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TRANSMISSION OF ELECTRONIC EFFECTS IN CERTAIN POLYENES

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Abstract—The effect of substituent variation in compounds of the general type $R(CH{=}CH)_nCHO$ (1) or p-$RC_6H_4(CH{=}CH)_nCHO$ (2) on the stretching vibrations of the CHO group (ν_{CO}), the dipole moments (μ), the long wave maxima (λ_{max}), and the halfwave potentials ($E_{1/2}$) for the polarographic reduction of the CHO group have been studied as well as the influence of variation of substituent R on the rate constants (k) of the alkaline hydrolysis of polyenic esters $R(CH{=}CH)_nCOOEt$ (3). A linear relationship between the σ^+, σ_c^0 or σ_c^+ values and the experimental values of ν_{CO}, μ, λ_{max}, $E_{1/2}$ and k has been established, which indicates the importance of the mesomeric mechanism of the transmission of electronic effects through the chain of conjugated double bonds in compounds 1, 2 and 3. Transmission coefficients (π') for one (π'_{1F}), two (π'_{2F}), three (π'_{3F}), and four (π'_{4F}) double bonds were calculated, and it was found that these values are bound together by the ratio: $(\pi'_{1F}):(\pi'_{2F}):(\pi'_{3F}):(\pi'_{4F}) = (\pi'_{1F}):(\pi'_{1F})^2:(\pi'_{1F})^3:(\pi'_{1F})^4$, i.e. the influence of substituents R is decreased in a geometrical progression when the number of double bonds increases. The distribution of the electronic density in 1 was calculated by the LCAO SCF method in the Pariser-Parr-Pople approximation, and it was found that the π-electronic density values at the O atoms of the CHO group correlates well with σ_c^0 constants and the calculated values of π'_{1F}, π'_{2F}, and π'_{3F} are bound together by the above ratio.

The quantitative estimation of the transmission of electronic effects through a system of conjugated double bonds and the investigation of the nature of the transmission process are of great theoretical importance and attract the attention of many chemists. A general approach to this problem may be based on the application of the Hammett equation to the series R—X and $R{-}(CH{=}CH)_n{-}X$, where R is a variable substituent and X is a reaction centre. The determination of the reaction constants ρ for both series provides a means of calculating the transmission coefficients (π') as the ratio ρ_n/ρ_0, where ρ_0 is the reaction constant of the series R—X and ρ_n is the reaction constant of the series $R{-}(CH{=}CH)_n{-}X$. π' Characterizes the effectiveness of transmission of electronic effects across the bridge $-(CH{=}CH)_n-$. This approach was found very fruitful for certain unsaturated and aromatic series in the estimation of the π' values for one double bond ($\pi'_{1F} = 0{\cdot}50 \pm 0{\cdot}02$), a phenylene group ($\pi'_{-C_6H_4-} = 0{\cdot}27 \pm 0{\cdot}03$) and a styrylene group ($\pi'_{-C_6H_4CH=CH-} = 0{\cdot}24 \pm 0{\cdot}05$) by the correlation analysis of kinetic or equilibrium data of such systems.[1] Recently[2] we carried out a correlation analysis of the values of relative intensities of the common benzoyl ion in the mass spectra of chalcones and their vinylogues of the general type p-$RC_6H_4(CH{=}CH)_nCOPh$ and calculated the π' values for one, two, and three double bonds ($\pi'_{1F} = 0{\cdot}72$, $\pi'_{2F} = 0{\cdot}25$, and $\pi'_{3F} = 0{\cdot}11$). However, as it was established later,[3] these compounds are not planar and therefore the results obtained may be not valid for other series.

In the present work we have systematically studied the substituent effects on the CO stretching frequencies (ν_{CO}), on the dipole moments (μ), the long wave maxima (λ_{max}), the halfwave potentials ($E_{1/2}$) of polyenales $R(CH{=}CH)_nCHO$ (1) and p-$RC_6H_4(CH{=}CH)_nCHO$ (2) and on the rate constants (k) of the alkaline hydrolysis of polyenic esters $R(CH{=}CH)_nCOOEt$ (3) with a view to elucidating the question of electronic effect transmission through the chain of conjugated double bonds in planar compounds.[4] In addition, calculation of the distribution of π-electronic density in some compounds (1) were carried out using the SCF method in the Pariser-Parr-Pople approximation.

IR spectra of 1 *and* 2. Compounds 1 and 2 were prepared[5-7] and were purified prior to measurement by repeated crystallization from an appropriate solvent or by repeated distillation. Polyenales 1 and 2 possess the *trans* configuration at the double bonds[5-7] and are planar.[4]

IR spectra of 1 and 2 were recorded in $CHCl_3$ on an UR-20 spectrometer. The calibration was made with the use of polystyrene (the sharp, strong peak at 1604 cm^{-1}) immediately after the spectrum of each compound. The frequencies registered are accurate to ±1 cm^{-1}.

ν_{CO} of **1** and **2** are given in Table 1.

As can be seen from the data of Table 1, the accumulation of double bonds in compounds **1** and **2** leads to a lowering of the ν_{CO} values. However, the ν_{CO} values of **1** ($R = Me_2N$, n = 3,4) are considerably larger than those of the foregoing members of the series. As a result the ν_{CO} values of all series become close to each other. For instance, the difference between the ν_{CO} values of **1** (R = COOEt, CN, and Me_2N, n = 4) is no more than 3 cm^{-1}, and that between the ν_{CO} values of **2** (R = H, Br, MeO, and NO_2) is 2–5 cm^{-1}. The convergence of the ν_{CO} values indicates that the sensitivity of the stretching vibrations to the influence of substituents R (electron-donating or electron-withdrawing) decreases with the extention of the conjugated chain. The decrease and the convergence of the ν_{CO} values were observed earlier in the case of compounds **3**,[8] and the IR spectra of **1** ($R = Me_2N$) have been discussed.[9]

Table 1. ν_{CO} in cm^{-1} ($CHCl_3$) of **1** and **2**

	I				II					
n	Me	COOEt	CN	Me_2N	H	Cl	Br	MeO	NO_2	NMe_2
0	1715	1712		1675	1702	1708	1707	1687	1712	1668
1	1690	1702	1703	1615	1677	1678	1678	1678	1685	1655
2	1680	1689	1692	1584	1675	1670	1670	1675	1680	
3	1678	1682	1687	1640	1675					
4		1681	1678	1681						

The correlation analysis of the data obtained using the equation $\nu_{CO} = \rho\sigma_c^0$ (1) ($\sigma_c^0 = \sigma^0 - \sigma_I$; σ_c^0 characterizes the summary mesomeric and π-inductive effects of substituents R[10]) revealed a rather poor linear relationship between the ν_{CO} values of polyenals **1** and **2** and σ_c^0 constants of substituents R. Parameters of the correlation equation (1) are shown in Table 2.

Though the correlation between ν_{CO} and σ_c^0 is rather poor the existence of such correlation demonstrates that the transmission of electronic effects through the chain of conjugated double bonds in the ground state of molecules of **1** and **2** can probably the accounted for almost entirely on the basis of an mesomeric effect mechanism.

Table 2. Parameters of the correlation equation (1)[a]

n	ρ	r^b	S^c
0	158	0·835	10·5
1	110	0·865	8·7
2	78	0·907	4·5
3	46	0·837	7·1

[a] Least square and statistical treatment of the data were carried out in accordance with Ref 1. [b] Correlation coefficient. [c] Standard deviation.

With a view to estimate more exactly the contribution of the inductive and mesomeric effects we have used for the correlation analysis of the ν_{CO} values the multiparameteric equation: $\nu_{CO}^R = \nu_{CO}^H + \rho_I\sigma_I + \rho_c^0\sigma_c^0 + \rho_{I,c}^0\sigma_I\sigma_c^0$ (see ref 1) and found the following expressions for **1** and **2**: n = 0, $\nu_{CO}^R = 1743 - 1182\ \sigma_I + 329{\cdot}1\ \sigma_c^0 - 795{\cdot}8\ \sigma_I\sigma_c^0$ (r = 0·984); n = 1, $\nu_{CO}^R = 1690 - 1105\ \sigma_I + 101{\cdot}2\ \sigma_c^0 + 145{\cdot}3\ \sigma_I\sigma_c^0$ (r = 0·911); n = 2, $\nu_{CO}^R = 1674 + 10{\cdot}22\ \sigma_I - 36{\cdot}76\ \sigma_c^0 + 362{\cdot}9\ \sigma_I\sigma_c^0$ (r = 0·954); n = 3. $\nu_{CO}^R = 1677 + 14{\cdot}1\ \sigma_I + 8{\cdot}74\ \sigma_c^0$ (r = 0·896) (in the last case the calculation was carried out without a cross-member).

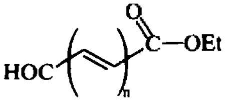
The comparison of the absolute values of ρ_I and ρ_c^0 indicates a considerably contribution of the mesomeric effect in the case of **1** and **2** (n = 2). In the case of **1** and **2** (n = 0,1) the absolute values of ρ_c^0 which shows that here the inductive effect is significant. It should be noted that in all cases the values of non-additive interactions are large.

Dipole moments of **1**. Dipole moments of **1** were measured in benzene at 25°.[11] The dipole moments measured are accurate to ±0·05 D. The data obtained are listed in Table 3.

In the only work[14] in which dipole moments of **1** ($R = Me_2N$, n = 0-4) were measured, it was concluded (based on data obtained) that the influence of each terminal substituent is extended to no more than three double bonds.

As it can be seen from our data (Table 3) dipole moments of compounds **1** (R = Me, Ph, Me_2N) increase with the extension of a polyenic chain. However, μ of compounds **1** (R = COOEt) change irregularly. This may be accounted for by the equilibrium between S-*cis* and S-*trans* conformation of **1** (R = COOEt) which may change depending on the number n.

Quantum-chemical calculation (the SCF method, PPP approximation) of both conformations revealed that S-*cis* conformation is energetically more preferable than S-*trans* conformation. In the case of **1** (R = COOEt, n = 2) the difference in free


S-*cis*

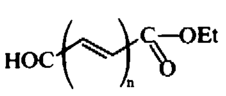

S-*trans*

Table 3. Experimental and calculated values of μ in D of I[a]

n	μ	Me	Ph	COOEt	Me_2N
0	Experimental (exp.)	2·60	3·00	1·88	3·86
	Calculated[2] (calc.)	2·49	2·30	1·42	3·29
	Calculated[3] (calc.)	3·77	3·62	1·05	3·76
	Interaction[4] (interac.)	0·11	0·70	0·46	0·57
1	Exp.	3·49	4·08	3·15	6·24
	Calc.[b]	2·49	2·30	1·42	3·29
	Calc.[c]	4·20	4·02	3·19	6·78
	Interac.[d]	1·00	1·32	1·85	2·95
2	Exp.	3·98	4·08	3·19	7·62
	Calc.[b]	2·49	2·30	1·42	3·29
	Calc.[c]	4·38	4·14	2·85	8·05
	Interac.[d]	1·49	1·78	1·77	4·33
3	Exp.	4·47	4·35	3·40	8·24
	Calc.[b]	2·49	2·30	1·42	3·29
	Calc.[c]	4·51	4·19	3·03	8·95
	Interac.[d]	1·98	2·05	1·98	4·95
4	Exp.	4·95		3·35	8·50
	Calc.[b]	2·49		1·42	3·29
	Calc.[e]	4·54		3·12	9·60
	Interac.[d]	2·46		1·87	5·21

[a] I(R = CN): n = 2, $\mu_{exp.} = 3{\cdot}14$ D, $\mu_{calc.}$ [b]$= 2{\cdot}88$ D, $\mu_{calc.}$ [c]$= 3{\cdot}20$, $\mu_{interac.}$ [d]$= 0{\cdot}26$; n = 3,4 are very poor soluble in benzene and therefore their dipole moments could not be measured. [b] Calculated using ordinary vector scheme.[12] [c] Calculated by quantum-chemical method.[13] [d] $\mu_{interac.} = \mu_{exp.} - \mu_{calc.}$[b]

energy of S-*cis* and S-*trans* conformers is 0·0248 eV (650 cal/mole) and a mixture equilibrated at 25° consists of 75% S-*cis* and 25% S-*trans* conformers.

The interaction between terminal groups in compounds 1 (R = Ph, Me_2N) weakens with the extension of polyenic chains. For instance, the difference between the μ_{exp} values of neighbouring members of the series 1 (R = Me_2N) decreases from 1·38 D/μ(n = 2) − μ(n = 1)/ to 0·26 D/ μ(n = 4) − μ(n = 3)/. In the case of 1 (R = COOEt), where extended conjugation cannot be operative but only acceptor group perturbation of the adjacent π-system of double bonds, the difference between μ of neighbouring members of the series is very small and irregular (0·05–0·21 D). μ of 1 (R = Me) increases regularly from 0·48–0·49 D with the introduction of each additional double bond in the chain. Such regular changes in the dipole moments of 1 (R = Me) is apparently connected only with an increase of the dipole shoulder.

The correlation of the experimental values of μ was carried out using the Exner equation:[15] $\mu/d = \rho\sigma$ (2) where d is the distance between the centres of the charges at the CHO group and at substituents R in Å (these values were determined from molecular diagrammes of compounds I). The best correlation was found with σ^+ or σ_c^0 constants. This appears to be evidence of the importance for a mesomeric mechanism of the transmission of substituent effects through the conjugated system of double bonds. Correlation parameters of the Exner equation are presented in Table 4.

Electronic spectra of 1 and 2. UV spectra of 1 and 2 were registered in alcohol on an Unican SP 700 spectrophotometer. Positions of long wave maxima are given in Table 5.

The λ_{max} of polyenales 1 (R = Me, COOEt, CN) with an equal number of double bonds are very close to each other as well as λ_{max} of polyenales 2 (R = H, Cl, Br, NO_2, n = 1.2). However, the difference between λ_{max} of 1 (R = Me_2N) and other polyenales (1) is considerable and reaches 68–130 nm.

The increment for each introduced double bond becomes smaller as the polyenic chain extends. Thus, the difference between λ_{max} of compounds 1 (n = 2, R = Me, COOEt, CN, Ph) and those of compounds 1 (n = 1, R = Me, COOEt, CN, Ph) is

Table 4. Correlation parameters of the equation (2).

n	σ	ρ	r	S
0	σ^+	−0·60	0·950	0·320
	σ_c^0	−2·06	0·993	0·265
1	σ^+	−0·47	0·930	0·190
	σ_c^0	−1·54	0·938	0·141
2	σ^+	−0·39	0·970	0·111
	σ_c^0	−1·39	0·970	0·115
3	σ^+	−0·34	0·983	0·072
	σ_c^0	−1·10	0·972	0·093
4	σ^+	−0·26	0·999	0·022
	σ_c^0	−0·89	0·999	0·025

Table 5. Long wave maxima in nm (alcohol) of 1 and 2

n	1				2					
	Me	COOEt	CN	Me$_2$N[a]	H[b]	Cl	Br	MeO	Me$_2$N	NO$_2$
0					247	258	264	277	339	263
1	218	208	204	286	288	299	302	323	289	303
2	274	268	263	366	330	329	333	353		333
3	317	309	305	425	361			382[c]		
4	351	341	336	466				403[c]		

[a] In CHCl$_3$ (data for solutions in CH$_2$Cl$_2$).[16] [b] Data for solutions in CH$_2$Cl$_2$.[17] [c] Data.[18]

56–60 nm while the difference between λ_{max} of 1 (n = 4, R = Me, COOEt, CN, Ph) and those of compounds 1 (n = 3, R = Me, COOEt, CN, Ph) is only 31–34 nm. The same trend was noted previously in the case of compounds 3.[19] The observed bathochromic shifts seem to be caused mainly by the extension of the conjugated chain of double bonds but not by the influence of substituents R.

The addition of each double bond in the molecules of 1 (R = Me$_2$N) or 2 (R = Me$_2$N) leads to much larger bathochromic shifts than those in the above case, though these shifts also decrease as the polyenic chain extends. For example, the increment for one double bond when n in compounds 1 (R = Me$_2$N) is changed from 1 to 2 is 78 nm, while it is only 41 nm as n is changed from 3 to 4. The peculiar spectral behaviour of polyenales 1 (R = Me$_2$N) may be accounted for by the extention of the conjugation on account of the dimethylamino group.

Correlation analysis of the data obtained (Table 5) was carried out using the equation $1/\lambda_{max} = \rho\sigma$ (3) and the best results were obtained with σ_c^+ constants of substituents R($\sigma_c^+ = \sigma^+ - \sigma_I$. σ_c^+ characterizes the summary π-inductive effect, mesomeric effect, and the effect of the direct polar conjugation).[15] The correlation with σ_c^+ indicates that the transmission of electronic effects through the conjugated double bonds in the case of the lower electronically excited states of compounds 1 and 2 is brought about mainly by the mesomeric mechanism.

Correlation parameters of the equation (3) are presented in Table 6.

Polarographic reduction of 1 *and* 2. Polarographic curves were recorded with a pen-recording polarograph EPR-315 (USSR). At working height of the mercury reservoir (40 cm) the capillary with a beak[20] had m = 1·1 mg/sec and t = 0·36 sec. An external saturated calomel electrode served as a reference electrode. The measurements were made with 0·1 mmole/l solutions of compounds 1 or 2 in 0·05 M buffer of pH 2 (HCl—KCl) in 50% dimethylformamide at 25 ± 0·2°. Under these conditions all polyenales 1 and 2 form one reversible diffusion wave corresponding to one-electron process[21] according to the following scheme:

Table 6. Correlation parameters of the equation (3)

m	$\rho \cdot 10^2$	r	S . 10^2
1	67·7	0·995	7·9
2	52·0	0·984	10·4
3	46·6	0·991	8·5
4	42·1	0·971	11·5

$$\mathrm{R(CH{=}CH)_nCHO + e + H^+ \rightleftarrows}$$
$$\mathrm{R(CH{=}CH)_n\dot{C}HOH \rightarrow [R(CH{=}CH)_nCH(OH)]_2}$$

Halfwave potentials ($E_{1/2}$) of polyenales 1 and 2 are given in Table 7.

Table 7. $E_{1/2}$ of 1 and 2 in mV against SCE

R n	0	1	2	3	4
Compounds 1					
Me		1060	771	598	472
COOEt		388	473	455	400
CN		482	518	401	220
Me$_2$N		[a]	1013	791	646
Compounds 2					
H	1007	725	507	400	
Cl	948	628	468		
Br	902	616	450		
MeO	1068	744	544		
Me$_2$N	1080	772			

[a] Non reducible.

As can be seen from Table 7, the introduction of electron-accepting or electronegative substituents facilitates the reduction of 1 and 2 at the dropping mercury electrode, while the introduction of electron-donating substituents impedes the reduction process.

A linear relationship was found between the $E_{1/2}$ values and σ_c^0 constants of substituents R, though this correlation is rather poor. Correlation parameters of the equation $E_{1/2} = \rho\sigma_c^0$(4) are shown in Table 8.

Table 8. Correlation parameters of the equation (4)

n	ρ (mV)	r	S
0	853	0·945	29·4
1	765	0·883	32·3
2	620	0·950	19·2

With a view to separate the inductive and mesomeric effects we used the multiparameter equation: $E^R_{1/2} = E^H_{1/2} + \rho_I\sigma_I + \rho_c^+\sigma_c^+ + \rho_{I,c}\sigma_I\sigma_c^+$ (5). The results of statistical treatment of the equation (5) are presented in Table 9.

Comparison of the absolute values of ρ_I and ρ_c^+ shows that in the case of compounds 1 and 2, n = 1 the inductive effect is of great importance,

Table 9. Parameters of the equation (5)

n	ρ_I mV	ρ_c^+ mV	$\rho_{I,C}$ mV	r	S	$E_{1/2}$, mV calc.	$E_{1/2}$, mV exp.
1	−1125·7	66·5	1212·5	0·876	168·8	900·1	914
2	−253·7	−701·1	4045·2	0·986	51·7	490·2	
3	−198·5	−664·3	4220·2	0·985	32·4	368·7	
4	−310·1	−119·3	[a]	0·957	62·8	455·5	

[a] This calculation was carried out without cross-member.

Table 10. Inductive (I), mesomeric (M), direct polar conjugation (C) and non-additive (I,C) interaction contributions of free energy ($\Delta\Delta G$), kcal/mole

Compounds 1

n	Contribution	Me	COOEt	CN	Me_2N	Ph
1	I	−1·31	8·90	14·7		2·62
	M	1·18	−31·45	−34·86		−12·56
	C	−0·24	0·00	0·38		0·13
	I,C	0·37	1·35	1·58		0·79
2	I	−0·29	2·01	3·30	0·59	0·59
	M	−0·90	−15·96	−16·65	24·43	−6·30
	C	−0·04	0·00	0·05	−0·37	0·02
	I,C	1·23	4·55	5·30	−17·0	−2·64
3	I	−0·23	1·58	2·60	0·46	0·46
	M	−0·01	−10·78	−14·44	23·74	−3·96
	C	−0·05	0·00	0·07	−0·94	0·02
	I,C	1·29	4·75	5·55	−17·18	2·77
4	I	−0·36	2·43	4·08		0·72
	M	0·54	−4·70	−12·30		8·28
	C	−0·18	0·00	0·27		−3·50
	I,C	0·00	−2·27	−7·95		5·50

Compounds 2

n	Contribution	Cl	Br	MeO	NO_2	Me_2N
1	I	5·24	5·29	2·88	7·33	1·17
	M	−17·69	−18·42	−10·83	−22·61	−10·86
	C	−0·25	−0·19	−0·64	0·25	−2·20
	I,C	−0·90	−0·73	−1·41	0·53	−1·01
2	I	0·59	1·18	1·18	0·65	
	M	−7·66	−8·79	−2·99	−14·09	
	C	−0·04	−0·03	−0·09	0·04	
	I,C	−3·03	−2·46	−4·73	1·80	

while in the case of 1 and 2, n = 2,3 the mesomeric effect is prelevant. It should be mentioned that the non-additive members of the equation (5) attain considerable values which often exceed the summary values of inductive and mesomeric effect and that of the direct polar conjugation. These non-additive interactions increase when the polyenic chain extends.

In accordance with the literature,[21] we presented the free energy ($\Delta\Delta G$) of the polarographic reduction as a sum of contributions of inductive (I), mesomeric (M), direct polar conjugation (C), and non-additive (I,C) interactions: $\Delta\Delta L = -2/303\ RT\Delta E_{1/2} = 1 + M + C + I,C$ and calculated these contributions by the methods given.[21,22] The results obtained are given in Table 10.

Analysis of the data obtained (Table 10) revealed that the contribution of mesomeric interaction in most cases exceeds that of the inductive interaction though the latter plays a great part in the case of compounds with one double bond. The contribution of the direct polar conjugation interaction is small for all compounds 1 and 2.

Alkaline hydrolysis of 3. Alkaline hydrolysis of esters 3 was carried out in 60% dioxane under nitrogen at equal initial concentration 0·025 M of alkali (KOH or NaOH) and esters 3 in a thermostat (±0·2°). Hydrolysis was followed by back titration of samples withdrawn at suitable time intervals from the reaction mixture and poured into an excess of 0·1 N HCl. Rate constants were calculated according to the usual equation of the second order reaction with an accuracy 1–2%. Activation parameters were found by the usual procedure.[23] Kinetic and thermodynamic parameters of alkaline hydrolisis of esters 3 are given in Table 11.

The investigated series 3 has an isoenthropic character which was confirmed using the ordinary procedure.[24,25] Since the isokinetic temperature (395 ± 20°) of the alkaline hydrolysis of esters 3 considerably exceeds the experimental temperature (7–62°), the kinetic data may be subjected to correlation analysis. Parameters of the equation $\lg k = \rho\sigma$ (5) are presented in Table 12.

The best correlation is achieved when σ^+, σ_c, or σ_c^+ constants are applied (Table 12). This implies that the mesomeric mechanism plays the

Table 11. Kinetic and thermodynamic parameters of alkaline hydrolysis of esters 3

n	R	Lgk (298°K)	ΔE‡ kcal/mole[a]	ΔS‡ eu[b]
0	Ph	−2·33	12·4	−29·9
	p-ClC_6H_4	−1·88	12·8	−26·6
	p-BrC_6H_4	−1·79	12·4	−27·4
	p-$O_2NC_6H_4$	−0·65	10·0	−30·4
	p-$MeOC_6H_4$	−3·02	14·6	−25·7
1	Me	−2·44	13·0	−28·4
	OEt	−3·32	14·8	−26·0
	Ph	−2·17	13·4	−25·8
	p-ClC_6H_4	−1·94	13·4	−24·7
	p-BrC_6H_4	−2·03	13·8	−23·8
	p-$O_2NC_6H_4$	−1·27	14·0	−19·6
	p-$MeOC_6H_4$	−2·64	14·2	−25·4
	p-$Me_2NC_6H_4$	−3·22	14·4	−27·2
2	Me	−2·60	13·6	−27·2
	OEt	−3·10	12·8	−32·0
	Ph	−2·35	13·6	−26·0
	p-ClC_6H_4	−2·23	13·2	−26·6
	p-BrC_6H_4	−2·31	13·8	−25·2
	p-$O_2NC_6H_4$	−1·83	13·0	−25·6
	p-$MeOC_6H_4$	−2·61	13·6	−27·0
	p-$Me_2NC_6H_4$	−3·00	14·2	−27·0
3	Me	−2·60	13·6	−27·2
	Ph	−2·46	13·2	−27·7
	p-ClC_6H_4	−2·43	13·6	−26·4
	p-BrC_6H_4	−2·42	13·6	−26·4
	p-$MeOC_6H_4$	−2·60	13·6	−27·3

[a]±0·5 kcal/mole. [b]±1 eu.

Table 12. Parameters of the correlation equation[5]

	n = 1			n = 2			n = 2			n = 4		
σ	ρ	r	S	ρ	r	S	ρ	r	S	ρ	r	S
σ_p	5·3	0·990	0·13	2·90	0·940	0·19	1·60	0·900	0·20	0·77	0·980	0·04
σ_I	10·9	0·930	0·36	4·80	0·800	0·32	2·70	0·820	0·09	1·13	0·900	0·07
σ^+	3·2	0·895	0·13	1·75	0·990	0·12	1·13	0·985	0·07	0·48	0·925	0·03
$\sigma_c{}^a$	7·3	0·970	0·21	3·45	0·965	0·18	2·20	0·990	0·06			
σ^0	5·6	0·920	0·27	3·50	0·925	0·17	2·00	0·900	0·09	0·77	0·900	0·07
$\sigma_c^{\pm}$	4·4	0·990	0·11	1·83	0·965	0·10	1·10	0·960	0·13			

$^a\sigma_c = \sigma_p - \sigma_1$, this constant characterizes I, M and C effects.[26]

chief part in the transmission of substituent effects of compounds 3 in the excited reactive state.

We estimated also the contributions of I, M and C interactions in the free energy ($\Delta\Delta G$) of the alkaline hydrolysis of esters 3.[21,22] The results obtained are shown in Table 13.

The results (Table 13) are in agreement with the above conclusion concerning the prevalence of the mesomeric mechanism in the transmission of substituent effects. In all cases with the exception of series 3 (n = 0) the summary contribution of the M and C interaction exceeds that of I interaction and only in the case of esters 3 (n = 0) the contribution of I interaction is almost equal or even more than that of the M and C contributions.

Table 13. I, M, and C interaction contributions of $\Delta\Delta G$, kcal/mole

n	R in 3	I	M	C
0	Ph	−0·57	0·57	−0·13
	p-ClC$_6$H$_4$	−1·13	0·78	−0·34
	p-BrC$_6$H$_4$	−1·13	0·68	−0·35
	p-O$_2$NC$_6$H$_4$	−1·58	0·60	−1·27
	p-MeOC$_6$H$_4$	−0·63	0·64	0·53
1	Me	0·13	0·13	−0·35
	OEt	−0·70	0·96	0·80
	Ph	−0·26	0·26	−0·42
	p-ClC$_6$H$_4$	−0·52	0·31	−0·51
	p-BrC$_6$H$_4$	−0·52	0·32	−0·35
	p-O$_2$NC$_6$H$_4$	−0·73	0·14	−0·98
	p-MeOC$_6$H$_4$	−0·29	0·41	0·05
	p-Me$_2$NC$_6$H$_4$	−0·12	0·26	0·75
2	Me	0·07	−0·02	−0·11
	EtO	−0·38	0·51	0·55
	Ph	−0·14	0·14	−0·25
	p-ClC$_6$H$_4$	−0·28	0·17	−0·32
	p-BrC$_6$H$_4$	−0·28	0·16	−0·21
	p-O$_2$NC$_6$H$_4$	−0·40	0·05	−0·55
	p-MeOC$_6$H$_4$	−0·15	0·21	−0·07
	p-Me$_2$NC$_6$H$_4$	−0·03	0·23	0·33
3	Me	0·03	0·03	0·05
	Ph	−0·06	0·06	−0·08
	p-ClC$_6$H$_4$	−0·12	0·07	−0·07
	p-BrC$_6$H$_4$	−0·12	0·07	−0·08
	p-MeOC$_6$H$_4$	−0·07	0·09	0·13

Quantum chemical calculation of 1. The SCF method in the PPP approximation was applied to the calculation of π-electronic density in the molecules of polyenales 1. These calculations were carried out using the program[27] and details will be published elsewhere. π-electronic densities (q_0) at atoms of polyenales 1 are given in Table 14.

Thus (Table 14), the highest π-electronic density is concentrated at the O atom of the aldehyde group with the exception of polyenals 1 (R = COOEt), where the highest π-electronic density localizes at the O atom of the CO group of the ester function.

q_0 at the O atom of the aldehyde group decreases in polyenals 1 (R = Me, or Me$_2$N) and increases on polyenals 1 (R = CN, or COOEt) with the accumulation of double bonds; in polyenals 1 (R = Ph) and q_0 values at the O atoms remain practically constant, as a result the q_0 values converge when n = 4.

We carried out a correlation analysis of the q_0 values and found the best correlation between the q_0 values and σ_c^0 constants of substituents R by the equation $q_0 = \rho\sigma_c^0$, (6) parameters of which are shown in Table 15.

It should be mentioned that the alternation of the charges at the C atoms of the polyenic chain are not observed in the case of 1 (R = Me$_2$N, CN, and COOEt) (Table 14). For instance, the alternation does not take place on the C atoms 5-6 (1, R = Me$_2$N, n = 2), 5-6-7-8 (1, R = Me$_2$N, n = 3), and 5-6-7, 9-10 (1, R = Me$_2$N, n = 4): all these atoms are negatively charged. Analogously, the alternation is not observed at the atoms 2-3-4-5-6 (n = 2), 2-3-4 (n = 1), 4-5-6-7 (n = 3), 6-7-8-9 (n = 4) of

Table 14. π-Electronic densities (q_0) at atoms of polyenales

$\mathrm{H_3C{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}O}$

11 10 9 8 7 6 5 4 3 2 1

Atom	q_0				
1	−0·330	−0·327	−0·326	−0·326	−0·326
2	0·290	0·283	0·282	0·282	0·282
3		−0·015	−0·012	−0·010	−0·010
4		0·045	0·041	0·040	0·039
5			−0·017	−0·009	−0·007
6			0·019	0·015	0·014
7				−0·015	−0·007
8				0·011	0·008
9					−0·014
10					0·008
11	−0·113	−0·101	−0·098	−0·097	−0·096
H_3	0·153	0·120	0·112	0·108	0·107

$\mathrm{Ph{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}O}$

10 9 8 7 6 5 4 3 2 1

1	−0·324	−0·325	−0·325	−0·325	−0·325
2	0·283	0·282	0·281	0·282	0·282
3		−0·010	−0·009	−0·009	−0·009
4		0·039	0·040	0·040	0·040
5			−0·007	−0·006	−0·005
6			0·014	0·014	0·014
7				−0·003	−0·003
8				0·006	0·006
9					−0·002
10					0·003

$\mathrm{Me_2N{-}CH{=}CH{-}CH{=}CH{-}CH{-}CH{=}CH{-}CH{=}CH{=}O}$

11 10 9 8 7 6 5 4 3 2 1

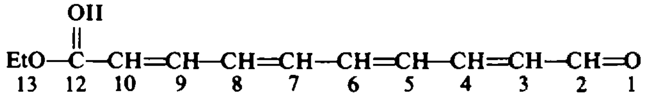
1	−0·355	−0·336	−0·330	−0·328
2	0·271	0·280	0·281	0·282
3	−0·145	−0·045	−0·023	−0·015
4	0·008	0·047	0·045	0·043
5		−0·145	−0·042	−0·020
6		−0·113	−0·023	−0·020
7			−0·143	−0·040
8			−0·017	0·016
9				−0·142
10				−0·019
11	0·221	0·210	0·206	0·204

$\mathrm{N{\equiv}C{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}O}$

12 11 10 9 8 7 6 5 4 3 2 1

1	−0·317	−0·321	−0·324	−0·325
2	0·282	0·282	0·281	0·281
3	0·021	0·001	−0·005	−0·007
4	0·028	0·035	0·037	0·038
5		0·023	0·004	−0·001
6		0·001	0·009	0·011
7			0·025	0·007
8			−0·071	0·001
9				0·027
10				−0·001
11	0·166	0·168	0·169	0·169
12	−0·180	−0·188	−0·191	−0·192

Table 14. (*cont.*)



$EtO{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}O$

13 12 10 9 8 7 6 5 4 3 2 1

	(S-*cis* Conformer)				(S-*trans*-Conformer)			
1	−0·314	−0·319	−0·323	−0·322	−0·205	−0·320	−0·322	−0·322
2	0·279	0·280	0·280	0·280	0·293	0·280	0·280	0·280
3	0·041	0·008	−0·002	−0·060		0·004	−0·003	−0·006
4	0·028	0·032	0·037	0·382		0·035	0·037	0·038
5		0·054	0·011	0·006		0·030	0·007	0·000
6		−0·015	0·006	0·010		0·008	0·009	0·011
7			0·058	0·014			0·032	0·003
8			−0·032	−0·029			0·000	0·001
9				0·059				0·039
10				−0·026				−0·004
11	0·298	0·284	0·284	0·282	0·291	0·284	0·284	0·284
12	−0·376	−0·383	−0·386	−0·387	−0·352	−0·379	−0·381	−0·382
13	0·058	0·058	0·058	0·057	0·003	0·058	0·058	0·058

Table 15. Parameters of the equation (6)

n	ρ	r	S
1	0·063	0·942	0·0076
2	0·025	0·961	0·0012
3	0·012	0·976	0·0005
4	0·0064	0·992	0·0001

compounds **1** (R = CN), which are positively charged. The same picture is observed in **1** (R = COOEt). These results may be accounted for by the displacement of π-electronic density due to the introduction of substituent in the molecule mainly within the bonds which are nearest to this substituent.

DISCUSSION OF RESULTS

The existence of a good linear relationship between the experimental values of ν_{CO}, μ, λ_{max}, $E_{1/2}$ and k and the values of substituent constants σ^+, σ_c^0, or σ_c^+ indicates the importance of the mesomeric mechanism of the transmission of electronic effects through the chain of conjugated bonds in compounds **1**, **2**, and **3** in the ground state as well as in the excited state of the molecule. This conclusion is in accordance with other investigations on the transmission of electronic effects through double bond.[28–33]

With a view to estimate the effectiveness of transmission of electronic effects across the system of conjugated double bonds in dependence on the number of double bonds we calculated the π' values for one, two, three and four double bonds as a ratio ρ_n/ρ_{n-1}. In Table 16 we presented the data obtained in our work and some values found in literature or calculated using literature data.

A careful analysis of the π' values in Table 16 reveals a very interesting feature: the π' values for one, two, three and four double bonds obtained by the correlation analysis of the same property (ν_{CO}, μ, $\lambda_{max.}$, $E_{1/2}$, or k) of different series are bound together by the ratio: $(\pi'_{1F}):(\pi'_{2F}):(\pi'_{3F}):(\pi'_{4F}) = (\pi'_{1F}):(\pi'_{1F})^2:(\pi'_{1F})^3:(\pi'_{1F})^4$ (7). This ratio implies that the substituent effects decrease in geometrical progression with an increasing of the number of double bonds. The only exception from this rule is the series $ArCO(CH{=}CH)_nAr$; however the compounds of these series are non-planar.[3]

The existence of the ratio (7) indicates also that transmission capability of the ethylene link at least in planar compounds does not depend on its position in the polyenic chain, and that the mesomeric effect as well as the inductive effect decrease rapidly and regularly with the extention of polyenic chain. These results are in accordance with the results obtained by Eaborn *et al*[38,39] in an excellent investigation on the transmission of electronic effects through a system of conjugated triple bonds. The authors measured the kinetic of cleavage of $XC_6H_4(C{\equiv}C)_nGeEt_3$ compounds by aqueous methanolic perchloric acid and carried out a correlation analysis of the data obtained. They found that the relative values of $\rho(\rho_{rel})$ rapidly decrease with the increasing of the number of triple bonds; $\rho_{rel} = 1$ (n = 0), 0·66 (n = 1), 0·30 (n = 2), and 0·18 (n = 3), and that the balance of inductive and resonance effects remained fairly constant as n was varied from 1 to 2 to 3. As it can be seen from our data (Table 16) such balance is observed also in the case of polyenes.

Table 16. The π' values of —(CH=CH)$_n$— (n = 1, 2, 3, 4) for certain polyenes containing a CO group

n	The series (n for standard and investigated series)	Correlated value	π'	Reference
1	Ar(CH=CH)$_n$CHO (0, 1)	ν_{CO}	0·74	29
	Ar(CH=CH)$_n$CHO (0, 1)	λ_{max}	0·79	Our data
	Ar(CH=CH)$_n$CHO (0, 1)	$E_{1/2}$	0·85	Our data
	Ar(CH=CH)$_n$COOH (0, 1)	ν_{CO}	0·58	34
	Ar(CH=CH)$_n$COOH (0, 1)	pK_a	0·47	35
	Ar(CH=CH)$_n$COOEt (0, 1)	ν_{CO}	0·64	30
	Ar(CH=CH)$_n$COOEt (0, 1)	k (alkaline hydrolysis)	0·54	35
			0·58	Calculated with data from ref 36
	R(CH=CH)$_n$CHO (0, 1)	ν_{CO}	0·67	Our data
	R(CH=CH)$_n$CHO (0, 1)	μ	0·87	Our data
	R(CH=CH)$_n$CHO (0, 1)	q_0	0·47	Our data
	R(CH=CH)$_n$CHO (0, 1)	λ_{max}	0·85	Our data
	R(CH=CH)$_n$COOEt (0, 1)	ν_{CO}	0·64	30
	R(CH=CH)$_n$COOEt (0, 1)	k (alkaline hydrolysis)	0·52	Our data
	R(CH=CH)$_n$COOEt (1, 2)	ν_{CO}	0·66	Calculated with data from refs 30, 19
	ArCO(CH=CH)$_n$Ar (0, 1)	ν_{CO}	0·75	7
	ArCO(CH=CH)$_n$Ar (0, 1)	μ	0·84	3
	ArCO(CH=CH)$_n$Ar (0, 1)	Z/Z_0[a]	0·72	2
	ArCO(CH=CH)$_n$Ar (1, 2)	λ_{max}	0·82	7
	Ar(CH=CH)$_n$COMe (0, 1)	k (isotope exchange)	0·50	37
2	Ar(CH=CH)$_n$CHO (0, 2)	λ_{max}	0·63	Our data
	Ar(CH=CH)$_n$CHO (0, 2)	$E_{1/2}$	0·73	Our data
	R(CH=CH)$_n$CHO (0, 2)	ν_{CO}	0·46	Our data
	R(CH=CH)$_n$CHO (0, 2)	μ	0·68	Our data
	R(CH=CH)$_n$CHO (0, 2)	q_0	0·22	Our data
	Ar(CH=CH)$_n$COOEt (0, 2)	k (alkaline hydrolysis)	0·33	Calculated with data from ref 36
	R(CH=CH)$_n$COOEt (1, 3)	ν_{CO}	0·42	Calculated with data from ref 19
	R(CH=CH)$_n$COOEt (1, 3)	k (alkaline hydrolysis)	0·28	Our data
	ArCO(CH=CH)$_n$Ar (1, 3)	λ_{max}	0·55	7
	ArCO(CH=CH)$_n$Ar (1, 3)	Z/Z_0	0·25	2
3	R(CH=CH)$_n$CHO (0, 3)	ν_{CO}	0·29	Our data
	R(CH=CH)$_n$CHO (0, 3)	μ	0·56	Our data
	R(CH=CH)$_n$CHO (1, 4)	λ_{max}	0·62	Our data
	R(CH=CH)$_n$CHO (1, 4)	q_0	0·10	Our data
	R(CH=CH)$_n$COOEt (0, 3)	ν_{CO}	0·25	Calculated with data from ref 19, 30
	R(CH=CH)$_n$COOEt (0, 3)	k (alkaline hydrolysis)	0·13	Our data
	ArCO(CH=CH)$_n$Ar (0, 3)	Z/Z_0[n]	0·11	2
4	R(CH=CH)$_n$CHO (0, 4)	μ	0·43	Our data
	R(CH=CH)$_n$CHO (0, 4)	ν_{CO}	0·13	Calculated with data from refs 19, 30

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[a] Z/Z_0 is the relative intensity of benzoyl ion in mass-spectra of the series NuCO CCu = Cu/nC$_6$NuR

Table 17. Calculated and experimental values of ν_{max} (cm^{-1}) and $E_{1/2}$ (V *vs* SCE) for certain polyenes

Ph(CH=CH)$_n$CHO

n	ν_{max}		$E_{1/2}$		n	ν_{max}		$E_{1/2}$	
	Exp.[17]	Calc.	Exp.[17]	Calc.		Exp.[17]	Calc.	Exp.[17]	Calc.
0	40·7		1·36		4	25·6	23·4	0·70	0·69
1	34·5	34·6	1·09	1·15	5	24·6	21·6	0·60	0·59
2	30·9	30·5	0·89	0·98	6	23·0	20·9		
3	28·0	25·2	0·77	0·83					

R(CH=CH)$_n$COOEt

R n	1		2		3		4	
	ν_{max}							
	Exp.[19]	Calc.	Exp.[19]	Calc.	Exp.[19]	Calc.	Exp.[19]	Calc.
Me[a]	43·0		38·8	36·5	33·2	31·1	29·9	26·4
CHO[b]	44·5		37·2	37·8	31·6	32·0	28·4	27·6
COOEt[c]	47·6		37·9	40·5	33·0	34·2	29·9	29·5
NO_2	45·0		35·6	38·2	30·6	32·3	27·5	27·9

[a] ν_{max}, n = 5: 27·4 (exp.), 22·4 (calc.). [b] ν_{max}, n = 5, 25·4 (exp.), 23·1 (calc.). [c] ν_{max}, n = 55, 27·4 (exp.), 25·0 (calc.).

It is of interest that the above found values of ρ_{rel} are in the following ratio: (0·66):(0·30)(0·18) = (0·66):(0·66)^3:(0·66)^4. Taking into account their results, Eaborn *et al.* suggest that "in conjugation systems the variation in the transmission of inductive and conjugative effects are not as independent as assumed in treatment of the Dewar–Grisdale type". This conclusion is especially true for polyenes. All our attempts to use the F,R method for the correlation analysis of our data gave poor results, and the separation of I and M effects according to Taft,[40] using the multiparameter equations, in all cases led to very large values of non-additive interactions, which indicate the interdependency of the transmission of inductive and conjugative effects.

Eaborn *et al.* observed also that the values of ρ_{rel} are roughly proportional to the degree of positive charge located in the aromatic ring in the transition state. We found that the π' values found by the correlation analysis of the q_0 values as well as those found by the correlation analysis of certain experimental values (ν_{CO}, μ, λ_{max}, $E_{1/2}$, k) are bound by the same ratio (7). These results indicate that this ratio (7) reflects some general regularities connected with the distribution of electronic density in molecules of polyenes.

The difference between the π' values calculated for different properties may be explained by the different sensitivity of various properties toward substituent changes. In addition transmission effects which are operative in excited states may not be operative in ground states.

The above ratio (7) may be applied to the calculation of the quantitative characteristics of polyenes when π'_{1_F} is known. In Table 17 we give some calculated and experimental values of long wave maxima and halfwave potentials of 2 (R = Ph) and certain compounds (3). As can be seen from the data of Table 17 the calculated and experimental values of ν_{max} and $E_{1/2}$ are close to each other.

In conclusion we would like to note that our results in this article, as well as those recorded[2,3,9,13] in addition to the result of other authors[14,17,27–34,38,39] indicate that the traditional view of substituent effects currently held by a majority of organic chemists becomes more and more insufficient and needs a modification.

REFERENCES

[1] Yu. A. Zhdanov and V. I. Minkin, *Correlation Analysis in Organic Chemistry* (Russian), Rostov-na-Donu (1966)

[2] B. M. Zolotarev, L. A. Yanovskaya, B. Umirzakov, O. S. Chizhov and V. F. Kucherov, *Org. Mass Spectrometry* 5, 1643 (1971)

[3] M. G. Grunfest, Yu. V. Kolodyazhny, O. A. Osipov, L. A. Yanovskaya, B. Umizakov, V. F. Kucherov and L. G. Vorontsova, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2662 (1972)

[4] L. G. Vorontsova, *Zh. Struct. Khim.* in press

[5] L. A. Yanovskaya, R. N. Stepanova, G. A. Kogan and

V. F. Kucherov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 857 (1963)

[6] L. A. Yanovskaya, R. N. Stepanova and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1334 (1967)

[7] L. A. Yanovskaya, B. Umerzakov, I. P. Yakovlev and V. F. Kucherov, *Izv. Akad. Naur SSSR, Ser. Khim.* 2447 (1971)

[8] G. A. Kogan, L. A. Yanovskaya, R. N. Stepanova and V. F. Kucherov, *Experiment. Teoretich. Khim.* **1**, 414 (1965)

[9] L. A. Yanovskaya, G. V. Kryshtal, I. P. Yakovlev and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 172 (1973)

[10] R. W. Taft, S. Ehrenson, I. C. Levais and R. E. Glick, *J. Am. Chem. Soc.* **81**, 5352 (1959)

[11] M. G. Kogan, V. S. Pustovarov, Yu. V. Kolodyazhny, S. N. Nazarova and O. A. Osipov, *Zh. Org. Khim.* **4**, 12 (1968)

[12] V. I. Minkin, O. A. Osipov and Yu. A. Zhdanov, *Dipole Moments in Organic Chemistry* (Russian), *Khimia*, Moscow (1968)

[13] G. V. Kryshtal, L. A. Yanovskaya, V. F. Kucherov, V. A. Bren and V. I. Minkin, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2362 (1972)

[14] M. H. Hutchinson and L. E. Sutton, *J. Chem. Soc.* 4382 (1958)

[15] O. Exner, *Coll. Czech. Chem. Commun.* **25**, 642 (1969)

[16] S. S. Malhotra and M. C. Whiting, *J. Chem. Soc.* 3212 (1960)

[17] W. Kraus, F. Scheidel and G. J. Wagner-Bartek, *Ber. Bunsen Ges. Physik. Chem.* **21**, 452 (1961)

[18] D. Marshall and M. C. Whiting, *J. Chem. Soc.* 4082 (1956)

[19] G. A. Kogan, L. A. Yanovskaya, R. N. Stepanova and V. F. Kucherov, *Experiment. Teoretich. Khim.* **1**, 411 (1965)

[20] S. G. Mairanovsky, L. A. Yanovskaya, N. V. Kondratova and G. V. Kryshtal, *Elektrokhim.* **4**, 1127 (1968)

[21] V. I. Minkin, V. A. Bren and E. N. Malysheva, *Reakts. Sposobn. Org. Soedin.* (Reactivity Org. Comp.) **5**, 565 (1968)

[22] V. A. Bren, E. N. Malysheva and V. I. Minkin, *Ibid.* (Reactivity Org. Comp.) **4**, 523 (1967)

[23] N. M. Emanuel and D. G. Knorre, *Manual of Chemical Kinetics* (Russian), Vysshya Shkola, Moscow (1969)

[24] G. V. Kryshtal, L. A. Yanovskaya and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2364 (1972)

[25] K. B. Wiberg, *Physical Organic Chemistry*. Wiley, New York (1964)

[26] R. W. Taft, *J. Am. Chem. Soc.* **79**, 1045 (1957)

[27] G. I. Kogan, I. N. Fundyler and G. I. Kogan, *Experiment. Teoretich. Khim.* **2**, 589 (1966)

[28] J. N. Juchnovski, *Dokl. Bolg. Akad. Nauk* **20**, 33 (1967)

[29] J. N. Juchnovski, *Ibid.* **20**, 97 (1967)

[30] J. Juchnovski, *Dokl. Akad. Nauk SSSR* **168**, 1117 (1966), **186**, 878 (1969)

[31] J. N. Juchnovski, D. Dumanov and A. Mincheva, *Izv. Bulgar. Akad. Mauk*, **4**, 39 (1967)

[32] W. L. Silver and D. W. Boykin, *J. Org. Chem.* **35**, 759 (1970)

[33] W. F. Winecoff and D. W. Boykin, *Ibid.* **37**, 674 (1972)

[34] J. Juchnovski and N. Christov, *Dokl. Bolg. Akad. Nauk* **22**, 1401 (1969)

[35] H. H. Jaffe, *Chem. Rev.* **53**, 191 (1953)

[36] H. Wang, C. H. Wang., *J. Org. Chem.* **36**, 3178 (1971)

[37] L. M. Litvinenko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1737 (1962)

[38] C. Eaborn, H. Eastmond and D. R. M. Walton, *J. Chem. Soc.* (B), 753 (1970)

[39] C. Eaborn, R. Eastmond and D. R. H. Walton, *Ibid.* (B). 127 (1971)

[40] R. W. Taft and I. C. Levais, *Tetrahedron* **8**, 1689 (1959)