine the relative efficiencies of the transmission of polar influences via *cis*- and *trans*-vinyl groups or via ethynyl linkages compared with the corresponding saturated bridges; (2) by calculating the so called transmission factor[1-3], which makes it possible to estimate the degree of attenuation of the influence of the substituent on molecular properties when a multiple bond is interposed between the substituent and the rest of the molecule.

In its initial form, the transmission factor was defined as the ratio of the reaction constants ρ for the given series X–M–Y [X is the variable substituent, Y the fixed part of the molecule, and M the bridge, i.e. $-(CH=CH)_n-$ or $-(C\equiv C)_n-$] and ρ_0 for a standard (reference) series X–Y:

$$\pi'=\rho/\rho_0. \qquad (2)$$

Thus π' shows to what extent the influence of the substituent is weakened when a multiple bond is inserted between X and the remaining part of the molecule Y, i.e. is a measure of the transmission of electronic effects via the bridge M. Apart from π', the transmission factor is sometimes designated in the literature by the symbols Z and τ.

For a quantitative estimation of the influence of substituents, a transmission factor designated by the symbol γ and defined by the ratio[1,7]

$$\gamma_M=\rho_M/\rho_{-C_6H_4-}, \qquad (3)$$

is sometimes used. Here ρ_M is the reaction constant for the series X–M–Y, and $\rho_{-C_6H_4-}$ the reaction constant for the p-XC_6H_4Y series.

In this case, the attenuation of the influence of the substituent is estimated relative to the *p*-phenylene group, the electronic conductivity of which is assumed to be unity. Thus γ is a measure of the transmission of electronic effects via the bridge M relative to the *p*-phenylene system. It follows from Eqns. (2) and (3) that

$$\gamma\text{-}C_6H_4M\text{-} = \pi'_M.$$

The average accuracy of the transmission factors is to within ±15% (in the range between 1.6 and 33%).[1,10]

The quantitative estimate of the influence of polar substituents with the aid of transmission factors is fairly general and rigorous. However, this procedure involves a number of difficulties due primarily to the difficulty of selecting a suitable reference series. In order to obtain correct results, it is necessary to maintain the following conditions: (1) The reference series and the series being compared must differ only in the structure of the bridge in the latter. (2) All the members of the selected series must have the same or similar conformations. (3) The properties compared must be of the same type. For example, in the correlation analysis of kinetic data, the mechanisms of the reactions of the reference series and the series being compared must be identical or, in the correlation analysis of ultraviolet spectroscopic data, the maxima analysed must correspond to the same electronic transitions, etc. (4) The properties Q to be correlated must be determined by the same method under strictly identical conditions. These rules must be observed also in those cases where, owing to the absence of a reference series, the polar influence of the substituents is estimated by comparing the values of ρ for analogous saturated and unsaturated series.

It is noteworthy that cases are frequently encountered where the transmission factors are determined by the ratio of the values of ρ for the test series and ρ_0 for incorrectly chosen reference series. For example, in the determination of π' per double bond (π'_{1F}), acetophenones $XC_6H_5COCH_3$ were chosen as the reference series for the series of chalcones $XC_6H_4CH{=}CHCOC_6H_5$ instead of benzophenones $XC_6H_4COC_6H_5$, which should have been selected[11]. In another study[12] π'_{1F} was found from the ratio of the values of ρ for the chalcols $XC_6H_4CH{=}CHCH(OH)C_6H_5$ (test series) and the chalcols $C_6H_5CH{=}CHCH(OH)C_6H_4X$ (reference series) instead of the $XC_6H_4CH(OH)C_6H_5$ series.

In order to reach a conclusion about the nature and mechanism of the transmission of the influence of substituents via multiple bonds, it is necessary to be able to separate the σ and π effects in correlation analysis. The overall polar effect (P) of a substituent at a multiple bond consists of the sum of the σ and π effects:

$$P = I_\sigma + I_\pi + F + M + C,$$

where I_σ (σ-inductive effect), I_π (π-inductive effect), and F (field effect) refer to the σ effects, while M (mesomeric effect) and C (the effect of direct polar conjugation) refer to the π effects.

Unfortunately the problem of the complete separation of the σ and π effects has not been completely solved[1-3,7,13-16]. However, an approach to this problem is available and makes it possible to infer to some extent whether the σ or π effects makes the dominant contribution to the electronic effect of the substituent and hence the nature and mechanism of the influence of the substituent can be deduced.

This approach consists in the employment of the two-parameter Hammett equation in the form proposed by Taft and Lewis[17-19]:

$$Q = \alpha\sigma_I + \beta\sigma_R; \qquad (4)$$

where α and β are reaction constants reflecting the sensitivity of the property Q to the inductive and mesomeric effects respectively. The two-parameter equation proposed by Swain and Lupton[20] has a somewhat different significance. In agreement with Dewar and Grisdale[21], these workers assume that, among the σ effects, the main role is due to the field effect F:

$$Q = fF + rR, \qquad (5)$$

where F is the field effect constant of the substituent, R its resonance (mesomeric) constant, and f and r are the regression coefficients for F and R respectively.

The contribution of the resonance influence of the substituent to the correlated property Q is expressed in the form

$$P_R = \frac{\beta \cdot 100}{\alpha + \beta} \qquad (6)$$

when Eqn. (4) is used and in the form

$$R = \frac{r \cdot 100}{f + r} \qquad (7)$$

when Eqn. (5) is used. P_R and R in Eqns. (6) and (7) represent the resonance (mesomeric) contribution (expressed as a percentage) to the overall polar effect P of the substituent X. The main difference between Eqns. (4) and (5) consists in the set of constants employed.

An approximate estimate of the resonance influence of substituents can be obtained in correlation analysis in terms of the usual one-parameter equation [Eqn. (1)] with the substituent constants varied until the optimum correlation is achieved. The values of P_R are zero for σ_I, 25% for σ_M, 40% for σ_n^0, 50% for σ_n, 62% for σ_n^+, 60% for σ_n^-, and 100% for σ_R.

The number of studies which have now been made on the correlation analysis of the properties of series of the type $X(CH{=}CH)_nY$ and $X(C{\equiv}C)_nY$ is fairly large. For certain types of unsaturated compounds, correlation analysis has been used successfully in relation to vibrational spectra[7,10,11,22-48], proton[7,12,49-56] ^{13}C[56] and ^{19}F[57,58] nuclear magnetic resonance, dipole moments[7,27,44,45,59-62], ultraviolet spectra[7,44,45,60,63], mass spectra[7,64-66], basicity and acidity[7,8,11,37,67-86], polarographic reduction[7,44,45,87-94], reaction kinetics[7,44,67,95-115], and finally the electron densities at the oxygen atom (q_O) of certain carbonyl compounds[89,116].

III. GENERAL CHARACTERISTICS OF THE INFLUENCE OF POLAR SUBSTITUENTS ON THE PROPERTIES OF UNSATURATED COMPOUNDS

1. Vibrational Spectra

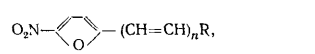
The positions of the characteristic absorption bands in the infrared spectra for a constant substituent Y in compounds of the type $X(CH{=}CH)_nY$ and $X(C{\equiv}C)_nY$ depend primarily on the force constant of the C–Y bond, which is determined by the electron distribution about the bond. It is assumed that infrared spectra are very sensitive to structural changes in the molecule and the method is therefore widely used to investigate the mutual influence

of substituents. Carbonyl compounds have been particularly widely investigated among unsaturated compounds, because the stretching vibrations of the carbonyl group are relatively insensitive to the mass of the substituents attached to the carbon atom of the carbonyl group.

Among carbonyl compounds, ketones have been most thoroughly investigated. Thus studies have been made on the infrared spectra of the series $XC_6H_4(CH=CH)_n.COCH_3$ [38,41,117,118], $XC_6H_4(CH=CH)_nCOC_4H_9$-n [30], and $XC_6H_4(CH=CH)_nCOC_4H_9$-t [42] and particularly detailed studies on the series of chalcones and their vinylogues $XC_6H_4(CH=CH)_n.COC_6H_4X'$ [10,11,27,29,33,37,40,45,60,119,120] as well as numerous heteroanalogues of chalcones: 1-(2′-furyl)-3-phenylpropenones [29,121], 3-phenyl-1-(2′-thienyl)propenones [24,29], 3-phenyl-1-(2′-pyrrolyl)-propenones [28], 3-phenyl-1-(2′-selenolyl)propenones [34], 3-phenyl-1-(2′-quinolyl)propenones [122], 3-α (or β)-naphthyl-1-(2′-thienyl)propenones [123], etc. as well as the ferrocene analogues of chalcones [32,33]. In addition, there are infrared spectroscopic data for one series of diketones (2-arylideneindan-1,3-diones) [36] and a single series of acetylenic ketones of the type $C_6H_5COC{\equiv}CC_6H_4X$. [46]

The influence of substituents on the absorption band of the carbonyl group [ν(CO)] in aldehydes has been studied much less, but purely aliphatic aldehydes of the type $X(CH=CH)_nCHO$ [43,44,124] and aliphatic-aromatic aldehydes of the series $XC_6H_4(CH=CH)_nCHO$ [25,26,42-44,124,125] have been investigated. There have also been several studies on the influence of substituents on ν(CO) for acids and esters in the aliphatic series $X(CH=CH)_nCOOR$ (R = H or C_2H_5) and the aliphatic-aromatic series $XC_6H_4(CH=CH)_n.COOR$ (R = H or C_2H_5) [9,22,28,35,126]. The influence of substituents on other groups has been studied very little. These investigations are restricted to the XC_6H_4CN, $XC_6H_4CH=C(C_6H_5)CN$, and $XC_6H_4CH=CHCH=C(C_6H_5)CN$ series [31,39,127,128] and there has been a single study of the influence of substituents on the symmetrical and asymmetric vibrations of the nitro-group in the series of ω-substituted α-(5-nitro-2-furyl)polyenes [129].

Table 1 gives a selection of typical examples of the influence of substituents on ν(CO) for some of the series listed above. It shows that the introduction of electron-accepting substituents increases ν(CO) compared with unsubstituted compounds and $\Delta\nu(CO) = \nu(CO)^X - \nu(CO)^H$ decreases with increase of the number of double bonds, $\Delta\nu$(CO) for compounds with 3-4 double bonds hardly exceeding the error of the measurement, which is ± 1-2 cm^{-1} (see Table 1, series 1, 4, and 6). On the other hand, the introduction of electron-donating substituents decreases ν(CO) and a tendency towards a decrease of $\Delta\nu$(CO) down to zero is also observed (Table 1, series 1, 4, and 6). Similar results have been obtained for nitriles [31,39,127,128]. The stretching vibration wave-numbers of the nitro-group in the series of α-(5-nitro-2-furyl)polyenes (series 1) are relatively insensitive to the nature of substituents and an increase in chain length does not affect $\nu(NO_2)^{sym}$:



where R = CHO, $COCH_3$, COOH, COOR′, $CH(OCOCH_3)_2CH=NNHCOCH_2CN$, etc. On the other hand, like ν(CO) and ν(CN), $\nu(NO_2)^{asym}$ increases appreciably when the proton is replaced by an electron-accepting group. An increase in chain length in this case also leads to a decrease of $\Delta\nu(NO_2)^{sym}$ down to zero.

Interesting features have been observed in series containing a variable substituent X in the benzene ring. In the first place, the influence of X on ν(CO) is in this case less marked than in aliphatic series (see, for example, series 1 and 2 in Table 1), which can be accounted for by an appreciable weakening of the influence of X during its transmission through the benzene ring. Furthermore, a strong influence of the conformation of the compound on ν(CO) has been noted, in particular ν(CO) for the *cis*-conformers is always smaller than the value for the *trans*-conformers (series 3 and 4 in Table 1). The most interesting feature is that the transition in series 3 and 4 from members of the series with $n = 0$ to members with $n = 1$ is seen to entail an appreciable increase of ν(CO) for the *cis*-conformers, sometimes reaching 10 cm^{-1}, instead of the expected decrease with increase in the length of the conjugation chain. The increase of the rigidity of the C=O bond following its relative approach to the double bond in *S-cis*-conformers can probably be accounted for by the strong interaction of these bonds [131,132]:

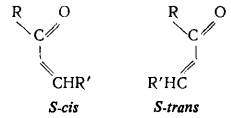


Table 1. Typical examples of the influence of substituents on the ν(CO) (cm^{-1}) of certain series of unsaturated compounds.

1	2	3	4	5	6	7	8	9	10	11	12
№	Series	n	H	CH_3	$CO_2C_2H_5$	NO_2	Cl	OCH_3	$(CH_3)_2N$	Remarks	References
1	$X(CH=CH)_nCHO$	0	—	1715	1712				1675	$CHCl_3$	43,44
		1	1730*	1690	1702				1615		
		2	—	1680	1689				1584		
		3	—	1678	1682				1640		
		4	—	—	1681				1681		
2	$X(CH=CH)_nCHO$ **	0	1702	—		1712		1687	1668	$CHCl_3$	43,44
		1	1677	—		1685		1675	1655		
		2	1675	—		1680		1675	—		
		3	1675	—		—		—	—		
3	$XC_6H_4(CH=CH)_nCOCH_3$	0	1691	—		1700		1683		CCl_4	41,47,118
		1	1697	—		1702		1693		*S-cis*	
		1	1674	—		1681		1670		*S-trans*	
4	$XC_6H_4(CH=CH)_nCOC_6H_5$	0	1666	—		—	—	—		CCl_4	33,130
		0	1660	—		—	1656	1654		$CHCl_3$	40,45
		1	1672	—		—	—	—		CCl_4, *S-cis*,	33,130
		1	1653	—		—	—	—		*S-trans*	
		1	1665	—		1670	1666	1660		$CHCl_3$, *S-cis*	40,45
		2	1660	—		1662	1659	1657			
		3	1654	—		1660	1658	1656			
5	$XC_6H_4(CH=CH)_nCO_2H$	0	1741			1724			1751	CCl_4	52
		1	1733			1724			1740		
6	$X(CH=CH)_nCO_2C_2H_5$***	1	1730*	1724		1735			1685	$CHCl_3$	22
		2	—	1718		1727			1680		
		3	—	1714		1721			1710		
		4	—	1715		1717			1712		
7	$XC_6H_4(CH=CH)_nCO_2C_2H_5$	0	1723			1731		1717		CCl_4	35,124
		1	1716			1722		1714			
8	$XC_6H_4(C{\equiv}C)_nCOC_6H_5$	0	1666				1650	1658		CCl_4	46,130
		1	1649			1654	1651	1645			

*Carbon tetrachloride [124].

**The following values of ν(CO) (in CCl_4) have been published [125] for X = C_6H_5 (the values of *n* are given in brackets): 1710 (0), 1689 (1), 1688 (2), 1685 (3), 1684 (4), and 1683 (5); the values of ν(CO) (CH_2Cl_2) are: 1704 (0), 1679 (1), 1677 (2), 1675 (3), 1674 (4), and 1673 (5, 6).

***The following values of ν(CO) (CCl_4) have been published [22] for X = $COOC_2H_5$ (the values of *n* are given in brackets): 1730 (1), 1721 (2), 1715 (3), 1714 (4), and 1713 (5, 6).

This feature can probably be used as an additional criterion for the assignment of an α-carbonyl β-unsaturated compound to the *S-cis*- or *S-trans*-form, apart from the usual criteria (the ratio of the intensities of the stretching vibrations of the C=O and C=C bonds and their difference [133]). This means that, when ν(CO) increases after the insertion of a double bond between the carbonyl group and the remainder of the molecule, the isomer obtained belongs to the *S-cis*-series and, when ν(CO) decreases, the isomer belongs to the *S-trans*-series.

In all cases, except for amino-derivatives, the accumulation of double bonds (see series 1 and 8) leads to a decrease of ν(CO). For amino-derivatives, a decrease of ν(CO) is initially observed, but subsequently it increases. The difference between the wavenumbers for adjacent members of the series diminishes and tends to zero.

In relation to the wavenumbers of functional groups or substituents, Eqn. (1) becomes

$$\Delta\nu = \nu - \nu_0 = \rho\sigma, \tag{1a}$$

or

$$\nu = \rho\sigma + \nu_0, \tag{1b}$$

where $\Delta\nu$ is the difference between the wavenumbers for the substituted and unsubstituted members of the series.

A correlation analysis has also been carried out for the intensities A of the vibrational bands, which are functions of the changes in the dipole moments and lengths of the vibrating bonds. The problem of the correlation of A still remains unresolved. Eqn. (1) was used in the following forms:

$$\lg(A/A_0) = \rho\sigma; \tag{1c}$$

$$\Delta A^{1/2} = \rho\sigma; \tag{1d}$$

$$\frac{A^2 - A_0^2}{A_0^2} = \rho\sigma. \tag{1e}$$

It has been noted that the application of Eqns. (1*c*), (1*d*), and (1*e*) frequently yields identical results [39,127,128].

Best results in the correlation analysis of series 1–8 (Table 1) were obtained when the constants σ^+ of σ_R^0 were used.

A new correlation equation has been proposed recently [134] for the interpretation of ν(CO) data for aromatic and aliphatic-aromatic carbonyl compounds:

$$\nu(\mathrm{CO}) = 1583 + 38{,}2\,[X(\mathrm{R}') + X(\mathrm{R}'')]\ (\mathrm{cm}^{-1}), \tag{8}$$

where X(R′) and X(R″) are constants which depend on the nature of R′ and R″ in the carbonyl compounds R′COR″. The new constants X(R) and the Hammett–Taft substituent constant are linked by the relation

$$\delta' = 0{,}482\,\sigma^*,\ \delta' = X(\mathrm{R}) - X(\mathrm{CH_3}),\ \text{and}\ \delta = \beta\sigma/10,$$

where $\delta = X(\mathrm{R}) - X(\mathrm{C_6H_5})$ and β depends on the type of substituent in the aromatic ring (*para*- or *meta*-) and on the nature of the substituent (electron-donating or electron-accepting). Somewhat later [10,135] Eqn. (1) was extended to unsaturated aliphatic-aromatic compounds of the type RCOCR′ = CR″R‴, the constants X(R) being replaced by new constants X^+(R) (calculated from the electrophilic constants σ^+), which yield an appreciably higher correlation coefficient than the Hammett σ constants. The new constants X^+(R) are empirically related to the σ^+ constants by the equation

$$X^+(\mathrm{R}) = 0{,}238\,\sigma^+ + 1{.}077, \tag{9}$$

and when the benzene ring contains more than one substituent, we have

$$X^+(\mathrm{R}) = 0{,}238\sum_{n=1}^{n}\sigma_i^+ + 0{,}007n + 1{.}070.$$

The values of X^+(R) for many substances have been calculated by Eqn. (9) and their applicability to 287 compounds of the type R′CH=CHCOR″ with *meta* and *para*-substituents in the benzene ring has been demonstrated.

It is noteworthy that both Eqns. (1*a*) and (1*b*) and Eqn. (8) with the constants X^+(R) proved to be inapplicable to members of series 4 with $n = 2$ or 3 (Table 1). This distinguishes series 4 from series 1, 2, and 6, which obey the Hammett equation also for members with $n = 2$–4.

Table 2. The fundamental wavenumbers (cm^{-1}) in the Raman spectra of the $C_2H_5O_2C(CH{=}CH)_nCO_2C_2H_5$ series (solvent—acetone, exciting light—blue mercury line, $\nu = 22\,938\ \mathrm{cm}^{-1}$).

n	ω_1	ω_2	ω_3	n	ω_1	ω_2
1	1210	1664	1733	5	—	1570
2	1135	1644	1726	6	1142	1562
3	1139	1621	1721	7	1140	1550
4	1139	1596	1717	8	1137	1540

Raman Spectra

Analysis of the Raman spectra of series of polyene esters $C_2H_5O_2C(CH{=}CH)_nCO_2C_2H_5$ (n = 1–8) showed that the vibrational wavenumbers for these compounds change little with increase in chain length [136]. It follows from the data in Table 2 that, with increase of chain length, the addition of each new unit has an increasingly smaller effect on the wavenumbers, i.e. the mutual influence of the atomic groups is weakened.

NMR Spectra

Since chemical shifts characterise the electron density, including the π-electron density, NMR has also found application in the study of the influence of substituents at a multiple bond in unsaturated compounds. The influence of substituents on the chemical shift of olefinic protons has been studied in the *trans*-$CH_3CH{=}CHX$ and *trans*-$C_6H_5CH{=}CHX$ series [49–51], methyl esters of *trans*-α- and *trans*-β-substituted cinnamic acids [50,51], *trans*-β-substituted methyl vinyl ketones and acryloyl chlorides [51], *cis*- and *trans*-cinnamic acids [51–53], chalcols [12,54], substituted styrenes $XC_6H_4CH{=}CH_2$ [55], and 1-arylpropynes [56]. Table 3 presents typical examples of the influence of substituents on the chemical shifts of the hydrogen atom in the β-position relative to the substituent. It shows that electron-accepting substituents cause an upfield displacement of the

signal due to the proton in the β-position with respect to the substituent, while electron-donating substituents have the opposite effect.

Table 3. Typical examples of the influence of substituents on the chemical shifts δ (p.p.m.) of hydrogen atoms in selected series of unsaturated compounds [solvent—CCl_4, internal standard—tetramethylsilane (TMS)].

$XCH=\underline{CH_2}$*[51]

CH_3	H	C_6H_5	Cl	Br	$COOCH_3$	$COCH_3$	CN
4.96	5.33	5.71	5.52	5.88	6.22	6.09	5.91

$XCH=\underline{CHC_6H_5}$[50]

H	Cl	NO_2	CH_3	CHO	COOH	$COOCH_3$	CN	C_6H_5
6.67	6.54	7.92	6.24	7.43	7.72	7.57	7.32	6.99

$XCH=\underline{CHCOOCH_3}$[51]

CH_3	H	C_6H_5	Cl	Br	$COOCH_3$	$COCH_3$	COCl
5.76	5.99	6.31	6.16	6.48	6.74	6.57	6.96

$p\text{-}XC_6H_4CH=\underline{CH_2}$[53,55]

	OCH_3	CH_3	H	Cl	NO_2
cis-	5.07	5.14	5.23	5.28	5.51
trans-	5.61	5.70	5.75	5.81	6.05

$p\text{-}XC_6H_4CH=\underline{CH}COOH$[53]

	OCH_3	CH_3	H	Cl	NO_2
cis-	5.82	5.92	6.00	6.03	6.31
trans-	6.35	6.47	6.54	6.56	6.74

*The chemical shifts of the underlined hydrogen atoms in the β-position with respect to the substituent are quoted.

Apart from ^1H NMR, the influence of substituents in unsaturated compounds has been investigated by ^{13}C NMR.[56] Table 4 presents the chemical shifts of ^{13}C in the β-position with respect to the aryl group containing the substituent for the series of 1-arylprop-1-enes and 1-arylprop-1-ynes. The introduction of electron-donating substituents causes an upfield shift of the ^{13}C signal, while electron-accepting substituents give rise to a downfield shift.

Table 4. The chemical shifts of the β-^{13}C atoms in the unsaturated group (δ in p.p.m., standard—TMS, no solvent)[56].

Series	X					
	p-CH_3O	*p*-CH_3	H	*m*-CH_3O	*p*-Cl	*m*-Cl
$XC_6H_4CH=\underline{C}HCH_3$	*cis*-125.2	125.9	126.9	—	127.8	—
	trans-123.6	124.6	125.7	126.1	127.1	—
$XC_6H_4C\equiv\underline{C}CH_3$	84.7	85.6	86.4	—	87.7	88.2

Finally, studies have been made[57,58] on the influence of substituents on the chemical shift of the ^{19}F nuclei in $XC_6H_4CH=CHC_6H_4F$-*p* (Table 5). In this case substituents have an appreciable influence on the position of the ^{19}F signal, electron-donating and electron-accepting substituents producing opposite effects on the position of the signal.

A satisfactory correlation has been observed when Eqn. (1) was used in the form

$$\Delta\delta = \delta - \delta_0 = \rho\sigma,$$

where Δδ is the difference between the ^1H, ^{13}C, or ^{19}F chemical shifts for substituted and unsubstituted members of the series.

Table 5. The ^{19}F chemical shifts in $XC_6H_4CH=CHC_6H_4F$-*p* [δ (p.p.m.) relative to 1,1,2,2,3,3,4,4,-octafluorobutane, solvent—benzene].

X	*p*-OCH_3	H	*m*-Cl	*p*-Cl	*m*-CF_3	*m*-NO_2	*p*-NO_2
δ	1.38	0.71	−0.02	−0.17	−0.36	−0.76	−1.35

Dipole Moments

The dipole moment is a direct characteristic of the electronic structure of the molecule. A change in the structure or the introduction of the substituent involves a redistribution of electron density and a change in the dipole moment. In unsaturated compounds, the relative contribution of the conjugation effects is expressed by the mesomeric effect (μ_m), defined as the difference between the dipole moments of the corresponding saturated and unsaturated compounds[137]. With increase in the length of the conjugated system, μ_m also increases[138,139] for all substituents except halogens, whose mesomeric effect is small[140].

Table 6. The dipole moments of certain disubstituted compounds of the type $X(CH=CH)_nCHO$ (μ, D; solvent—benzene).[62]

n	1		2		3		4	
X	μ_{exp}	μ_{int}	μ_{exp}	μ_{int}	μ_{exp}	μ_{int}	μ_{exp}	μ_{int}
CH_3	3.49	1.00	3.98	1.49	4.47	1.98	4.95	2.46
$COOC_2H_5$	3.15	1.85	3.49	1.77	3.40	1.98	3.55	1.78
$(CH_3)_2N$	6.24	2.95	7.62	4.33	8.24	4.95	8.50	5.21

The presence at the ends of the conjugated system of substituents of different types (electron-donating and electron-accepting) causes a displacement of electrons from the electron-donating to the electron-accepting groups, which leads to the appearance of an additional dipole moment. The vector difference between the experimental and calculated dipole moments is called the interaction moment (μ_{int}).[141]

It has been shown for a series of substituted benzenes XC_6H_4Y and styrenes $XC_6H_4CH=CHY$ that the values of μ_{int} are higher for ethylenic compounds when X and Y are of different electronic types and lower when X and Y are both powerful electron acceptors[142,143]. The same rule holds also for the series of linear polyene aldehydes[62,144]. The insertion of a multiple bond between the substituents

in the disubstituted compounds probably promotes the mutual enhancement of conjugation for electron-donating and electron-accepting substituents and weakens the conjugation for two electron-accepting substituents owing to the competitive interaction of the functional groups with the π-electron system of the multiple bonds. The above features of the influence of substituents on the dipole moments of unsaturated compounds are illustrated by examples in Table 6. It is noteworthy that high interaction moments (μ_{int}) are observed for all aliphatic polyenes, the moments increase with chain length in an acceptor–donor system, change little in an acceptor–acceptor system, and increase regularly in a methyl–acceptor system.

A completely different behaviour is observed in systems of the type $XC_6H_4(CH{=}CH)_nCOC_6H_5$ (Table 7). In this case, the dipole moments of compounds with n = 1–3 are very close to those for substituted benzophenones, and the μ_{int} are very low, except for amino-derivatives. The features of chalcones and their vinylogues noted above indicate a weak interaction between the carbonyl group and the π-electron system of the C_6H_4X-*p* group (except for amino-derivatives). This can be explained both by the appreciable weakening of the influence of the group X owing to the benzene ring and by the non-planar structure of such compounds. X-Ray diffraction and Rayleigh light scattering data for benzophenones [146] and X-ray diffraction analysis of chalcones and their vinylogues [147,148] have shown that the rings are rotated by an angle of 30–31° in benzophenone, 36–37° in *p*-bromochalcone, 51° in the vinylogue with n = 2, and 3° in the vinylogue with n = 3. Furthermore, the angle between the plane of the ring of p-BrC_6H_4 and the plane of the double bond is 27° in *p*-bromochalcone, 16° in the vinylogue with n = 2, and 18° in the vinylogues with n = 3. Thus the compounds are non-planar and the transmission of the electronic influence via the mesomeric mechanism should be weakened, i.e. the values of μ_{int} should also be small, which is in fact observed experimentally. The high values of μ_{int} for amino-derivatives can be attributed to the direct polar conjugation between the amino- and carbonyl groups, which presupposes an appreciably smaller (owing to the $=C-C_{Ar}$ bond order) deviation from the planar conformation in the amino-derivative compared with other substituted derivatives.

Table 7. The dipole moments of certain members of the *trans*, *cis*-*p*-$XC_6H_4(CH{=}CH)_nCOC_6H_5$ series.[45,61,145].

n	0	1		2		3	
X	μ_{exp}	μ_{exp}	μ_{int}	μ_{exp}	μ_{int}	μ_{exp}	μ_{int}
H	2.99	3.07	0.11	3.05	0.09	3.39	0.43
NO_2	4.23	4.16	−0.02	4.19	0.01	4.30	0.12
OCH_3	—	3.60	0.28	3.62	0.30	3.61	0.29
Cl	2.95	2.56	−0.33	2.58	−0.31	2.59	−0.30
$(CH_3)_2N$	—	5.22	2.66	5.44	1.88	—	—

The applicability of the Hammett equation in form (1) to the correlation of the dipole moments of non-aromatic unsaturated compounds was first demonstrated by Charton [59]. The optimum correlation is achieved using the constants σ_R^+ for electron-donating substituents and σ_R^- for electron-accepting substituents. Apart from Eqn. (1) in the form

$$\Delta\mu = \rho\sigma,$$

use is made of Eqn. (1*f*) (where account is taken of the distances d^X and d^H between the centres of the substituent Y and the variable substituent X or H at the ends of the unsaturated chain), which was proposed by Exner [149] on the basis of the analysis of numerous dipole moments of aromatic compounds:

$$\frac{\mu^X - \mu^H}{d^X - d^H} = \rho\sigma. \qquad (1f)$$

Ultraviolet Spectra

The characteristics of the electronic structures of linear conjugated molecules are manifested most clearly in the ultraviolet absorption spectra. It has been established that the introduction of each new double bond causes a shift of the absorption bands in the spectra of series of disubstituted unbranched polyenes [150–165] towards the visible part of the spectrum, the shift diminishing with increase of the number of double bonds. The dependence of the wavelength of the main absorption maximum on the number of double bonds in the molecule is expressed fairly satisfactorily by the semi-empirical equation of Lewis and Calvin [166]:

$$\lambda^2_{max} = kn.$$

Examples are quoted in a number of communications [123,154,157–159,167–169].

Table 8. The principal absorption maxima in the spectra of certain linear polyenes (λ, nm).

(a) $X(CH{=}CH)_nY$

X	Y	Solvent	n				
			1	2	3	4	5
H	H	Hexane	—	—	274.5[158]	310[158]	341[158]
CH_3	CH_3	»	—	227[167]	267.5[158]	304[158]	334[158]
CH_3	$COOC_2H_5$	Alcohol	206[160]	258[160]	301[160]	334[160]	365[160]
NO_2	$COOC_2H_5$	»	222[160]	281[160]	327[160]	363[160]	—
$(CH_3)_2N$	$COOC_2H_5$	Chloroform	283[182]	345[182]	400[182]	430[182]	—
$COOC_2H_5$	$COOC_2H_5$	Alcohol	210[160]	264[160]	303[160]	335[160]	365[160]

(b) $XC_6H_4(CH{=}CH)_nCOC_6H_5$ (in toluene) (Ref.45)

n	X					
	H	CH_3O	$(CH_3)_2N$	Cl	Br	NO_2
1	311	342	407	317	319	318
2	345	369	435	347	347	358
3	370	400	—	370	372	383

(c) $XC_6H_4(CH{=}CH)_nCOH$ (in alcohol) (Ref.44)

n	X					
	H	CH_3O	$(CH_3)_2N$	Cl	Br	NO_2
0	247	277	339	258	264	263
1	288	323	389	299	302	303
2	330	353	—	329	333	333
3	361	382	—	—	—	—

The following characteristic features have also been noted for linear disubstituted polyenes. The replacement of an ethyl group in dimethylpolyenes by an electron-accepting or electron-donating substituent causes a bathochromic shift of the main absorption maximum,

which increases in the following sequence of substituents: $C_2H_5O < COOC_2H_5 < CHO \leqslant COCH_3 < NO_2$. The replacement of the methyl group in the methylpolyenals $CH_3(CH=CH)_nCHO$ or the polyenoic esters $CH_3(CH=CH)_nCOOC_2H_5$ by an electron-accepting substituent results in small bathochromic or hypsochromic shifts. The replacement of the methyl group by an electron-donating group leads to significant bathochromic shifts (see Table 8, *a*). A similar behaviour has also been observed in the $XC_6H_4(CH=CH)_nCHO$ and $XC_6H_4(CH=CH)_n.COOC_2H_5$ series[63] (Table 8, *b*).

A detailed study of the ultraviolet spectra of chalcones and their vinylogues[40,45,170-173] and also of the heteroanalogues of chalcones and their vinylogues[174-181] showed that an increase in the length of the conjugated chain also leads to a bathochromic shift of the principal absorption maximum, the shift being particularly marked when electron-donating and electro-accepting groups are introduced simultaneously at the opposite ends of the molecules. Regardless of the nature of the substituents, substitution in the *para*-position of the cinnamoyl part of the molecule leads to a bathochromic shift of the absorption maximum, which increases in the sequence $H < Cl=Br < NO_2 < OCH_3 < N(CH_3)_2$ (Table 8).

The correlation of the ultraviolet spectroscopic data leads to satisfactory results when the σ^+ constants are used in Eqn. (1) in the form

$$\frac{1}{\lambda_H} - \frac{1}{\lambda_X} = \rho\sigma.$$

Mass Spectrometry

The possibility of the correlation of the ionisation potentials with the Hammet σ constants when the two-parameter Eqn. (4) is used for substituted ethylenes and unsaturated carbonyl compounds was observed by Charton[7,64]. On the other hand, the correlation between the relative intensity of the common ion peak and the Hammett σ constants in terms of the simple Eqn. (1) in the form

$$\lg Z/Z_0 = \rho\sigma,$$

where Z and Z_0 are respectively the relative intensities of the peaks of the common fragment ion peaks in substituted and unsubstituted compounds, was established by Bursey and McLafferty[183] in relation to benzophenones (with a common benzoyl ion) and was later extended to chalcones and their vinylogues[45,65,66]. An excellent correlation was achieved using the Hammett σ constants for the entire $C_6H_5CO(CH=CH)_nC_6H_4X$ series (where $n = 1-3$).

The mass-spectrometric method has a number of advantages compared with methods based on measurements in solutions, where it is extremely difficult to take into account quantitatively the interactions between the solvent and solute (the solvation and steric interactions), which distorts the results obtained. Fragmentation in the mass-spectrometer takes place in the gas phase at pressures guaranteeing the absence of collisions of molecules with one another. Thus the use of the mass-spectrometric method makes it possible to determine the exact quantitative characteristics of the efficiency of the transmission of electronic influences by various bridge systems.

Basicity and Acidity

The influence of substituents on the basicity and acidity of unsaturated compounds has been investigated in fair detail. Particularly systematic studies have been made on chalcones and their analogues. Investigation of the comparative basicities of chalcones by the measurements of the shift of the stretching vibration wavenumber of the hydroxy-group in phenols [ν(OH)] in carbon tetrachloride in the presence of chalcones owing to the formation of an intermolecular hydrogen bond[11,79] showed that the introduction of electron-donating substituents [CH_3, CH_3O, and $(CH_3)_2N$] increases the basicity of chalcones [increases $\Delta\nu$(OH)], while the introduction of electron-accepting substituents lowers their basicity [decreases $\Delta\nu$(OH)]. The constants K_{ass} for the association of phenol with chalcones have also been determined from the change in the intensity of the stretching vibration band of the phenolic OH group in the presence of chalcones[82]. As a result, it has been established that K_{ass} increases following the introduction of electron-donating substituents and decreases in the presence of electron-accepting substituents in chalcones.

A dependence of $\Delta\nu$(OH) on the nature of the substituents similar to that noted above has also been observed in the study of the hydrogen bonds between 2,3,4,6-tetrachlorophenol and chalcones[83] and between trifluoroacetic acid and chalcones[84]. In the latter case $\Delta\nu$(OH) is particularly sensitive to the electronic effects of the substituents. The influence of the nature of the substituent on basicity [based on $\Delta\nu$(OH) or the constants K_{ass} for association with phenols] has also been investigated for furan, thiophen, selenophen[79,82-84,184,185], and pyrrole[79,184,185] analogues of chalcones. The same relations as for chalcones have been observed for all the compounds.

Table 9. The values of pK_{BH^+} for certain aminostilbenes and tolanes and the values of pK_a for certain hydroxystilbenes and tolanes.

Series	X			References
	H	H_2N	NO_2	
p-$XC_6H_4CH=CHC_6H_4NH_2$-*p* (*trans*-)	3.78	3.95	3.43	76
p-$XC_6H_4C\equiv CC_6H_4NH_2$-*p*	3.04	3.18	2.74	77
p-$XC_6H_4CH=CHC_6H_4OH$-*p* (*trans*-)	10.73	10.84	10.13	78
p-$XC_6H_4C\equiv CC_6H_4OH$-*p*	10.31	10.37*	9.97	78

*X = OCH_3.

The basicities in certain other series, particularly in amino-[76,77] and hydroxy-derivatives[78] of *trans*-stilbenes and tolanes, have also been determined. Table 9 lists the basicities (in 50% alcohol) of certain compounds. It is seen that a slight but clear influence of the substituents on basicity is observed in this group of compounds too. Electron-donating substituents increase pK_{BH^+} or pK_a, while electron-accepting substituents cause a decrease. The influence of the substituent is more pronounced in the series of stilbenes.

A number of studies have been made on the influence of substituents on the acidity of unsaturated carboxylic acids of the type XCH=CHCOOH, RCX=CHCOOH, or $XC\equiv CCOOH$[7,8,68-75,80,81,85-87]. Typical examples are compiled in

Table 10. The introduction of electron donors in the β-position of the unsaturated acid lowers its acidity, while electron acceptors increase it.

The majority of the series investigated exhibit a satisfactory correlation with the σ^- and σ^+ constants in terms of Eqn. (1) in the form

$$\lg K/K_0 = \rho\sigma.$$

Table 10. The pK_a values for certain unsaturated acids.

Series	Solvent	X					References
		H	CH_3	COC_6H_5	*n*-OCH_3	*n*-O_2N	
XCH=CHCOOH, *cis*-	80% $CH_3OCH_2CH_2OH$	6.50	7.07	5.33	—	—	87
trans-	ditto	—	6.77	5.78	—	—	87
$XC_6H_4C{\equiv}CCOOH$	50% alcohol	3.40	—	—	3.63	2.87	70

Polarographic Reduction

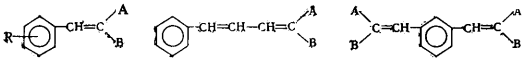
Polarographic reduction constitutes a convenient method for the investigation of the reactivities of unsaturated compounds containing polarographically active groups. The electrochemical reduction of linear polyenals of the type $X(CH{=}CH)_nCHO$ (n = 1–5) and p-$XC_6H_4(CH{=}CH)_nCHO$ (n = 0–3) [7,44,93,125,186] and unsaturated ketones of the type $C_6H_5CO(CH{=}CH)_nC_6H_4X$ (n = 0–3) [45,87,89,90,91,94] has been investigated. It has been noted for both aldehydes and ketones that the accumulation of double bonds facilitates reduction, the increment per double bond decreasing with increase in chain length. Other conditions being equal, electron-accepting substituents facilitate reduction while electron-donating substituents hinder it. As double bonds accumulate, the influence of substituents is abolished (Table 11).

Table 11. The influence of substituents on the half-wave potentials (mV) in selected series of carbonyl compounds (relative to the saturated calomel electrode).

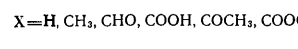
Series	*n*	CH_3	$(CH_3)_2N$	CN	References
$X(CH{=}CH)_nCHO$	1	1060	*	482	44,93,186
	2	771	1013	518	
	3	598	791	401	
	4	472	646	220	
		H	CH_3O	Cl	
p-$XC_6H_4(CH{=}CH)_nCHO$	0	1007	1068	948	44,93
	1	725	744	628	
	2	507	544	468	
p-$XC_6H_4(CH{=}CH)_nCOC_6H_5$	1	557	584	513	45,94
	2	446	452	428	
	3	354	390	376	

*Not reduced.

Similar relations have been observed for heteroatomic systems [187] of the type



Apart from the investigation of carbonyl compounds, the polarographic method has been used to study the transmission of the polar effect via the furan ring and other bridges, including the vinyl group, in the series of α-nitrofuryl-α′-vinyl derivatives [88,92]:

X=H, CH_3, CHO, COOH, $COCH_3$, $COOCH_3$. 

There is no unanimous view concerning the interpretation of the dependence of half-wave potentials on the structure of organic compounds [188–191]. Lagutskaya and Dadali [190] believe that the influence of the electronic structure of the substituent and its position in the molecule is reflected in different ways in the electron density at the reaction centre and in the energy levels. They suggest that the free energy of the stage determining the potential of the polarographic process depends primarily on the electron affinity of the molecule and that the influence of substituents on the half-wave potential should be treated from the standpoint of the change in the energy of the lowest vacant molecular orbital. Thus the correlation of the half-wave potentials with the Hammett constants is possible only when there is a direct proportionality between the change in electron density at the reaction centre and in the positions of the energy levels, which happens only for a limited range of substituents. Indeed, the correlation between the half-wave potentials and the σ constant is observed solely within narrow series of the same type [44,45].

Eqn. (1) in the form

$$\Delta E_{1/2} = \rho\sigma, \qquad (1g)$$

or the two-parameter Yukawa-Tsuno equation

$$\Delta E_{1/2} = \rho(\sigma + r\Delta\sigma^+_R) \qquad (9a)$$

are used for the correlation. In particular, Eqn. (1g) has proved applicable to chalcones using the σ^0 constants and aldehydes of the $R(CH{=}CH)_nCHO$ series using the σ^0_R constants Eqn. (9a) yielded satisfactory results for the $C_6H_5CO(CH{=}CH)_nC_6H_4X$ (n = 1–3) series.

Reaction Kinetics

The study of the influence of substituents on the reactivity of unsaturated compounds is of particular interest. For this purpose, one can use the influence of substituents on the rate of reaction of a functional group in the $X(CH{=}CH)_nY$ series, where Y is a functional group, or on the rate of addition of an addend to the double bond in the $X(CH{=}CH)_nY$ system, where Y = H or a fixed substituent.

The kinetics of the esterification of unsaturated acids [67,95,101,198] and of the hydrolysis of esters [44,112,192,193] as well as deuterium exchange in monosubstituted acetylenes [99,100,103,194] and in the methyl group of benzylideneacetones [195] have been studied on the widest scale. There are also data for the kinetics of the conversion of benzylideneacetones into oximes [111], the acetylation of aminostilbenes [99] and aminochalcones [110], the formation of complexes of monosubstituted acetylenes with diethylacetamide [108], and also the acid and alkaline cleavage of the $XC_6H_4(C{\equiv}C)_nMR_3$ systems (M = Si or Ge) [96,97,107,197,198]. The influence of substituents on addition to double bonds has been much less investigated. Here one may note studies on the addition of dichlorocarbene to compounds of the type $XC_6H_4(CH{=}CH)_nH$ (n = 1 or 2) [113,115] and the addition of HX in aqueous dioxan to $XC_6H_4C{\equiv}CCOOH$ [106] and of diazomethane to p-$XC_6H_4C{\equiv}CH$. [114]

Table 12. The rates of certain reactions involving the functional group R in the $X(CH=CH)_nR$ and $X(C\equiv C)_nR$ systems.

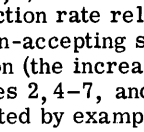
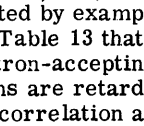
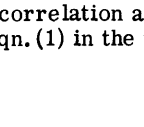
Reaction	Rate characteristic	X					References
1. $XCH=CHCOOH+CH_3OH \xrightarrow{H^+,\ 35^\circ} XCH=CHCOOCH_3$	10^2k, s^{-1}	H	OCH_3	CH_3	Cl	O_2N	
cis-isomers		2.00	—	3.87	3.40	—	103
trans-isomers		—	4.70	9.07	5.13	2.62	
2. $XC_6H_4(CH=CH)_nCOOC_2H_5 \xrightarrow{OH^-} XC_6H_4(CH=CH)_nCOOH$	lg k (298° K)	H	OCH_3	Cl		O_2N	
(*trans*-isomers) $n=0$		−2.33	−3.02	−0.65		−1.88	44
$n=1$		−2.44	−2.64	−1.27		−1.94	
$n=2$		−2.60	−2.61	−1.83		−2.23	
$n=3$		−2.60	−2.60	—		−2.43	
3. $XC_6H_4C\equiv CCOOH+(C_6H_5)_2CN_2 \rightarrow XC_6H_4C\equiv CCOOCH(C_6H_5)_2$	10^2k, litre $mole^{-1}$ s^{-1}	H	p-OCH_3		p-NO_2		
		0.53	0.56		0.25		67
4. $XC\equiv CCOOC_2H_5 \xrightarrow{OH^-} XC\equiv CCOOH$	k, litre $mole^{-1}$ s^{-1}	H	CH_3		$COOC_2H_5$		
		4.68	0.568		69.0		193
5. $XCH=CHCOOC_2H_5 \xrightarrow{OH^-} XCH=CHCOOH$	k, litre $mole^{-1}$ s^{-1}	H	CH_3		$COOC_2H_5$		
trans-isomers		0.0779	0.043		4.47		193
6. $XC\equiv CH \xrightarrow[NH_3,D]{KNH_2} XC\equiv CD$	k_{rel}	H	OCH_3		CF_3		
		1	0.5		10 000		99
7. $XC_6H_4CH=CHCOCH_3+NH_2OH \xrightarrow[pH\ 7,6]{} \rightarrow XC_6H_4CH=CHC(=NOH)CH_3$	k, min^{-1}	H	p-OCH_3		p-NO_2		
		0.5	0.45		2.6		111
8. $XC_6H_4(C\equiv C)_nGe(C_2H_5)_3 \xrightarrow[CH_3OH]{HClO_4\ (30^\circ)} XC_6H_4(C\equiv C)_nH$	10^3k, min^{-1}	H	p-OCH_3		p-NO_2		
$n=2$		110	255		20.7		107
$n=3$		34.7	148		6.15		
9. $XC_6H_4(C\equiv C)_nSi(C_2H_5)_3 \xrightarrow[30^\circ]{KOH\ (CH_3OH)} XC_6H_4(C\equiv C)_nH$	k_{rel}	H	p-OCH_3		p-NO_2		
$n=2$		1	0.55		5.54		198
$n=3$		1	0.59		3.33		

Table 12 presents typical examples of kinetic data for certain reactions involving functional groups in unsaturated compounds, while Table 13 lists data for the reactions involving double or triple bonds. Depending on the nature of the reaction, the introduction of electron-donating substituents either reduces (Table 12, examples 2, 4, 6, 7, 9) or increases (Table 12, examples 1, 3, and 8) the reaction rate relative to the unsubstituted compound. Electron-accepting substituents act in the opposite direction (the increase of the rate is illustrated by examples 2, 4–7, and 9 in Table 12 and its decrease is illustrated by examples 1, 3, and 8). It is seen from the data in Table 13 that electrophilic reactions are retarded by electron-accepting substituents, while nucleophilic reactions are retarded by electron-donating substituents.

The correlation analysis of kinetic data is carried out using Eqn. (1) in the form

$$\lg K/K_0 = \rho\sigma.$$

Table 13. The rates of addition to multiple bonds (some examples of the influence of substituents).

Reaction	Reagent (reaction conditions)	Rate characteristic	X			References
			H	n-CH_3O	n-NO_2	
$XC_6H_4CH=CHCOCH_3 \rightarrow$ 	NH_2OH (90% methanol; pH 7,6; 17,5°)	k, min^{-1}	3.60	2.55	5.40	111
$XC_6H_4CH=CHCH=CH_2 \rightarrow$ 	: CCl_2 ($Cl_3COOC_2H_5$, CH_3ONa, O°, petroleum ether)	k_{rel}	1	2.08	0.47	115
$XC_6H_4C\equiv CH \rightarrow$ 	CH_2N_2 (ether)	k, litre $mole^{-1}$ s^{-1}	0.099	0.078	3.225	114

IV. THE CHARACTERISTICS AND MECHANISM OF THE TRANSMISSION OF THE INFLUENCE OF POLAR SUBSTITUENTS VIA MULTIPLE BONDS

The quantitative characteristics of the transmission of the influence of substituents via multiple bonds are based on correlation analysis (see Section II) and on the determination of transmission factors. It is noteworthy that, whereas there have been numerous studies on correlation analysis, the transmission factors have been determined in a much smaller number of instances, which is explained mainly by the difficulty of selecting suitable reference series. Table 14 lists the transmission factors for one (π'_{1F}), two (π'_{2F}), three (π'_{3F}), and four (π'_{4F}) double bonds and for one (π'_{1F}), two (π'_{2F}), and three (π'_{3F}) triple bonds.

Although the total number of series investigated is not as yet very large (21 series) and certain types of compounds have not been studied at all or have been studied inadequately, nevertheless analysis of the data in Table 14 yields information about certain characteristic features of the transmission of influences via multiple bonds. In the first place, the long range of variation of the values of π'_{1F} [from 0.42 (series 9) to 0.87 (series 1)] is probably evidence that π' for the $X(CH=CH)_nY$ systems depends not only on the nature of the bridge [1,199] but also on the nature of the unchanged part of the molecule Y. Thus the values of π'_{1F} found from the correlation analysis of ν(CO) or ν(CN) are 0.74 (series 2), 0.62 (series 6, *S-cis* in CCl_4), 0.82 (series 6, *S-trans* in CCl_4), 0.64 (series 10), and 0.61 (series 17). It is therefore hardly useful to

combine in a single series compounds of different types, as has been done in series 21, which includes all carbonyl compounds regardless of their nature (aldehydes, ketones, carboxylic acids, and their esters and amides).

Table 14. Transmission factors.

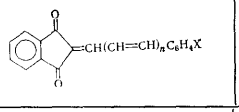
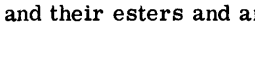
Series	Property	σ	π′	Remarks	Refs
1. X $(CH=CH)_n$CHO *trans-*	μ	σ^+ or σ^0_R	0.87 (1F) 0.68 (2F) 0.56 (3F) 0.43 (4F)		44
»	λ_{max}	σ^+_R	0.85 (1F) 0.75 (2F) 0.62 (3F)		44
»	q_0	σ^0_R	0.47 (1F) 0.22 (2F) 0.10 (3F)		44
2. $XC_6H_4(CH=CH)_nCHO$ *trans-*	ν(CO)	σ^+	0.74 (1F) 0.58 (1F) 0.69 (1F)	In CCl_4 In $CHCl_3$ Association of phenol with CO	25, 26 44 199
»	λ_{max}	σ^+_R	0.79 (1F) 0.63 (2F)		44
»	$E_{1/2}$	σ^0_R	0.86 (1F) 0.63 (2F) 0.70 (1F)	50% DMF, pH 2 Abs. DMF, R_4NI	44 199
3. X′ $(CH=CH)_n$CHO X′=X, XC_6H_4, *trans-*	ν(CO)	σ^0_R	0.67 (1F) 0.49 (2F) 0.29 (3F) 0.13 (4F)	$CHCl_3$, CCl_4	44
4. $XC_6H_4(CH=CH)_nCOCH_3$ *trans-*	ν(CO)	σ^+	0.47 (1F) 0.54 (1F)	CCl_4, *S-cis* *S-trans*	41
»	$\Delta\nu$(OH..OCR_2)	σ	0.76 (1F)		199
»	$E_{1/2}$	σ	0.76 (1F)		199
5. $XC_6H_4(CH=CH)_nCOC_4H_9$-t *trans-*	$\Delta\nu_{OH...OCR}$	σ	0.75 (1F)		199
»	$E_{1/2}$	σ	0.73 (1F)		199
6. $XC_6H_4(CH=CH)_nCOC_6H_5$	ν_{CO}	σ^+	0.62 (1F) 0.82 (1F) 0.79 (1F) 0.82 (1F)	CCl_4, *S-cis* *S-trans* $CHCl_3$, *S-cis* *S-trans*	11 45
»	ν(OH...OCR_2)	σ^+	0.70 (1F)		199
»	ν(OH...OCR_2)	σ	0.8 (1F)		78
»	K_{ass}	σ	0.7 (1F)		81
»	μ	σ^+	0.82 (1F)		45
»	$E_{1/2}$	σ^+	0.71 (1F)		199
»	λ_{max}	σ^+	0.72 (1F) 0.55 (2F)		45
»	Z/Z_0	σ	0.72 (1F) 0.25 (2F) 0.11 (3F)		45
7. 	ν(CO)	σ^+	0.72 (1F) 0.76 (1F)	sym. asym.	36 »
8. $XC_6H_4(C\equiv C)_nCOC_6H_5$	ν(CO)	σ^+	0.58 (1F)		41
9. $XC_6H_4(CH=CH)_nCOOH$ *trans-*	pK_a	σ	0.47 (1F)		8
»	*k*	σ	0.44 (1F)	Esterification	71
10. X $(CH=CH)_nCOOC_2H_5$ *trans-*	ν(CO)	σ^+	0.64 (1F) 0.42 (2F) 0.25 (3F)		22 » »
11. $XC_6H_4(CH=CH)_nCOOC_2H_5$ *trans-* *cis-* *trans-*	*k*	σ^+	0.52 (1F) 0.33 (2F) 0.13 (3F) 0.43 (1F) 0.50 (1F) 0.54 (1F)	Alkaline hydrolysis, 66% dioxan Ditto, 50% alcohol » Ditto » Ditto, 88% alcohol	44 » » 71 » 200

Table 14 (continued).

Series	Property	σ	π′	Remarks	Refs.
12. 	$E_{1/2}$	σ	0.50 (1F) 0.60 (1F)	DMF, R_4NI water, pH 12	92 »
13. $XC_6H_4C\equiv CCOOH$	pK_a	σ	0.35 (1F) 0.33 (1F)	85% alcohol 50% alcohol	200 71
»	*k*	σ	0.33 (1F)	Esterification, $(C_6H_5)_2CN_2$	72
14. $XC_6H_4C\equiv CCOOC_2H_5$	*k*	σ	0.42 (1F)	Alkaline hydrolysis, 50–88% alcohol	67, 200
15. Ar $(C\equiv C)_nHg$	*k*	σ	0.35 (1F)	HCl in dioxan, demercurisation	201
16. $XC_6H_4(C\equiv C)_nGe(Ce_2H_5)_3^*$ $n=0$ $n=1$ $n=2$ $n=3$	*k*	σ	 1 0.66 1.30 0.18	$HClO_4$, degermylation	107
17. $XC_6H_4(CH=CH)_nCN$	ν(CN)	σ^+	0.61 (1F) 0.58 (1F)	CCl_4 $CHCl_3$	31, 39, 127
18. Ar $(CH=CH)_nH$	*k*	σ^+	0.68 (1F)	Addition: CCl_2 l_2	113
19. $XC_6H_4(CH=CH)_nCH=NC_6H_4Y$	pK_a	σ^+	0.76 (1F) 0.72 (1F)	Y=H Y=*n*-OCH_3	202
20. Ar $(CH=CH)_nArNH_2$	*k*	σ	0.63 (1F) 0.67 (1F)	Acylation	98
21. $R_1(CH=CH)_nCOR_2^{**}$ *S-cis-* *S-trans-*			 0.766± 0.012 (1F) 0.855± 0.024 (1F)		10

*The values of ρ_{rel} are quoted.

**Series 21 includes cinnamaldehydes, chalcones, styrylketones, cinnamic acids and their esters, dimethylamides, etc.

The dependence of the π'_{1F} on the nature of the property being correlated is very clearly manifested. Thus π'_{1F} for the ketones $XC_6H_4(CH=CH)_nCOCH_3$ amounts to 0.47 (*S-cis*-conformers) or 0.54 (*S-trans*-conformers) on the basis of the correlation analysis of ν(CO) and 0.76 on the basis of the correlation of half-wave potentials. The difference between the values of π'_{1F} is apparently determined by the different sensitivities of the properties to the influence of substituents.

The dependence of the values of π'_{1F} on the conformation of the molecules was already noted above (see, for example, series 4, 6, and 22 in Table 14): *S-trans*-conformers are appreciably more sensitive to the influence of substituents. This apparently applies also to geometrical isomers: a *trans*-double bond transmits the influence of a substituent more effectively than a *cis*-double bond (series 11).

In some cases π'_{1F} is affected by the solvent in which the property to be correlated has been determined [see the difference between the values of π'_{1F} found from the correlation analysis of the ν(CO) determined in CCl_4 and $CHCL_3$ (series 2 and 6) or between the values found from the correlation analysis of the half-wave potentials determined in water and dimethylformamide (series 12)]. This may be associated with the different degrees of solvation of the bridge or of the reaction centre or with the specific interaction of the substance with the solvent.

The values of π'_{1F}, π'_{2F}, π'_{3F}, and π'_{4F}, obtained from the correlation analysis of the same parameters [$\nu(CO)$, μ, λ_{max}, $E_{\frac{1}{2}}$, and k] of the polyene series 1, 2, 3, 10, and 11, are linked by the relation [44]

$$\pi'_{1F} : \pi'_{2F} : \pi'_{3F} : \pi'_{4F} = \pi'_{1F} : (\pi'_{1F})^2 : (\pi'_{1F})^3 : (\pi'_{1F})^4. \quad (10)$$

Thus the influence of substituents diminishes in a geometrical progression with increase of the number of double bonds.

This conclusion agrees fully with data obtained by Bowden [71], who believed that π' is a power function of the type

$$\pi' = \varepsilon^n, \quad (11)$$

where ϵ is the transmission factor of the atomic group entering into the composition of the bridge and n the number of such atomic groups, and calculated on the basis of the analysis of 17 reaction series the values of ϵ for the carbon atom in the sp^3 (0.48 ± 0.04), sp^2 (0.67 ± 0.02), and sp (0.57 ± 0.01) states, and found that π'_{1F} for the –CH=CH– group is equal to ϵ^2 (C_{sp^2} = 0.45). If Eqn. (11) holds, then evidently $\pi'_{2F} = (\pi'_{1F})^2$, $\pi'_{3F} = (\pi'_{1F})^3$, and $\pi'_{4F} = (\pi'_{1F})^4$, i.e. Eqn. (10), found in the correlation analysis of the experimental properties of polyenes, is obtained. The validity of Eqn. (10) indicates the equivalence of the double bonds with respect to the transmission of the influence of substituents in these polyenes.

It is of interest that the values of ρ_{rel} (see Table 14, series 16) [107] are in the following proportions:

$0.66 : 0.30 : 0.18 = 0.66 : (0.66)^3 : (0.66)^4$.

Table 15. The calculated and experimental values of $10^3\,\nu_{max}$ (cm^{-1}) and $E_{\frac{1}{2}}$ (V) for certain series of $C_6H_5(CH=CH)_n$·CHO polyenes.

Property	n						
	0	1	2	3	4	5	6
ν_{max} (expt.)	40.7	34.5	30.9	28.0	25.6	24.6	23.0
ν_{max} (calc.)	—	34.6	30.5	25.2	23.4	21.6	20.9
$E_{\frac{1}{2}}$ (expt.)	1.36	1.09	0.89	0.77	0.70	0.60	
$E_{\frac{1}{2}}$ (calc.)	—	1.15	0.98	0.83	0.69	0.59	
$(CH_3)_2N(CH=CH)_n$CHO							
ν_{max} (expt.)	—	35.4	27.7	23.7	21.8	20.4	19.2
ν_{max} (calc.)	—	—	30.3	25.4	21.6	18.6	15.8
p-$CH_3OC_6H_4(CH=CH)_n$CHO							
ν_{max} (expt.)	—	31.1	28.4	26.2	24.9	23.6	22.7
ν_{max} (calc.)	—	—	26.3	24.0	22.2	21.0	20.0

However, Eqn. (10) does not hold for series 6 (see Table 14, data for the correlation of Z/Z_0), which can probably be explained by the different deviations of members of this series from coplanarity [45,147,148].

One should also note that, whereas the π-electron densities q_0 at the carbonyl oxygen atom in the aldehyde series 1 are correlated with the σ_R^0 constants and the values of π'_{1F}, π'_{2F}, and π'_{3F} found from these data obey Eqn. (10), the π-electron densities at the oxygen atom of the keto-group in chalcones and their vinylogues (series 6) are almost independent of the nature of the substituent X. [45]

Comparison of the values of π'_{1F} and π'_{1E} determined for similar series (Table 14, series 6 and 8, 9 and 13, and 11 and 14) in the correlation analysis of identical properties shows that the efficiency of the transmission of influences via a double bond is somewhat greater than via a triple bond.

Using Eqn. (10) and knowing the value of π'_{1F} for the given series, it is possible to calculate beforehand the properties of compounds with 2–5 and even 6 double bonds. Table 15 presents examples of such calculations [44]. Evidently the agreement between calculation and experiment is satisfactory.

As regards the mechanism of the transmission of influences, analysis of the data in Table 14 shows that the best correlation is achieved in most cases when the σ^+, σ_R^+, and σ_R^0 constants are used, i.e. the mesomeric mechanism is most important in the transmission of influences via multiple bonds. A detailed analysis of the two-parameter equation for aliphatic compounds with a single bond has been made by Charton [7]. Table 16 lists the contributions of the mesomeric effect (P_R) to the overall electronic effect of the substituent for a number of typical series. Evidently the contribution is large in most cases. It is striking that P can be influenced by the solvent in which the properties being correlated are determined (Table 16, series 4, 5, and 11).

Table 16. The mechanism of the transmission of influences via multiple bonds [the values of P_R (%) for certain series [7]].

Series	Property	P_R, %	Remarks
1. XCH = CH_2	μ	42	
	f	66–69	
	ν	78	Frequency in ^{1}H NMR spectrum
	δ	53	
	k	37	Addition of Cl_2 to CH_3COOH
	"	21	Addition of Br_2 to CH_3COOH
	"	52	Reaction with C_6H_5CH = CHCHO in dioxan
2. XCH = CHBr	μ	42	
	δ	64	
3. C_6H_5CH = CHX		44	
4. XCH = CHCOOH *trans-*	pK_a	48	In water
	"	56	In 80% methylcellosolve
	"	75	In 50% alcohol
	k	42–50	Esterification of $(C_6H_5)_2CN_2$ in alcohol
	"	51	Ditto in t-butyl alcohol or ethyl acetate
5. XCH = CHCOOH *cis-*	pK_a	39	In water
	"	71	In 50% alcohol
	k	55	Esterification of $(C_6H_5)_2CN_2$ in ethyl acetate
6. $CH_3C(X)$ = CHCOOH *cis-* *trans-*	pK_a	55	In water
	"	45	Ditto
7. $C_6H_5C(X)$ = CHCOOH *cis-* *trans-*	pK_a	49	In 50% alcohol
	"	59	Ditto
8. XCH = $CHCOOCH_3$	δ	50	Addition to 9,10-dimethylanthracene in dioxan
	k	95	
9. XCH = $CHCOOC_2H_5$	k	63	Alkaline hydrolysis in water
	"	52	Ditto in 70% dioxan

The two-parameter Eqn. (4) and a similar two-parameter equation including the cross term,

$$Q = Q_0 + \alpha\sigma_I + \beta\sigma_R^+ + \gamma\sigma_I\sigma_R^+, \quad (12)$$

have been used to estimate the contributions of the inductive and mesomeric effects for series 1, 3, and 6 (see Table 14) [44,45]. It was found that, in the

$X(CH=CH)_nCHO$ polyenal series 1, the inductive effect makes the greatest contribution ($n = 1$, $\rho_I \gg \rho_R^+$), while for the remaining series ($n = 2-4$) the mesomeric effect assumes the greatest importance, as expected, because of the rapid decay of the inductive effect. Similar data were obtained also for series 3. One should note that in all the examples application of Eqn. (12) yielded very high cross terms, which shows that the changes in the transmission of inductive and mesomeric effects are probably not quite so independent as is usually believed[20,21].

The application of the two-parameter Eqn. (12) to the series of chalcones and their vinylogues (Table 14, series 6) showed that the inductive effect predominates ($\rho_I > \rho_R^+$) in series with $n = 1-3$; this is consistent with the fact that these compounds are not planar.

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