

ELECTROSTATIC EFFECTS ON CONFORMATION EQUILIBRIA. ESTERS OF 2-HALOGENOBENZOIC ACIDS

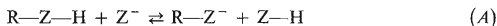
O. EXNER and Z. FRIEDL

*Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague 6 and
Department of Organic Chemistry,
Slovak Institute of Technology, 880 37 Bratislava*

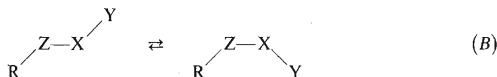
Received April 13th, 1977

The conformation equilibria ($E \rightleftharpoons Z$) of methyl and ethyl esters of 2-halogenobenzoic acids *I–VIII* were estimated in good agreement from dipole moments in benzene solution and from the IR carbonyl bands in decaline solution. At room temperature the *E* conformer slightly prevails but its abundance diminishes with the size of the halogen, reaching approximately 50% for iodine. The calculations of the electrostatic energy based on the point charges approximation predict well the population of conformers of fluorine derivatives, the deviations for heavier halogens being attributable to their steric effects. It is believed that conformation equilibria can be reasonably estimated on the basis of the electrostatic energy alone, provided that the non-bonded and torsional strains are absent.

The electrostatic theory of substituent effects has been devised for dissociation equilibria and tested on relative pK values, mostly of carboxylic acids^{1,2}. The reaction involved may be generally written:



Another application, much less used^{3–6}, is to conformation equilibria, *e.g.*:



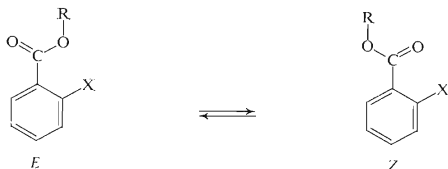
In any case there is a common presumption that the remaining substituent effects have been eliminated by the proper choice of the model. This concerns particularly non-bonded interactions (van der Waals strain) and mesomeric effects; in addition in (A) the bond energy of the $Z-H$ bond must be equal in either molecule and in (B) the torsional energy (Pitzer strain) equal in either conformation. Under these condi-

tions the electrostatic energy may be calculated from all charges (q) in the molecule and their distances (r), and equated to the reaction free enthalpy (ΔG°):

$$\Delta G^\circ = -RT \ln K = N \sum_{ijk} q_{ik} q_{jk} / \epsilon_{ef} r_{ijk} \quad (1)$$

The summation extends over all charges (i, j) in each molecule and over all molecules involved (k), the reactant being taken with the negative sign. Most frequently the charges are localized in the centres of atom nuclei. The effective dielectric constant ϵ_{ef} acquires a value between the macroscopic dielectric constant of the solvent and the assumed value for the reacting molecule⁷ (*i.e.* ~ 2 , although even the value $\epsilon = 1$ has been suggested⁸). The difficulties of the electrostatic theory are thus evident. In particular, if the above mentioned substituent effects are not eliminated rigorously, they may easily predominate the electrostatic energy (*e.g.*⁹). In the conformation analysis the electrostatic term is generally considered as one of the less important¹⁰.

The aim of this and of the forthcoming papers is to test the electrostatic theory on selected model compounds and to compare the two principal applications, which have been hitherto discussed in the literature separately and in different terms. In this paper we are concerned with the conformation equilibria of alkyl 2-halogenobenzoates I–VIII (Table I). In general, the conformation equilibria have the advantage against the ionization equilibria that no bond energies are involved; in addition the measurement in nonpolar solvents minimizes the problems with calculating ϵ_{ef} . Benzene bis-derivatives are then a suitable model system^{3,4} since the torsional energy may be assumed equal in different planar conformations. In *meta* derivatives (*e.g.* 3-chlorobenzaldehyde^{3,4}, 3-chloroacetophenone³, 1,3-diformylbenzene⁴) even the non-bond-



ing interactions are completely negligible but the electrostatic energy is also low, so that experimental as well as calculated equilibrium constants differ only slightly from unity; in the intention to achieve distinct results the experimental accuracy was sometimes overestimated³. For this reason we proceeded to *ortho* derivatives and chose a functional group with similar steric demands from other side. It was argued¹¹ that even the pure steric interactions of the two oxygen atoms of the ester group are not exactly equal, the effective size of the ether oxygen in the *E* form (CO-*trans*)

being greater than of the carbonyl oxygen in the *Z* form (CO-*cis*). We believed, however, that this difference is not important on the one hand, and that it can be revealed by comparing quantitatively derivatives with different halogens on the other hand.

The conformation of methyl 2-halogenobenzoates has been studied¹¹⁻¹⁴ by the ¹³C-NMR and IR spectroscopies. All the methods agree that two conformers are present at room temperature. The results obtained from the ¹³C-NMR spectra¹⁴ or from the doubled carbonyl band^{11,12} were only qualitative in character, but even

TABLE I

Dipole Moment and Spectral Data of Alkyl 2-Halogenobenzoates 2-XC₆H₄COOR

Compound	X R	n_D^{20}	$\nu(\text{C=O})^a$ <i>E</i> <i>Z</i> cm ⁻¹	α^b β^b	P_2^0 R_D^c	$\mu(5\%)^d$ $\mu(15\%)^d$	μ_{calc} <i>E</i> <i>Z</i>
<i>I</i>	F	1.5032	1 727	3.77	148.0	2.30	1.62
	CH ₃		1 745	-0.300	37.7	2.26	3.18
<i>II</i>	F	1.4910	1 722	3.27	146.7	2.24	1.62
	C ₂ H ₅		1 741	-0.278	42.4	2.19	3.18
<i>III</i>	Cl	1.5359	1 729	4.22	176.1	2.53	1.67
	CH ₃		1 747	-0.357	42.8	2.49	3.31
<i>IV</i>	Cl	1.5228	1 722	3.65	170.8	2.43	1.67
	C ₂ H ₅		1 741	-0.342	47.5	2.38	3.31
<i>V</i>	Br	1.5598	1 731	3.25	173.0	2.47	1.66
	CH ₃		1 747	-0.503	45.7	2.42	3.28
<i>VI</i>	Br	1.5438	1 724	3.02	176.7	2.46	1.66
	C ₂ H ₅		1 742	-0.460	50.4	2.41	3.28
<i>VII</i>	I	1.6042	1 731	2.67	172.9	2.41	1.56
	CH ₃		1 743	-0.613	51.1	2.36	3.01
<i>VIII</i>	I	1.5848	1 724	2.34	170.0	2.31	1.56
	C ₂ H ₅		1 739	-0.554	55.7	2.26	3.01

2-Chlorobenzaldehyde

1.5661	—	—	214.8	2.93 ^e	2.61 ^f
—	—	—	37.3	2.90 ^e	4.51 ^f

^a In decahydronaphthalene solution; ^b slopes of the Halverstedt-Kumler²⁵ plots of ϵ_{12} vs w_2 and d_{12}^{-1} vs w_2 , respectively; benzene solution 25°C; ^c calculated from increments as given in Experimental; ^d correction for the atomic polarization 5% or 15% of the R_D value, respectively; ^e literature^{4,19,21,27} gives 3.00, 2.92 (in CCl₄), 3.00, and 2.80 D, respectively; ^f the values of 3.21 and 4.50 D, respectively, were calculated²⁰, using a slightly different system of bond moments.

so they are at variance with the populations of conformers calculated from the ν_{16} ring stretching mode¹³. As to the exact geometry of the two conformers, they were mostly considered planar¹²⁻¹⁴, or alternatively some deviations were admitted¹¹ with respect to the crystal structure of 2-halogenobenzoic acids. In this study we measured dipole moments of compounds *I-VIII* in benzene solution and the integrated absorption intensities of the resolved carbonyl band in decahydronaphthalene solution. The experimental populations of the conformers *E* and *Z* were then compared with those calculated using Eq. (1). The comparison of corresponding methyl (*I, III, V, VII*) and ethyl (*II, IV, VI, VIII*) esters should serve merely to test the reliability and accuracy of the approach. For the same reason we investigated also 2-chlorobenzaldehyde whose conformation equilibrium had been established by the electron diffraction¹⁵ and by the IR spectroscopy in the gas phase¹⁶. In addition 2-halogenobenzaldehydes have been studied by a variety of methods¹⁷⁻²⁴. They were, however, not suitable to our purpose since the electrostatic effect is combined with the steric effect of carbonyl oxygen; the equilibrium is shifted to one side and sometimes the other conformer has even escaped detection^{4, 17, 19, 21, 23, 24}.

EXPERIMENTAL AND RESULTS

Materials: Alkyl 2-halogenobenzoates *I-VIII* were prepared from commercially available acids by extractive esterification in tetrachloromethane. Their purity was checked by vapour phase chromatography and measurement of refractive indices (Table I).

Measurements of dipole moments: Dielectric constants and densities of benzene solutions were measured at 25°C, the former on a heterodyne apparatus at a frequency of 1.2 MHz. Usually five solutions were prepared in the concentration range $5 \cdot 10^{-3}$ – $5 \cdot 10^{-2}$ M. The dipole moments were calculated according to Halverstadt and Kumler²⁵, the molar refractions R_D were calculated from increments²⁶ (valid at 20°C) using additional increments (exaltations) of 0.7 cm^3 for the conjugation $\text{C}_6\text{H}_5\text{—COOR}$, 1.2 cm^3 for $\text{C}_6\text{H}_5\text{—CHO}$, 0.1 cm^3 for $\text{C}_6\text{H}_5\text{—Cl}$ or $\text{C}_6\text{H}_5\text{—Br}$, and 0.2 cm^3 for $\text{C}_6\text{H}_5\text{—I}$. The atomic polarization was accounted for by a correction of 5% or 15%, respectively, of the R_D value. The experimental results are listed in Table I.

Theoretical dipole moments, expected for the planar conformations *E* and *Z* of compounds *I-VIII*, were calculated using the simple bond moment scheme with the standard values²⁸ (in D units): H—C_{al} 0.3, H—C_{ar} 0, C=O 2.5, C—O 0.74, $\text{C}_{\text{ar}}\text{—F}$ 1.47, $\text{C}_{\text{ar}}\text{—Cl}$ 1.60, $\text{C}_{\text{ar}}\text{—Br}$ 1.57, $\text{C}_{\text{ar}}\text{—I}$ 1.30. The conjugation of the alkoxycarbonyl or formyl group with the benzene nucleus was accounted for by mesomeric moments of 0.25 and 0.5 D, respectively. The bond angles within the alkoxycarbonyl group ($\text{C}_{\text{ar}}\text{—C=O}$ 123°, O—C=O 124°, C—O—C 116°) were in agreement with the averaged X-ray data for 2-halogenobenzoic acids²⁹⁻³¹, while in the case of 2-chlorobenzaldehyde the angles on C were 120° according to the ED data¹⁵. The benzene nucleus was assumed hexagonal. The calculated dipole moments are listed in Table I, last column. The population of conformers was calculated according to the equation

$$N_E = (\mu_Z^2 - \mu_{\text{exp}}^2) / (\mu_Z^2 - \mu_E^2) \quad (2)$$

The results are given in Table II. Their accuracy may be estimated from the statement that standard deviations of 0.05 D in the experimental and of 0.1 D in the calculated dipole moments would in

combination produce a standard deviation of 5% (absolutely) in N_E . Hence the values found were rounded off to 1%. The populations given in the literature³ to 0.1% would require a quite unrealistic accuracy of measured as well as of calculated dipole moments.

Spectral measurements: The IR spectra of compounds *I*–*VIII* in the region 1550–1800 cm^{-1} were recorded in 0.015M decahydronaphthalene solution at the temperatures 40 and 110°C ($\pm 0.3^\circ$). A Perkin-Elmer 621 instrument and NaCl cells 1.0 mm were used. The solvent was purified by boiling with sodium and vacuum rectification under nitrogen; it contained 53% of *trans*-decahydronaphthalene. The band separation and calculation of integral absorption intensities was accomplished by means of a program for the HP 9830 A calculator, based upon the Lorentz-type band shape. Assuming equal molar absorptivities the population of conformers was obtained with an average standard deviation of 0.6%. Finally it was extrapolated to the temperatures 25 and 110°C using the linear dependence of $\log K$ on T^{-1} . The results are listed in Table II.

The ^{19}F -NMR spectra of *I* and *II* were recorded at 94.1 MHz on a Varian XL-100-15 spectrometer with heteronuclear decoupling and with fluorobenzene as internal reference. The temperature dependence was followed between 37 and 120°C in hexachlorobutadiene (chemical shifts $\delta = 4.38$ and 4.19 for *I* and *II*, respectively) and between 0 and -80°C in [1,1,1,3,3,3- ^2H]acetone. The observed changes with temperature were not significant.

Electrostatic calculations: The relative electrostatic energy of the *E* and *Z* conformers was calculated according to Eq. (1) which for the equilibrium $E \rightleftharpoons Z$ takes the form:

$$\Delta E_{\text{elst}} = E_Z - E_E = \frac{N}{\epsilon_{\text{ef}}} \left(\sum_Z \frac{q_i q_j}{r_{ij}} - \sum_E \frac{q_i q_j}{r_{ij}} \right) \quad (3)$$

The dielectric constant ϵ_{ef} was that of benzene (2.274). The summations extend over the whole molecule but many terms cancel. The charges q on individual atoms were obtained by dividing the bond moments by the bond length and summing up at each atom. The alkyl groups were represented by a negative charge on C and a positive one in the middle between the three H atoms; hence the results for corresponding methyl and ethyl derivatives are identical. The mesomeric moments and the mesomeric components of the $\text{C}_{\text{ar}}-\text{X}$ bonds were represented — somewhat arbitrarily — by charges on the carbonyl carbon or halogen atom, respectively, and in the middle of the benzene ring. Most of these fractional charges are the same for either conformer and cancel when calculating ΔE_{elst} . The remaining mesomeric corrections are small, so that this arbitrariness does not affect the results significantly. The bond lengths in compounds *I*–*VIII* were^{29–31} (in Å): C–C (ring) 1.39, $\text{C}_{\text{ar}}-\text{C}$ 1.50, C=O 1.20, (O)C–O 1.32, C–O 1.47, $\text{C}_{\text{al}}-\text{H}$ 1.09, C–F 1.33, C–Cl 1.70, C–Br 1.85, C–I 2.05. For 2-chlorobenzaldehyde the bond lengths¹⁵ from ED were adopted: $\text{C}_{\text{ar}}-\text{C}$ 1.47, (O)C–H 1.06, C–Cl 1.73. The bond angles were the same as in the preceding paragraph. The uncertainty in the geometrical parameters is generally not critical for the final values.

The population of conformers at 298 K was calculated from Boltzmann law with ΔE_{elst} equal to ΔG° . The calculations were carried out for planar *E* and *Z* forms, as well as for slightly distorted forms with dihedral angles $\tau = 7$ – 22° ; the results are listed in Table II. In addition, another modification of calculations was examined in which either the C–X dipole or the COOR group dipole moment³ was represented by the point dipole approximation. The results differed no more than by 6% (absolutely) in N , in average by 3%, and are not tabulated.

DISCUSSION

The experimental evidence obtainable from the two applied methods is different in character. The effective dipole moments cannot be interpreted unambiguously: either one nonplanar conformation is possible, or the equilibrium of two forms, planar or nonplanar. In the case of two forms their abundance may be determined only roughly but there are as a rule no doubts about the assignment, *i.e.* which is the prevailing conformer. From the doubled carbonyl band in the IR spectra, from the changes of relative intensities with temperature, and from other spectroscopic arguments, one can conclude that two conformers are present. Their ratio is obtained relatively accurately — provided the molar absorptivities are actually equal — but their geometry is more or less hypothetical; even wrong assignments have not been rare. In previous qualitative studies^{11,12} of 2-halogenobenzoates the assignment was based on the general experience that the alignment of C=O and C—X dipoles results in higher frequency; it was corroborated by the observed solvent shifts and by changes in the series F—Cl—Br—I. If we adopt these arguments, we can combine the evidence from dipole moments and from the IR spectroscopy to get completely consistent results for compounds *I–VIII* (Table II). The only uncertainty concerns the exact planarity of the two conformers. Although the planar forms were preferred several times^{13,14}, twisted conformations were also advocated¹¹ with reference to the X-ray analysis^{29–31} of 2-halogenobenzoic acids, which reports dihedral angles $\tau = 7, 14, 18,$ and 22° (the last value extrapolated), respectively, according to the halogen present. Distortions of this order would not affect the results from dipole moments at all and the electrostatic calculations but slightly (Table II). Therefore, we shall consider the two conformers as planar or nearly planar in further discussion.

The consistency of experimental data of Table II is actually as good as could be anticipated considering their relatively large errors. This concerns not only the agreement of the two methods, but also of the two limiting values from the dipole moment approach (5% or 15% correction, respectively, for the atomic polarization), and of the corresponding methyl and ethyl esters. Even this discrepancy represents in our opinion merely the experimental error than a real difference between the two compounds. Also, the temperature dependence of the data from IR spectroscopy is as expected since the equilibrium constant is shifted with increasing temperature towards unity. Further confirmation of our approach was obtained from the conformer population of 2-chlorobenzaldehyde which accords satisfactorily with the approximate but principally dependable data from electron diffraction¹⁵ (at 70°) and from the torsional frequency in the far infrared¹⁶ (at 95°C). In such a position even the failure of the ^{19}F -NMR spectroscopy, which did not reveal any difference between chemical shifts of the *E* and *Z* forms of *I* or *II*, is not decisive. Note that even the ^1H - and ^{13}C -NMR spectroscopies^{17,23,24} failed to detect the *Z* conformer of 2-chlorobenzaldehyde. The data of Table II express also with more precision previous quali-

tative findings^{11,12,14}. The only contradictory estimates obtained from the integrated intensities of the unresolved band of the ν_{16} ring stretching mode¹³ in IR spectra are to be ascribed to the applied approximate method which in some cases was disproved by later experiments^{15,16}, even of the same research group³.

TABLE II

Conformer Population, Calculated and Experimental, of Alkyl 2-Halobenzoates 2-XC₆H₄.COOR (298 K)

Compound	X R	Electrostatic calculations			Dipole moments	$\nu(\text{C}=\text{O})$ Intensities	
		τ	ΔE cal mol ⁻¹	N_E %	N_E^a %	N_E^b %	ΔH cal mol ⁻¹
I	F	0	439	68	64	63	290
	CH ₃	7	447	68	66	(60) ^b	
II	F	0	439	68	68	62	220
	C ₂ H ₅	7	447	68	70	(60) ^b	
III	Cl	0	404	66	54	56	350
	CH ₃	14	398	66	58	(53) ^b	
IV	Cl	0	404	66	61	54	200
	C ₂ H ₅	14	398	66	64	(52) ^b	
V	Br	0	376	65	58	54	150
	CH ₃	18	345	64	61	(53) ^b	
VI	Br	0	376	65	58	54	-50
	C ₂ H ₅	18	345	64	61	(55) ^b	
VII	I	0	288	62	48	43	-540
	CH ₃	22	259	61	51	(48) ^b	
VIII	I	0	288	62	54	40	-390
	C ₂ H ₅	22	259	61	58	(44) ^b	
2-Chlorobenzaldehyde		0	1026	85	86	^c	—
					88		
3-Chlorobenzaldehyde		0	-14	50 ^d	57.2 ^e	—	—
					56 ^e		

^a The two values were obtained from dipole moments μ (5%) and μ (15%), respectively, with different corrections for the atomic polarization; ^b the values in parentheses refer to 383 K; ^c we were not able to obtain reliable figures from the carbonyl frequency, ref.^{15,16} give c. 80% or 72% at 70 or 95°C, respectively, using other methods; ^d ref.³ gives 56% calculated by a different approximation, see Experimental; ^e ref.^{3,4}, respectively.

The electrostatic calculations have usually been performed with one of the two opposite approximations: either placing point charges at the centres of atom nuclei, or representing them by point dipoles in the middle of each bond. We preferred the former procedure which is in our opinion more versatile for complex molecules and in addition the better approximation³² as the point dipole concept presumes that the dipole lengths are negligible compared to the distance between them. Sometimes the two concepts were even mixed: in the case of 3-chlorobenzaldehyde, methyl 3-chlorobenzoate and of similar compounds the carbonyl was represented by a point dipole but the C—Cl dipole by point charges³ without any evident reason. With respect to the similarity to our problem we carried out some calculations of this type, too, and in addition the just reversed ones. These modifications had not very significant effect in the case of our compounds, hence we abode by the point charges approximation. On the other hand, this kind of calculation would influence the less clean-cut results on 3-chloro derivatives³, predicting *e.g.* for 3-chlorobenzaldehyde the population almost exactly 50 : 50 (Table II). We conclude that these *meta* derivatives are less suitable model for testing the electrostatic effects because these effects are small and the results are too sensitive both to the experimental accuracy and to the modifications of the theoretical approach.*

Another point of issue is the microscopic dielectric constant which must be assigned an effective value in Eqs (1) and (3). In benzene or decaline solutions the dielectric properties of the solvent and of the solute molecule are similar, hence we used the macroscopic dielectric constant of benzene. The recommended value⁸ $\epsilon_{\text{ef}} = 1$ is in our opinion unsound: even if no solvent molecule can get between the interacting dipoles, a great many lines of force do not go this shortest way but through the solute molecule and adjoining solvent molecules⁷.

The conformer population predicted from the point charges calculations agrees quite well with the experimental values. At a glance the theoretical approach seems justified. A more detailed examination must, however, consider also the effects of the halogen substituent and of temperature. Substituting ΔE_{c1st} for ΔG° into the Boltzmann equation we assume $\Delta S^\circ = 0$. The predicted dependence of $\log K$ on $1/T$ is thus represented by a line going through the origin (Fig. 1). For the comparison with experiment the fluoro derivatives *I*, *II* are decisive since no perceptible steric effects are involved. Fig. 1 shows also a satisfactory accord as far as the abundances *N* are concerned, which is certainly sufficient for the purpose of conformation analysis and is even not worse than the accord of the two experimental methods themselves. However, if the calculated (ΔE_{c1st}) and experimental (ΔG° in the respective solvent)

* In the paper quoted³ there is in addition a misprint²⁰ in the fundamental equation (6) on p. 1798. However, the calculations had been carried out according to the correct equation as we have now checked by repeating some of them. We thank Professor A. R. Katritzky for the correspondence to this point.

energies are compared, the relative error may attain to 30%. The assumption $\Delta S^\circ = 0$ is critical, even the minute value of $\Delta S^\circ = 0.2$ e.u. would manifest itself clearly (Fig. 1). In the case of chloro and bromo derivatives the deviations are more expressed and for iodo derivatives *VII* and *VIII* even the sign of the dependence on T^{-1} is doubtful; note that the agreement between the two methods and between the methyl and ethyl esters is also worse. Although some experimental factors may lower the accuracy in the case of the iodo derivatives, the results seem to corroborate the view¹¹ that the ether oxygen is bulkier than the carbonyl oxygen. Pure steric effects thus shift the equilibrium in favour of the *Z* conformer and testing of the electrostatic effects relies in fact upon the fluoro derivatives *I* and *II*.

Summarizing we can state that simple electrostatic formulae with the point charges approximation and with an effective dielectric constant may be applied reasonably to conformation equilibria of special model systems where non-bonded interactions and torsional strain are eliminated. In general, the attained accuracy seems better than in the classical application to dissociation equilibria¹ (except, say, some new improved calculations³³) but this apparent agreement is partly due to the position of equilibrium near to unity. Another reason may be the nonpolar solvent, greatly reducing the problems with the effective dielectric constant^{7,33}. We believe, however, that the critical point of the electrostatic theory, which has not yet received attention, may be the assumption of equal bond energies of the X—H bonds in the substituted and unsubstituted molecule, see Eq. (A). The decision between these possibilities can be obtained only by changing systematically the individual factors. Since it is difficult to study conformation equilibria in polar solvents as well as ionization equilibria in nonpolar solvents, new models are to be devised.

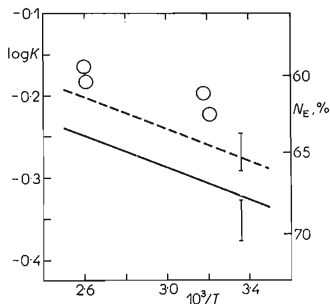


FIG. 1

Dependence of the Conformation Equilibrium $E \rightleftharpoons Z$ of Compounds *I* or *II* on the Reciprocal Temperature

Open points — IR experiments, abscissae — dipole moment experiments; full line — calculated from the electrostatic energy assuming $\Delta S^\circ = 0$, broken line — $\Delta S^\circ = 0.2$ e.u.

Thanks are due to Dr P. Fiedler from this Institute for measuring the IR spectra and calculating the integrated intensities according to a program written by Dr A. Vitek. We thank also Mrs M. Kuthanová and Dr P. Trška, Prague Institute of Chemical Technology, Prague, for measuring the dielectric constant and densities and for recording the ^{19}F -NMR spectra, respectively.

REFERENCES

1. Ehrenson S.: *Progr. Phys. Org. Chem.* **2**, 195 (1964).
2. Stock L. M.: *J. Chem. Educ.* **49**, 400 (1972).
3. Jones R. A. Y., Katritzky A. R., Ochkin A. V.: *J. Chem. Soc. B* **1971**, 1795.
4. Lumbroso H., Andrieu C. G.: *Bull. Soc. Chim. Fr.* **1973**, 1575.
5. Wennerström H., Forsén S., Ross B.: *J. Phys. Chem.* **76**, 2430 (1972).
6. Jehlička V., Floch L., Exner O.: *This Journal* **42**, 464 (1977).
7. Kirkwood J. G., Westheimer F. H.: *J. Chem. Phys.* **6**, 506 (1938).
8. Buckingham A. D.: Quoted according to³.
9. Janák P., Exner O.: *This Journal* **40**, 2502 (1975).
10. Altona C., Faber D. H.: *Topics Curr. Chem.* **45**, 1 (1974).
11. Eglinton G., Ferguson G., Islam K. M. S., Glasby J. S.: *J. Chem. Soc. B* **1967**, 1141.
12. Brooks C. J. W., Eglinton G., Morman J. F.: *J. Chem. Soc.* **1961**, 106.
13. Katritzky A. R., Sinnott M. V., Tidwell T. T., Topsom R. D.: *J. Amer. Chem. Soc.* **91**, 628 (1969).
14. Dhami K. S., Stothers J. B.: *Can. J. Chem.* **45**, 233 (1967).
15. Schaefer L., Samdal S., Hedberg K.: *J. Mol. Struct.* **31**, 29 (1976).
16. Miller F. A., Fateley W. G., Witkowski R. E.: *Spectrochim. Acta, Part A* **23**, 891 (1967).
17. Drakenberg T., Jost R., Sommer J. M.: *J. Chem. Soc., Perkin Trans. 2*, **1975**, 1682.
18. Wasylshen R., Schaefer T.: *Can. J. Chem.* **49**, 3216 (1971).
19. Aw C. T., Huang H. H., Tan E. L. K.: *J. Chem. Soc., Perkin Trans. 2*, **1972**, 1638.
20. Bruce E. A. W., Ritchie G. L. D., Williams A. J.: *Aust. J. Chem.* **27**, 1809 (1974).
21. Cheng C. L., Le Fèvre R. J. W., Ritchie G. L. D., Goodman P. A., Gore P. H.: *J. Chem. Soc. B* **1971**, 1198.
22. Bock E., Tomchuk E.: *Can. J. Chem.* **50**, 2890 (1972).
23. Karabatsos G. J., Vane F. M.: *J. Amer. Chem. Soc.* **85**, 3886 (1963).
24. Smith W. B., Deavenport D. L., Ihring A. M.: *J. Amer. Chem. Soc.* **94**, 1959 (1972).
25. Halverstadt I. F., Kumler W. D.: *J. Amer. Chem. Soc.* **64**, 2988 (1942).
26. Vogel A. I.: *J. Chem. Soc.* **1948**, 1842.
27. Ahmad S. I.: *Indian J. Pure Appl. Phys.* **1**, 434 (1963).
28. Exner O.: *Dipole Moments in Organic Chemistry*, p. 33. Thieme, Stuttgart 1975.
29. Krause J., Dunken H.: *Acta Crystallogr.* **20**, 67 (1966).
30. Ferguson G., Islam K. M. S.: *Acta Crystallogr.* **21**, 1000 (1966).
31. Ferguson G., Sim G. A.: *Acta Crystallogr.* **14**, 1262 (1961); **15**, 346 (1962).
32. Všetěčka V., Exner O.: *This Journal* **39**, 1140 (1974).
33. Ehrenson S.: *J. Amer. Chem. Soc.* **98**, 7510 (1976).

Translated by the author (O. E.).