

POLAR EFFECTS ON ^{13}C NMR CHEMICAL SHIFTS AND ROTATIONAL BARRIERS OF AMIDES. A DUAL SUBSTITUENT PARAMETERS ANALYSIS OF N,N-DIMETHYL-3-(5-SUBSTITUTED-2-FURYL)-ACRYLAMIDES*

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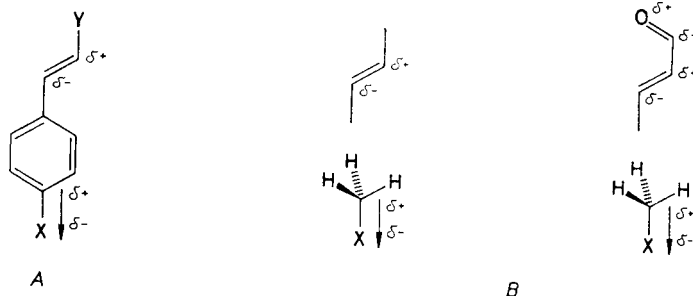
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^{13}C NMR chemical shifts were measured for sixteen N,N-dimethyl-3-(5-substituted-2-furyl)-acrylamides in CDCl_3 at 21°C ; the barriers of rotation about the C—N bond ΔG_c^\ddagger were determined by using the ^1H NMR coalescence method, and the positions of the IR bands of the $\nu(\text{C}=\text{O})$ stretching vibrations were measured. The dual substituent parameters (DSP) analysis of the ^{13}C NMR chemical shifts for atoms of the vinylcarboxamide side chain $-\text{C}(3)\text{H}=\text{C}(2)\text{H}-\text{C}(1)=\text{O}(-\text{N})$ gives evidence that the chemical shifts for the C-1 and C-3 atoms are controlled primarily by polar effects ($\delta(\text{C}-3) = -3.12\sigma_1 - 1.03\sigma_{\text{R}}$; $\lambda = \rho_1/\rho_{\text{R}} = 3.0$), which exert a reverse substituent effect on these atoms. Similarly, the DSP analysis of the ΔG_c^\ddagger and $\nu(\text{C}=\text{O})$ data shows that the dominant factor of the total substituent effect is the polar effect ($\lambda = 1.95$ and 1.70 , respectively). A confrontation of the results of the DSP analysis with the CNDO/2 calculated electron densities at the corresponding atoms demonstrates that the reactivity of the entire vinylcarboxamide side chain can be well explained in terms of a combination of the polar effect (π -electron polarization) with resonance effects.

Substituent effects on the reactivity of atoms of the side chains of vinylaromatic systems have been studied extensively¹⁻³; the most significant results have apparently been obtained by dual substituent parameters (DSP) analysis⁴ of ^{13}C NMR chemical shifts (CS) in terms of the polar (σ_1) and resonance (σ_{R}) constants. That this approach is physically warranted has been proved by factor analysis⁵⁻⁷ of an ample collection of ^{13}C CS data.

Recent results of DSP analysis of ^{13}C CS of β -substituted 4-X-styrenes⁸⁻¹¹ (Structure A) led to the formulation of the π -polarization mechanism of polar effect transfer³. Experimental study of the π -polarization has been combined with theoretical calculations for isolated molecules (Structure B) at the *ab initio* STO-3G level^{12,13}. Since resonance effects are ruled out in the isolated molecules, the identical changes in the π -electron distribution in Structures A and B can only be explained in terms of polar effects.

* This paper should be considered as Part CCXII in the series Furan Derivatives.



By introducing the N,N-dimethylcarboxamide group in the side chains of vinylaromatic systems, additional sensitive reaction centres are obtained, *viz.* the rotational barriers about the C—N bond and carbonyl stretching vibrations. The reactivity of the entire vinylcarboxamide chain has not been so far examined in total, attention having only been paid to the rotational barriers ΔG^\ddagger and IR bands of the $\nu(\text{C}=\text{O})$ vibrations in N,N-dimethyl-3-(4-substituted-1-phenyl)acrylamides^{14–16}. Of heterocyclic amides, only derivatives with an N,N-dimethylcarboxamide group bonded directly to the ring system have been examined (N,N-dimethyl-2-furamide^{17–20} and N,N-dimethyl-3-furamide^{18–20}).

In this paper, the results of DSP analysis of reactivity of the —C(3)H=C(2)H—C(1)=O(—N) vinylcarboxamide side chain are presented for sixteen (*E*)-N,N-dimethyl-3-(5-X-2-furyl)acrylamides (*I–XVI*). The ¹H and ¹³C CS, rotational barriers ΔG_c^\ddagger and IR band positions of the $\nu(\text{C}=\text{O})$ stretching vibrations were measured. For testing the kinetic data and comparing the reactivity of the furan and benzene rings, (*E*)-N,N-dimethyl-3-(4-X-1-phenyl)acrylamides *XVII–XIX* were prepared; their kinetic data, as well as those of the remaining amides *XX–XXV*, are available^{14–16}. The results of the DSP analysis were confronted with the CNDO/2 calculated σ , π and total electron densities at the corresponding atoms of the side chain.

EXPERIMENTAL AND RESULTS

Substances. Amides *I–VIII* and *X–XVIII* were synthesized from the corresponding acids, which were converted with thionyl chloride in benzene to the respective chlorides using dimethylformamide as catalyst, and the chlorides were reacted with aqueous dimethylamide in tetrahydrofuran to obtain the N,N-dimethylamides. Amides *IX* and *XIX* were prepared from 8 mmol of the corresponding methylates²¹ by aminolysis with 40 ml of 50 wt % dimethylamine in ethanol in the presence of 6.5 ml of 0.1 mol l⁻¹ sodium ethanolate in ethanol²².

An overview of the physical and analytical properties of amides *I–XVI* and *XIX* is given in Table I. The melting temperatures, measured with a Kofler stage, are uncorrected. The samples were dried over P₂O₅ at 25°C/10 Pa. Their identity was checked by melting temperature measurements, thin layer chromatography, elemental analysis and IR and ¹H NMR spectroscopy.

Physical measurements. ¹H NMR spectra of the substances in CDCl₃ solutions ($c = 0.25 \text{ mol l}^{-1}$, amide *VII*: 0.16 mol l^{-1}) were run on a Tesla BS 467 spectrometer at 25°C using tetramethylsilane as the internal standard. The concentration dependence of the CS was examined

for amide *I* over the region of 0.05–0.5 mol l⁻¹; only the methyl signals of the amide group were observed to be concentration dependent. The ¹H CS of amides *I–XVI* are given in Table II.

¹³C NMR spectra of the amides in CDCl₃ solutions (*c* = 0.1 mol l⁻¹) were scanned at 15.04 MHz on a Jeol FX 60 spectrometer at 21°C using tetramethylsilane as the internal standard. FT conditions: spectrum width 4 kHz, FID data accumulation 8 K, ¹³C{¹H} broadband decoupling 1 kHz, effective computer resolution 0.06 ppm. The signal assignment was performed by means of the selective ¹³C{¹H} decoupling, spectra of the heteronuclear NOE effect and spectra with all ¹H–¹³C interactions preserved, and confronted with the empirical relations for the calculation of the ¹³C CS (ref.²⁵) where the increments were obtained from the experimental data of 2-substituted furans²⁶, and the ¹³C CS of the unsubstituted amide *I* served as the starting values. The concentration dependence of the ¹³C CS was examined for amide *I* over the region of 0.05–0.5 mol l⁻¹, and changes were only observed for the CS of the methyl carbon atoms of the amide group. The ¹³C CS data for amides *I–XIX* are given in Table III.

The dipole moments were measured for amides *I* and *XVII* in benzene solutions at 25°C by the procedure described previously²⁷; the values are given in Table IV.

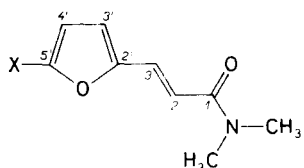
TABLE I

Physical and analytical data of compounds *I–XVI* and *XIX*

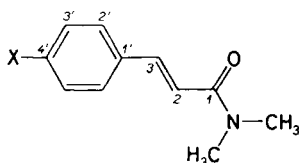
No	Compound ^a formula	Mol. wt.	M.p. °C	Yield %	Calculated/found		
					% C	% H	% N
<i>I</i>	C ₉ H ₁₁ NO ₂	165.19	70–71	77	65.43/65.60	6.70/6.61	8.48/8.40
<i>II</i>	C ₁₀ H ₁₃ NO ₂	179.21	60–61	65	67.02/67.31	7.31/7.36	7.82/7.59
<i>III</i>	C ₁₅ H ₁₅ NO ₂	241.28	108–109	75	74.66/74.90	6.27/6.48	5.81/6.05
<i>IV</i>	C ₉ H ₁₀ NClO ₂	199.64	126–127	66	54.14/54.03	5.05/5.15	7.02/7.30
<i>V</i>	C ₉ H ₁₀ NBrO ₂	244.09	119–120 ^b	66	44.28/43.84	4.13/4.08	5.74/5.55
<i>VI</i>	C ₉ H ₁₀ NIO ₂	291.09	127	72	37.13/36.86	3.46/3.39	4.81/4.64
<i>VII</i>	C ₉ H ₁₀ N ₂ O ₄	210.19	195–196 ^c	70	51.42/51.53	4.80/4.82	13.33/13.18
<i>VIII</i>	C ₁₀ H ₁₀ N ₂ O ₂	190.20	154–155	57	63.14/63.56	5.30/5.38	14.73/14.97
<i>IX</i>	C ₁₁ H ₁₆ N ₂ O ₂	208.25	87–88	66	63.43/63.60	7.74/7.60	13.45/13.10
<i>X</i>	C ₁₀ H ₁₃ NO ₄ S	243.28	133–134	24	49.37/49.66	5.38/5.45	5.76/5.97
<i>XI</i>	C ₁₅ H ₁₅ NO ₄ S	305.34	143–144	59	59.00/59.38	4.95/4.98	4.59/4.78
<i>XII</i>	C ₁₁ H ₁₃ NO ₃	207.22	136	23	63.75/64.07	6.32/6.57	6.76/7.19
<i>XIII</i>	C ₁₁ H ₁₃ NO ₄	223.22	122–122.5	30	59.18/59.33	5.87/6.21	6.27/6.68
<i>XIV</i>	C ₁₀ H ₁₃ NO ₂ S	211.28	57–57.5	70	56.84/57.26	6.20/5.90	6.63/6.96
<i>XV</i>	C ₁₅ H ₁₅ NO ₂ S	273.34	69.5–70	81	65.91/66.20	5.53/5.47	5.12/5.06
<i>XVI</i>	C ₁₅ H ₁₅ NO ₃	257.28	64–65	56	70.02/70.31	5.88/5.83	5.44/5.48
<i>XIX</i>	C ₁₃ H ₁₈ N ₂ O	218.29	132–133	76	71.52/71.62	8.31/8.48	12.84/13.03

^a Compounds *I*, *II*, *VII*, and *XV* crystallized from ethyl ether–hexane mixture, compounds *III–VI*, *VIII–XIII*, and *XVI* from ethyl acetate, compound *XIX* from ethanol; ^b ref.²³: 120°C (water); ^c ref.²⁴: 194–195°C (aqueous ethanol).

^1H DNMR spectra were recorded at 60 MHz on a Tesla BS 467 spectrometer. The temperature measurements were performed using a Tesla BP 4675 temperature probe. The precise temperature was measured before and after each experiment by means of standard Tesla tubes with ethylene glycol and/or methyl alcohol using Van Geet's relations²⁸; the accuracy was better than $\pm 1^\circ\text{C}$. The kinetic measurements were made with solutions in CDCl_3 at $c = 0.25 \text{ mol} \cdot \text{l}^{-1}$ ($0.16 \text{ mol} \cdot \text{l}^{-1}$ for amide VII) in the presence of 0.1 vol. % pyridine- d_5 for removing trace quantities of hydrogen chloride¹⁴. Hexamethyldisiloxane served as the internal standard. Prior to measurement the solutions were degassed by repeated freezing in a vacuum. The kinetically unaffected chemical shift differences $\Delta\nu_c$ at the temperature of coalescence t_c were determined²⁹ by extrapolation of the linear dependence of $\Delta\nu$ on the reciprocal absolute temperature. It was found that at temperatures $t_c - 30^\circ\text{C}$ and lower, $\Delta\nu$ is temperature independent, and so the temperature $t_c - 40^\circ\text{C}$ was used as the standard temperature for determining $\Delta\nu_c$ and the kinetically unaffected signal widths b_E . The values are given in Table V.



- | | |
|---------------------------------|---|
| I, X = H | IX, X = $\text{N}(\text{CH}_3)_2$ |
| II, X = CH_3 | X', X = SO_2CH_3 |
| III, X = C_6H_5 | XI, X = $\text{SO}_2\text{C}_6\text{H}_5$ |
| IV, X = Cl | XII, X = COCH_3 |
| V, X = Br | XIII, X = COOCH_3 |
| VI, X = I | XIV, X = SCH_3 |
| VII, X = NO_2 | XV, X = SC_6H_5 |
| VIII, X = CN | XVI, X = OC_6H_5 |



- | | |
|------------------------------------|-------------------------|
| XVII, X = H | XXII, X = Br |
| XVIII, X = NO_2 | XXIII, X = CN |
| XIX, X = $\text{N}(\text{CH}_3)_2$ | XXIV, X = CH_3 |
| XX, X = F | XXV, X = OCH_3 |
| XXI, X = Cl | |

Infrared absorption spectra of amides I–XIX in CHCl_3 solutions containing 0.1 vol. % pyridine were measured over the region of $1500\text{--}1700 \text{ cm}^{-1}$ on a Unicam SP 100 instrument; concentration $0.05 \text{ mol} \cdot \text{l}^{-1}$, optical path length 0.1 mm. The wavenumber scale was calibrated with a polystyrene foil and the reading accuracy was $\pm 0.5 \text{ cm}^{-1}$. The $\nu(\text{C}=\text{O})$ wavenumbers are given in Table V.

Kinetic calculations. The Gibbs energies of the rotational barrier at the temperature of coalescence, ΔG_c^\ddagger , were calculated by the modified Eyring equation

$$\Delta G_c^\ddagger = 8.314T_c[23.760 + \ln T_c/k_c], \quad (1)$$

where T_c is the absolute temperature of coalescence and k_c is the rate constant at this temperature, calculated³⁰ by using the equation

$$k_c = (\pi/2)(\Delta\nu_c - b_E) + b_E, \quad (2)$$

where $\Delta\nu_c$ is the difference of the kinetically unaffected chemical shifts and b_E is the kinetically unaffected bandwidth. The error $\Delta\Delta G_c^\ddagger$ was calculated according to the equation

$$\Delta\Delta G_c^\ddagger = 16.628 + 2 \Delta G_c^\ddagger/T_c + 4.708T_c/k_c, \quad (3)$$

where the errors $\Delta T_c = \pm 2$ K, $\Delta\Delta\nu_c = \pm 0.2$ Hz and $\Delta b_E = \pm 0.1$ Hz are included. The ΔG_c^\ddagger values along with the associated error $\Delta\Delta G_c^\ddagger$ are given in Table V.

The kinetically broadened signals of amides *I*, *VII*, and *IX* were simulated on an M 4030-1 computer using the modified³⁰ program of Neuman and Jonas³¹. The signal intensities in the experimental spectra at 25°C were recorded as a function of frequency and, by using the least squares method, compared with the normalized intensities calculated by variation of the set

TABLE II

¹H NMR chemical shifts (δ scale, ± 0.01 ppm) of compounds *I*–*XVI* in deuteriochloroform at 25°C

Compound	H-2 ^a	H-3 ^a	H-3' ^b	H-4' ^b	CON(CH ₃) ₂	
<i>I</i>	6.80	7.45	6.53	6.44	3.05	3.13
<i>II</i>	6.70	7.37	6.42	6.03	3.05	3.12
<i>III</i>	6.86	7.46	6.70	6.61	3.06	3.16
<i>IV</i>	6.77	7.32	6.53	6.27	3.04	3.13
<i>V</i>	6.78	7.32	6.46	6.36	3.04	3.13
<i>VI</i>	6.78	7.34	6.59	6.42	3.04	3.14
<i>VII</i>	7.15	7.43	7.34	6.69	3.07	3.19
<i>VIII</i>	7.01	7.40	7.11	6.59	3.06	3.17
<i>IX</i>	6.34	7.29	6.49	5.06	3.06	3.06
<i>X</i>	7.02	7.44	7.18	6.63	3.05	3.17
<i>XI</i>	6.91	7.35	7.19	6.57	3.02	3.13
<i>XII</i>	7.05	7.44	7.18	6.62	3.07	3.19
<i>XIII</i>	7.04	7.43	7.16	6.59	3.05	3.17
<i>XIV</i>	6.77	7.35	6.49	6.38	3.07	3.15
<i>XV</i>	6.83	7.39	6.72	6.57	3.02	3.09
<i>XVI</i>	6.64	7.34	6.48	5.51	3.04	3.08

^a ³J(H-2, H-3) = 15.5 Hz; ^b ³J(H-3', H-4') = 3.5 Hz.

of variables k , $\Delta\nu$, and b_E based on the Gutowsky-Holm equation³² for the total analysis of the line shape. The mean ΔG_{298}^\ddagger values were calculated from the simulated ΔG^\ddagger values, whose standard deviation was lower than 3% of the maximum intensity. The data are given in Table VI.

Quantum chemical calculations. The total energies, dipole moments and electron densities of amides *I–V* and *VII–XIX* were calculated by the semiempirical CNDO/2 method in the standard parametrization³³ and without geometry optimization; the Cl, Br, and S atoms were approximated in the *sp* orbital base. The use of the *spd* base led to nonreal results for all of the amides treated; and since for the iodo derivative *VI* also the *sp* base appeared inadequate, this compound was omitted from the treatment. The geometry of the coplanar 5-substituted furylacryl skeleton was composed of the optimized *ab initio* STO-3G geometry of the furan ring³⁴ and the standard bond lengths and angles for the substituent and the vinylcarboxamide group^{35,36}. The value of the interaction constant $^3J(\text{H-2, H-3}) = 15.5$ Hz (Table II) indicates that all of the amides *I–XIX* possess the *E*-configuration at the double bond of the side chain. The conformation at the (furan)—(C=C) bond inferred from the ^1H NMR spectra and dipole moments 5f amides *I* and *XVII* (Table IV) is (*E*)-*sp,sp*. The absence of the stereospecific interaction constant $^oJ(\text{H-3, H-4}')$ and the positive homonuclear NOE of the (H-3, H-3') protons rule out the (*E*)-*ap,sp* conformation, which agrees with the results obtained for most of *E*-furylethylenes studied^{37–39}.

TABLE III

^{13}C NMR chemical shifts (δ scale, ± 0.06 ppm) of compounds *I–XIX* in deuteriochloroform at 21°C

Compound	C-1	C-2	C-3	C-2'	C-3'	C-4'	C-5'	CON(CH ₃) ₂	
<i>I</i>	166.86	115.23	129.43	152.08	113.93	112.37	144.07	37.43	36.07
<i>II</i>	167.25	115.69	129.62	150.71	113.28	108.85	154.75	37.43	36.07
<i>III</i>	166.66	116.23	129.10	151.26	114.42	107.73	155.29	37.49	35.99
<i>IV</i>	166.20	115.59	128.13	151.39	115.26	108.96	138.26	37.43	35.99
<i>V</i>	166.54	115.69	128.32	154.04	116.08	114.25	124.48	37.50	36.07
<i>VI</i>	166.54	115.95	128.12	157.42	116.28	123.10	90.95	37.50	36.07
<i>VII</i>	164.97	121.69	127.02	153.47	114.94	113.31	151.94	37.55	36.13
<i>VIII</i>	165.29	120.26	127.15	155.68	113.44	123.64	126.31	36.06	34.83
<i>IX</i>	167.63	107.14	129.04	143.26	119.29	84.86	161.20	35.90	35.90
<i>X</i>	165.69	120.24	127.86	156.12	119.40	113.86	149.80	37.63	36.13
<i>XI</i>	165.69	120.11	127.86	156.31	119.40	113.93	150.32	37.56	36.07
<i>XII</i>	166.02	119.66	128.45	155.14	115.17	119.53	152.73	37.56	36.13
<i>XIII</i>	165.88	119.72	128.19	154.88	114.58	119.01	144.72	37.37	35.87
<i>XIV</i>	166.53	114.87	128.58	150.15	115.00	115.52	153.53	37.43	35.99
<i>XV</i>	166.16	115.25	128.43	145.06	121.16	116.49	154.99	37.33	36.04
<i>XVI</i>	166.99	113.21	129.17	144.59	116.21	90.75	158.59	37.43	36.00
<i>XVII</i>	166.48	117.33	142.02	127.57	128.62	129.32	135.18 ^a	37.18	35.78
<i>XVIII</i>	165.66	121.84	139.50	128.33	124.12	148.05	141.67 ^a	37.47	36.01
<i>XIX</i>	167.44	112.04	142.75	129.24	111.86	151.29	123.27 ^a	37.33	35.92

^a Corresponds to C-1' atom.

The (*E*)-*sp,sp* conformation also emerges as the most stable from CNDO/2 calculations (Table IV), although the difference in the total nonoptimized energies is insignificant. The *sp* conformation at the (C=C)—(C=O) bond of the vinylcarboxamide group has been established recently for amide *XVII* by X-ray diffraction analysis⁴⁰ ($\tau = 0 \pm 15^\circ$) and by IR and ¹H NMR spectroscopic study⁴¹ and is in agreement with the CNDO/2 calculations for amide *I*, the two *ap* conformers being about 1 000 kJ mol⁻¹ less stable (Table IV). Based on these results, a planar structure with the (*E*)-*sp,sp* conformation as shown above was assigned to amides *I—XVI* and the (*E*)-*sp* conformation, to amides *XVII—XIX*. The CNDO/2-calculated relative σ , π and total electron densities δQ at the atoms of the vinylcarboxamide side chain are given in Table VII.

DISCUSSION

Although this study is concerned with the DSP analysis of ¹³C CS, let us examine first the ¹H CS given in Table II. It has been shown² that ¹H CS of H- α and H- β protons in β -substituted 4-*X*-styrenes (Structure *A*) generally do not suit well to the study of the substituent effect because of the too complex mechanism of shielding, which is affected by the anisotropy of the adjacent aromatic ring, particularly for the α -position. The correlation of the δ (H-2) and δ (H-3) data with the CNDO/2 total charges at the H-2 and H-3 atoms is poor ($r = 0.741$ and 0.418 , respectively; $n = 15$) and no conclusions can be drawn from it. The DSP analysis⁴ of the δ (H-2) and δ (H-3) data was performed in terms of the two-parameter equation

$$\delta(y) = \rho_I \sigma_I + \rho_R \sigma_R + b \quad (4)$$

using the standard⁴² polar σ_I and resonance σ_{R0} constants; its results are given in

TABLE IV
Relative total CNDO/2 energies and dipole moments of *I* and *XVII* conformers

Conformer	ΔE_{tot}^a kJ mol ⁻¹	Dipole moment, 10 ⁻³⁰ Cm		
		calculated	observed ^b	
			5%	15%
<i>I</i> (<i>E</i>)- <i>sp, sp</i>	0	10.06 (12.16) ^c	11.44	11.31
(<i>E</i>)- <i>sp, ap</i>	1 088.7	10.08	—	—
(<i>E</i>)- <i>ap, sp</i>	1.0	14.07	—	—
(<i>E</i>)- <i>ap, ap</i>	1 088.5	8.38	—	—
<i>XVII</i> (<i>E</i>)- <i>sp</i>	—	11.08 (12.63) ^c	12.28	12.17

^a Relative to the most stable conformer; ^b benzene solution, 25°C; correction for atomic polarization 5% or 15% of R_D value; ^c CNDO/S calculation.

Table VIII. The quality of the $\delta(\text{H-3})$ data correlation, similarly as in the case of the total CNDO/2 charges, is unsatisfactory. Thus only the $\delta(\text{H-2})$ data have an explanatory power: the polar-to-resonance effect ratio $\lambda = \rho_{\text{I}}/\rho_{\text{R}} = 0.48$ indicates an enhanced resonance interaction in position 2 of the side chain. Since the ^1H CS reflect directly the electron situation at the carbon atoms to which the respective hydrogen atoms are bonded, we will return to the $\delta(\text{H-2})$ data during the discussion of the ^{13}C CS of the C-2 atom.

The results of the DSP analysis of ^{13}C CS of amides *I–XVI* are given in Table VIII. The iodo derivative *VI* was omitted from the treatment since there are two other halo derivatives included in the reaction series (Cl and Br), which is not recommended for DSP analysis^{3,4}. The DSP analysis was performed in terms of the two-parameter

TABLE V

^1H NMR coalescence data at 60 MHz for compounds *I–XIX* in deuteriochloroform solutions ($c = 0.25 \text{ mol l}^{-1}$) and wavenumbers of their $\nu(\text{C=O})$ infrared bands

Compound	t_c °C	$\Delta\nu_c^a$ Hz	b_E^b Hz	k_c s^{-1}	$\Delta G_c^{\ddagger c}$ kJ mol^{-1}	$\nu(\text{C=O})$ cm^{-1}
<i>I</i>	34	6.1	0.7	12.7	68.7	1 652.5
<i>II</i>	31	6.6	0.9	13.6	68.0	1 652
<i>III</i>	34	7.5	1.0	15.4	68.1	1 652
<i>IV</i>	43	6.4	0.8	13.2	70.7	1 654.5
<i>V</i>	42	6.6	0.8	13.7	70.5	1 654
<i>VI</i>	42	6.8	0.8	14.1	70.4	1 653
<i>VII</i>	56	7.8	0.6	16.6	73.1	1 657
<i>VIII</i>	52	7.4	0.8	15.5	72.3	1 657.5
<i>IX</i>	9	5.5	1.1	10.9	63.3	1 642
<i>X</i>	51	7.2	1.1	14.6	72.4	1 657.5
<i>XI</i>	47	7.0	0.8	14.6	71.3	1 658
<i>XII</i>	47	7.5	0.8	15.7	71.3	1 656
<i>XIII</i>	50	7.6	0.8	15.9	71.9	1 657
<i>XIV</i>	34	6.8	0.9	14.0	68.4	1 653
<i>XV</i>	35	4.8	1.1	9.3	69.7	1 654
<i>XVI</i>	27	4.4	1.0	8.6	68.2	1 653.5
<i>XVII</i>	33	6.4	0.6	13.5	68.4 ^d	1 655
<i>XVIII</i>	49	7.6	0.6	16.2	71.6 ^e	1 659
<i>XIX</i>	19	6.2	1.4	12.1	65.4	1 643

^a Kinetically unaffected chemical shift difference at t_c ; ^b kinetically unaffected signal width. ^c error $\Delta\Delta G_c^{\ddagger} = 0.6 \text{ kJ mol}^{-1}$; ^d ref.¹⁴: 68.4 kJ mol^{-1} , ref.¹⁶: 67.8 kJ mol^{-1} ; ^e ref.¹⁴: 70.5 kJ mol^{-1} , ref.¹⁶: 70.2 kJ mol^{-1} .

equation (4) using the resonance constants σ_{R0} as well as σ_{R+} which reflect better the resonance interaction with electron donor substituents. Since the N,N-dimethylcarboxamide group itself has an electron acceptor nature (for CONH_2 , $\sigma_1 = 0.28$, $\sigma_{R-} = 0.27$, ref.⁴²), it was the set of σ_1 and σ_{R+} constants that gave the best correlation both for ^{13}C CS and $\nu(\text{C}=\text{O})$ wavenumbers.

A conspicuous feature of the correlation parameters in Table VIII is the negative sign of the ϱ_I and ϱ_R slopes for the C-1 and C-3 atoms and the magnitude of the $\lambda = \varrho_I/\varrho_R$ ratio which is 1.2–3.4 for C-1 and 3.0–11.3 for C-3 according to the kind of the σ_R constants used. The dominance of the polar effect on the ^{13}C CS of atoms C-1 and C-3, which follows from these facts, is consistent with the results of DSP analysis of the rotational barriers ΔG_c^\ddagger and IR wavenumbers of the $\nu(\text{C}=\text{O})$ vibration ($\lambda = 1.95$ and 1.52, respectively). Comparing the absolute values $|\varrho_I|$ for the C-2 and C-3 atoms over the whole series we obtain $\varrho_I(\text{C-2})/\varrho_I(\text{C-3}) \approx 2.3$. All these observations indicate the occurrence of a reverse substituent effect whose intensity increases with increasing distance; they cannot be explained in terms of any of the classical polar effect transfer mechanisms (σ -inductive χ_σ or electrostatic F_D), because these involve a monotonic decrease in the effect intensity with increasing distance. Analogy of our observations with some results obtained recently can be illustrated on the DSP analysis of the ^{13}C CS of 4-substituted styrenes⁴³, (*E*)-3-(4-X-1-phenyl)-acrylonitriles³, (*E*)-3-(4-X-1-phenyl)-2-cyanoacrylamides⁴⁴, and (*E*)-3-(5-X-2-thienyl)-2-cyanoacrylamides⁴⁴.

DSP analysis of the ^{13}C CS of the C-2 atom (Table VIII) leads to the conclusion that in this position the substituent effect has the "normal" direction ($\varrho_I, \varrho_R > 0$) and an appreciable resonance interaction occurs ($\lambda < 1$). Also, a comparison of the ^{13}C CS for the C-1 through C-3 carbon atoms in amides *I*, *VII*, and *IX* with those in the structurally related amides *XVII*–*XIX* (Table III) gives evidence of the same substituent effect patterns at the side chain atoms of the two systems.

TABLE VI

Computer simulated data^a of 60 MHz $\text{CON}(\text{CH}_3)_2$ signals of compounds *I*, *VII*, and *IX* in deuteriochloroform solutions ($c = 0.25 \text{ mol l}^{-1}$) at 25°C

Compound	$\Delta\nu$ Hz	b_E Hz	k s^{-1}	ΔG_{298}^\ddagger kJ mol^{-1}
<i>I</i>	5.8	0.6	5.4	68.9 ± 0.1
<i>VII</i>	7.5	0.6	1.0	73.2 ± 0.4
<i>IX</i>	5.4	0.9	59.0	62.9 ± 0.2

^a Symbols used as in Table V.

TABLE VII
Relative CNDO/2 electron densities^a δQ at the $\text{---C(3)H=C(2)H-C(1)ON(CH}_3)_2$ atoms in compounds I—XIX^b

Compound	C-3			C-2			C-1			O			N		
	π	σ	tot	π	σ	tot	π	σ	tot	π	σ	tot	π	σ	tot
I ^c	9 340	30 380	39 720	10 477	30 260	40 738	8 189	28 373	36 561	13 657	49 756	63 413	18 039	33 730	51 769
II	-45	15	-30	81	-35	46	-10	7	-3	25	-5	20	5	-1	4
III	-24	12	-12	42	-19	23	-5	5	0	14	-2	12	4	-1	3
IV	68	-57	11	-68	32	-36	13	-12	1	-22	4	-18	-7	1	-6
V	25	-31	-6	-9	6	-3	4	-5	-1	-3	0	-3	-2	0	-2
VII	290	-150	140	-428	192	-236	69	-50	19	-136	31	-105	-28	3	-25
VIII	86	-46	40	-123	54	-69	20	-15	5	-38	7	-31	-9	2	-7
IX	-153	39	-114	309	-136	173	-37	24	-13	93	-20	73	18	-3	15
X	166	-87	79	-226	102	-124	35	-28	7	-68	13	-55	-19	5	-14
XI	55	-31	24	-70	52	-18	-3	5	2	4	10	14	-8	9	1
XII	69	-19	50	-121	48	-73	21	-14	7	-43	6	-37	-6	0	-6
XIII	116	-47	69	-192	85	-107	28	-18	10	-58	12	-46	-11	1	-10
XIV	-22	-1	-23	57	-27	30	-4	1	-3	13	-4	9	3	-1	2
XV	-39	6	-33	92	3	95	0	-4	-4	14	-9	5	-3	4	1
XVI	-50	-12	-62	135	-11	124	-2	-14	-16	24	-9	15	-5	7	2
XVII ^c	9 186	30 326	39 512	10 558	30 309	40 867	8 176	28 373	36 548	13 668	49 751	63 420	18 044	33 732	51 776
XVIII	207	-97	111	-303	125	-178	53	-39	14	-103	15	-88	-20	1	-19
XIX	-144	34	-110	281	-118	163	-36	21	-15	87	-17	70	14	-2	13

^a $\delta Q \cdot 10^4$ (e); positive values denote higher electron densities; ^b iodo derivative VI not included (see text); ^c $Q \cdot 10^4$ (e).

Before starting discussion of the kinetic data in Table V, their reliability, *i.e.*, the assumption of temperature and concentration independence of the Gibbs energies of the rotational barriers at the temperature of coalescence ΔG_c^\ddagger , must be tested. The rotational barriers of amides *I*, *VII*, and *IX* were therefore measured at 25°C by the TLS method; the Gibbs energies ΔG_{298}^\ddagger are given in Table VI. Comparing the ΔG_c^\ddagger and ΔG_{298}^\ddagger values we find that the errors $\Delta\Delta G^\ddagger$ in the rotational barriers obtained by the two methods are at the same level, so that the generally adopted assumption⁴⁵ that for the degenerate rotation of symmetrically N,N-disubstituted amides, $\Delta S^\ddagger \approx 0$, is also satisfied for amides *I–XVI*. The concentration dependence of ΔG_c^\ddagger was studied for amide *I* over the region of 0.1–0.5 mol l⁻¹ and was found virtually constant within the error $\Delta\Delta G_c^\ddagger$. This agrees with the rotational barriers of N,N-dimethyl-4-X-benzamides¹⁴ and amides *XVII–XXV* (refs^{14,16}), which appeared to be insensitive to concentration changes over the region of 0.25–1.0 mol . As it seems, ΔG_c^\ddagger in CDCl₃ solutions is most appreciably affected by traces of hydrogen chloride¹⁴, by the presence of which its magnitude is lowered. This effect can be eliminated by adding pyridine in trace amounts. It can be concluded that the ΔG_c^\ddagger data in Table V are mutually consistent and amenable to DSP analysis.

With regard to the close structural relation of amides *I–XVI* to the corresponding (*E*)-3-(5-X-2-furyl)acrylic acids²¹, the substituent effects on the reactivity of the

TABLE VIII
Correlation parameters in the equation $\delta(y) = \rho_1\sigma_1 + \rho_R\sigma_R + b$ for compounds *I–XVI*^a

<i>y</i>	σ_R	ρ_1	ρ_R	<i>b</i>	r^b	<i>S</i> ^c	λ^d
¹ H-2	<i>R</i> ⁰	0.38 ± 0.10	0.80 ± 0.10	6.84 ± 0.04	0.939	0.08	0.48
¹ H-3	<i>R</i> ⁰	-0.05 ± 0.04	0.23 ± 0.04	7.44 ± 0.02	0.848	0.03	0.22
¹³ C-1	<i>R</i> ⁰	-2.46 ± 0.30	-2.03 ± 0.31	166.83 ± 0.13	0.956	0.23	1.21
	<i>R</i> ⁺	-2.25 ± 0.39	-0.66 ± 0.15	166.80 ± 0.18	0.924	0.30	3.41
¹³ C-2	<i>R</i> ⁰	7.89 ± 1.36	14.82 ± 1.43	116.26 ± 0.61	0.964	1.07	0.53
	<i>R</i> ⁺	5.96 ± 1.37	5.42 ± 0.51	116.86 ± 0.63	0.965	1.05	1.10
¹³ C-3	<i>R</i> ⁰	-3.12 ± 0.38	-1.03 ± 0.40	129.35 ± 0.17	0.934	0.30	3.03
	<i>R</i> ⁺	-3.06 ± 0.44	-0.27 ± 0.16	129.37 ± 0.20	0.915	0.33	11.30
¹³ C-2'	<i>R</i> ⁰	6.39 ± 2.96	16.32 ± 3.12	151.92 ± 1.33	0.864	2.33	0.39
	<i>R</i> ⁺	4.03 ± 2.57	6.32 ± 0.96	152.80 ± 1.18	0.905	1.96	0.64
$\Delta G^{\ddagger e}$	<i>R</i> ⁺	6.07 ± 0.86	3.11 ± 0.32	69.03 ± 0.40	0.967	0.66	1.95
$\Delta G^{\ddagger f}$	<i>R</i> ⁺	3.43 ± 0.59	2.02 ± 0.23	68.62 ± 0.31	0.979	0.41	1.70
$\nu(C-O)^g$	<i>R</i> ⁺	7.69 ± 2.10	5.06 ± 0.79	1 653.34 ± 1.02	0.920	1.61	1.52

^a Iodo derivative *VI* not included, number of points *n* = 15; ^b multiple correlation coefficient; ^c standard deviation; ^d $\lambda = \rho_1/\rho_R$; ^e *n* = 16; ^f compounds *XVII–XXV*, *n* = 9.

C—N bond (ΔG_c^\ddagger) and of the O—H bond (ionization constants pK) can be expected to be roughly the same. By correlating the rotational barriers ΔG_c^\ddagger with the pK values²¹ in 50% ethanol at 25°C, the relation

$$\Delta G_c^\ddagger = -5.4 pK + 100.0 \quad (5)$$

($r = 0.961, n = 10$) was obtained; similarly, for ΔG_c^\ddagger of amides *XVII–XXV* (refs^{14,15}) and pK of (*E*)-3-(4-X-1-phenyl)acrylic acids⁴⁶ (50% ethanol, 25°C),

$$\Delta G_c^\ddagger = -5.2 pK + 99.2 \quad (6)$$

($r = 0.990, n = 6$). In view of the fact that at 25°C, $\Delta G^0 = -5.7 pK$ (in kJ mol^{-1}), Eqs (5) and (6) indicate that the substituent effects on ΔG_c^\ddagger and pK are approximately the same in both series *I–XVI* and *XVII–XXV*. This implies that the substituent effects in amides and in carboxylic acids are apparently of the same nature. The field effect of the dipolar substituent, generally characterized as the polar effect^{12,47}, then is the most appropriate explanation.

The other part of the amide group, the carbonyl group, was characterized by the wavenumbers of the $\nu(\text{C}=\text{O})$ stretching vibration (Table V). The close correlation of $\nu(\text{C}=\text{O})$ with ΔG_c^\ddagger ,

$$\nu(\text{C}=\text{O}) = (1.49 \pm 0.14) \Delta G_c^\ddagger + (1\,549.8 \pm 9.5) \quad (7)$$

($r = 0.946, S = 1.28, n = 16$), is of fundamental importance for estimation of the reactivity of the whole N,N-dimethylcarboxamide group. The fact that the slope of the regression straight line is positive gives evidence that the substituent effects on the C—N and C=O bonds are of the same sense, the bond orders being both either increased or decreased. These effects cannot be explained in terms of the generally adopted mesomeric structure $^-\text{O}-\overset{+}{\text{C}}=\text{NR}_2$, and so it is more appropriate, when studying the substituent effects on the amide group, to regard the group as an $n-\pi$ delocalized system.

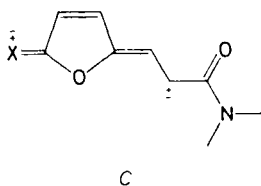
The results of DSP analysis of the N,N-dimethylcarboxamide part of the side chain in amides *I–XVI* and *XVII–XXV* are given in Table VIII. Let us first examine the differences in the reactivity of the furylacrylic derivatives *I–XVI* and their phenylacrylic analogues *XVII–XXV*. A higher effectiveness of the substituent effect transfer by the furan ring as compared with the benzene ring has been observed on the ionization equilibria of 5-X and 5-CH₂X substituted 2-furoic acids⁴⁸; the $\varrho_{\text{furan}}/\varrho_{\text{benzene}}$ ratio was 1.43 and 1.31, respectively. Correlation of the rotational barriers in series *I–XVI* and *XVII–XXV* gives $\Delta G_c^\ddagger(\text{furyl})/\Delta G_c^\ddagger(\text{phenyl}) = 1.60$, in a good agreement with the above relations. The slopes ϱ_1 and ϱ_R (Table VIII)

show that the higher effectiveness of the substituent effect transfer by the furan ring in comparison with the benzene ring is proportional both for polar (1.77) and resonance (1.54) effects. It can be concluded that polar effects are the dominant factor controlling the rotational barriers ΔG_c^\ddagger ($\lambda = 1.95$) as well as the wavenumbers of the $\nu(\text{C}=\text{O})$ vibrations ($\lambda = 1.70$). The simultaneously acting resonance effects attain approximately one-half intensity of the polar effects, and are more effective in the case of the $\nu(\text{C}=\text{O})$ vibrational wavenumbers ($\varrho_R(\nu(\text{C}=\text{O}))/\varrho_R(\Delta G_c^\ddagger) = 1.6$).

That the phenomenon operating in amides *I–XIX* really is the polarization of the π -electron system of the side chain is evidenced by the changes in the CNDO/2 electron densities (Table VII). In accordance with the results of DSP analysis, electron acceptor substituents increase the π -electron density at the C-1 and C-3 atoms, bringing about an upfield shift of the ^{13}C signals; the reverse is true of electron donor substituents. The total electron density Q_{tot} at an atom is the sum of the σ and π contributions, so that Q_σ and Q_π are proportionally interdependent. Comparing the δQ_{tot} values with the corresponding δQ_π and δQ_σ contributions (Table VII) we observe that it is invariably δQ_π that has the dominant effect on δQ_{tot} . This bears out the above conclusions that the substituent effects in amides *I–XVI* (and similarly in *XVII–XIX*) on the reactivity of the entire vinylcarboxamide chain are of π -electron nature.

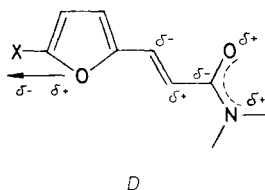
Recently, Fliszár and coworkers⁴⁹ revised the general concept of dependence of ^{13}C CS on the π -electron density for all types of carbon atoms, and set up a new scheme according to which for amides *I–XIX* the ^{13}C CS of the C-2 and C-3 atoms should be controlled by changes in Q_π whereas $\delta(\text{C-1})$ should be determined by changes in Q_σ . It is, however, evident from a comparison of the δQ_π and δQ_σ values in Table VII that it is the change in Q_π that is dominant with respect to the ^{13}C CS of all of the atoms C-1 through C-3. The reverse substituent effect on the carbonyl C-1 atom also disagrees with the scheme⁴⁹ whereas it is consistent with the π -electron polarization concept. A similar trend has been observed³ for a series of many phenyl-carbonyl derivatives of the type $\text{X}-\text{C}_6\text{H}_5-\text{CO}-\text{Z}$, for which the DSP analysis of the ^{13}C CS gave a negative slope ϱ_1 for the carbonyl carbon atoms.

In a similar fashion, the π -electron nature of the substituent effects on the C-2 carbon atom and the nitrogen and oxygen atoms of the carboxamide group is confirmed by the changes in the CNDO/2 π -electron densities Q_π (Table VII): $Q_\pi(Q_{\text{tot}})$ at these atoms is lowered by electron acceptor substituents, this lowering at the C-2 atom being more pronounced than the associated increase in $Q_\pi(Q_{\text{tot}})$ at the adjacent C-3 atom. DSP analysis describes these electronic effects in terms of the $\varrho_1(\text{C-2})/\varrho_1(\text{C-3})$ slope ratio which is greater than unity; for the resonance interaction, $\varrho_R(\text{C-2})/\varrho_R(\text{C-3}) \approx 3.3$. The λ value for the C-2 atom is 0.53, approaching that for the H-2 hydrogen atom ($\lambda = 0.48$). The reverse proportionality of the polar and resonance effects at the C-2 and C-3 atoms, and, at the same time, the higher intensity of the resonance effect at the C-2 atom can be illustrated by the mesomeric structure C,



reflecting the changes in the electron distribution of the furylethylene system induced both by electron acceptor (X^-) and electron donor (X^+) substituents. The preferential localization of the positive (negative) charge at C-2 is responsible for the higher sensitivity of this atom to resonance effects. The electron densities at the C-1 and C-3 atoms, on the other hand, are only partly affected by resonance interactions, the dominant effect in these positions being the π -polarization.

In summary, the polar effect transfer in amides I–XVI by the π -polarization mechanism in the side chain can be represented by structure D which reflects the changes in the electron distribution arising from the effect of the dipole of the electron acceptor substituent X.



The relative π and total electron densities δQ_π and δQ_{tot} at the atoms of the vinyl-carboxamide chain and the corresponding fractional charges in Structure D thus form a theoretical basis for the results of DSP analysis of the furylacrylamides studied.

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REFERENCES

1. Ewing D. F. in the book: *Correlation Analysis in Chemistry. Recent Advances* (N. B. Chapman and J. Shorter, Eds), p. 357. Plenum Press, New York 1978.
2. Ford G. P., Katritzky A. R., Topsom R. D. in the book: *Correlation Analysis in Chemistry. Recent Advances* (N. B. Chapman and J. Shorter, Eds), p. 269. Plenum Press, New York 1978.
3. Craik D. J., Brownlee R. T. C.: *Prog. Phys. Org. Chem.* **14**, 1 (1983).
4. Ehrenson S., Brownlee R. T. C., Taft R. W.: *Prog. Phys. Org. Chem.* **10**, 1 (1973).
5. Wiberg K. B., Pratt W. E., Bailey W. F.: *J. Org. Chem.* **45**, 4936 (1980).
6. Bailey W. F., Cioffi E. A., Wiberg K. B.: *J. Org. Chem.* **46**, 4219 (1981).

7. Reynolds W. F., Gomes A., Maron A., MacIntyre D. W., Maunder R. G., Tanin A., Wong H. E., Hamer G. K., Peat I. R.: *Can. J. Chem.* **61**, 2367 (1983).
8. Bromilow J., Brownlee R. T. C., Craik D. J., Fiske P. R., Rowe J. E., Sadek M.: *J. Chem. Soc., Perkin Trans. 2*, **1981**, 753.
9. Craik D. J., Brownlee R. T. C., Sadek M.: *J. Org. Chem.* **47**, 657 (1982).
10. Hamer G. K., Peat I. R., Reynolds W. F.: *Can. J. Chem.* **51**, 897 (1973).
11. Reynolds W. F.: *Prog. Phys. Org. Chem.* **14**, 165 (1983).
12. Reynolds W. F., Mezey P. G., Hamer G. K.: *Can. J. Chem.* **55**, 522 (1977).
13. Brownlee R. T. C., Craik D. J.: *J. Chem. Soc., Perkin Trans. 2*, **1981**, 760.
14. Spaargaren K., Korver P. K., Van der Haak P. J., De Boer T. J.: *Org. Magn. Reson.* **3**, 615 (1971).
15. Spaargaren K., Korver P. K., Van der Haak P. J., De Boer T. J.: *Org. Magn. Reson.* **3**, 605 (1971).
16. Spassov S. L., Dimitrov V. S., Agova M., Kantschowska I., Todorova R.: *Org. Magn. Reson.* **3**, 551 (1971).
17. Montaudou G., Maravigna P., Caccamese S., Librando V.: *J. Org. Chem.* **39**, 2806 (1974).
18. Davis M., Lakhan R., Ternai B.: *J. Org. Chem.* **41**, 3591 (1976).
19. Bernardi F., Lunazzi L., Zanirato P., Cerioni G.: *Tetrahedron* **33**, 1337 (1977).
20. Alberghina G., Bottino F. A., Fisichella S., Arnone C.: *J. Chem. Res., Synop.* **1985**, 108.
21. Kováč J., Štětinová J., Surá J., Špaček F., Brežný R.: *This Journal* **42**, 1871 (1977).
22. Freytag H., Möller F., Pieper G., Söll H. in the book: *Methoden der Organischen Chemie* (Houben-Weyl), Vol. 11/2, p. 20. Thieme, Stuttgart 1958.
23. Nazarova Z. N., Magakyan N. V.: *Zh. Obshch. Khim.* **34**, 4123 (1964).
24. Kurgan B. V., Giller S. A.: *Khim. Geterotsykl. Soedin.* **1966**, 323.
25. Pretsch E., Clerc T., Seibl J., Simon W.: *Tables of Spectral Data for Structure Determination of Organic Compounds*. Springer, Berlin 1983.
26. Gronowitz S., Johnson I., Hoernfeldt A.-B.: *Chem. Scripta* **7**, 211 (1975).
27. Exner O., Friedl Z.: *This Journal* **42**, 3030 (1977).
28. Van Geet A. L.: *Anal. Chem.* **40**, 2227 (1968); **42**, 679 (1970).
29. Holík M., Mannschreck A.: *Org. Magn. Reson.* **12**, 28 (1979).
30. Holík M., Mannschreck A.: *Org. Magn. Reson.* **12**, 223 (1979).
31. Neuman R. C. jr., Jonas V.: *J. Am. Chem. Soc.* **90**, 1970 (1968).
32. Gutowsky H. S., Holm C. H.: *J. Chem. Phys.* **25**, 1228 (1956).
33. Pople J. A., Beveridge D. L.: *Approximate Molecular Orbital Theory*, p. 163. McGraw-Hill, New York 1970.
34. John I. G., Radom L.: *J. Am. Chem. Soc.* **100**, 3981 (1978).
35. Pople J. A., Gordon M.: *J. Am. Chem. Soc.* **89**, 4253 (1967).
36. Chakrabarti P., Dunitz J. D.: *Helv. Chim. Acta* **65**, 1555 (1982).
37. Huckerby T. N.: *Tetrahedron Lett.* **1971**, 353.
38. Parr W. J. E., Wasylishen R. E., Schaefer T.: *Can. J. Chem.* **54**, 3216 (1976).
39. Dandárová M., Kováč J., Végh D., Žvak V.: *This Journal* **47**, 3412 (1982).
40. Meester M. A. M., Schenk H.: *Rec. Trav. Chim. Pays-Bas* **90**, 508 (1971).
41. Kruk C., Spaargaren K.: *Spectrochim. Acta A* **27**, 77 (1971).
42. Exner O. in the book: *Correlation Analysis in Chemistry. Recent Advances* (N. B. Chapman and J. Shorter, Eds), p. 439. Plenum Press, New York 1978.
43. Reynolds W. F., Dais P., MacIntyre D. W., Hamer G. K., Peat I. R.: *J. Magn. Reson.* **43**, 81 (1981).
44. Bhattacharyya S. P., De A., Chakravarty A. K., Brunskill J. S. A., Ewing D. F.: *J. Chem. Soc., Perkin Trans. 2*, **1985**, 473.

45. Jackman L. M. in the book: *Dynamic Nuclear Magnetic Resonance Spectroscopy* (L. M. Jackman and F. A. Cotton, Eds), p. 203. Academic Press, New York 1975.
46. *Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions* (V. A. Palm, Ed.). VINITI, Moscow 1975.
47. Friedl Z.: *Can J. Chem.* **63**, 1068 (1985).
48. Exner O., Simon W.: *This Journal* **29**, 2016 (1964).
49. Fliszár S., Cardinal G., Béraldin M.-T.: *J. Am. Chem. Soc.* **104**, 5287 (1982).

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