ELECTROSTATIC EFFECTS ON CONFORMATIONAL EQUILIBRIA: ALKYL 2-CYANOBENZOATES AND 3-CYANOPROPENOATES

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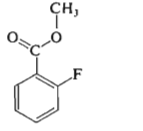
The conformational equilibrium *ap* ⇌ *sp* of the title compounds was investigated by two methods: dipole moment measurement in benzene solution and IR spectroscopy of the carbonyl band in decahydronaphthalene solution. Approximately 71% of the *ap* rotamers were found for 2-cyanobenzoates (*II*, *III*), and between 60 to 80% for (*Z*)-3-cyanopropenoates (*V*, *VI*). This result does not reveal any special attractive interaction between the carbonyl oxygen and cyano carbon atoms; on the other hand, it is in fair agreement with electrostatic calculations based on point charges calculated from bond moments. Any attractive interaction was not detected even on aliphatic cyano esters *VII*–*IX*. Comparison of several model compounds and several kinds of approximative calculations leads us to conclude that the electrostatic model works generally better for conformational equilibria than for ionization equilibria.

In several papers[1–3] we investigated the effect of electrostatic forces on conformational equilibria. The question was, inasmuch this effect can be approximated by a simple model, representing the solute molecule together with the surrounding solvent as a homogeneous continuum with a given effective permittivity ε_{ef}. The results had to be compared with the similar approach applied to ionization equilibria[4–7], usually referred to as the Kirkwood–Westheimer theory[8]. In terms of this theory the molecule is represented as a system of point charges z and/or point dipoles μ; the Gibbs energy is then equated to the electrostatic energy which is a function of z's, μ's, ε_{ef}, and of geometrical parameters (r and Θ):

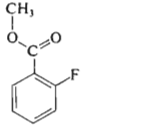
$$2{\cdot}303RT\log K = N_A f(z_i, \mu_i, r_i, \Theta_i, \varepsilon_{ef}) . \qquad (1)$$

The results obtained with the conformational equilibria[1–3,9–13] may be summarized as follows. The calculation reproduces the equilibrium constants reasonably well but non-bonded interaction (direct steric effect) and torsional strain must be eliminated by proper choice of model compounds. In general the theory has been relatively more successful than in the case of ionization equilibria. In our opinion this might be due particularly to two reasons: *a*) Conformational equilibria can be investigated

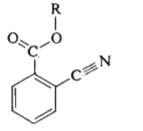
in non-polar solvents. This obviates problems with determining the effective permittivity ε_{ef} on the basis of sophisticated models[8,14] which represent the solute molecule as a regular-shaped cavity within the solvent. *b*) No bond is broken in the process of conformational change, so that cancellation of bond energies[5,6] need not be assumed.



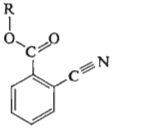
Iap



Isp



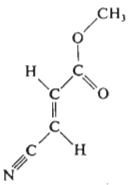
ap



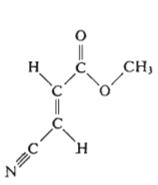
sp

II, R = CH_3
III, R = C_2H_5

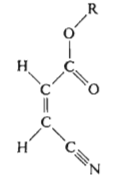
On the other hand, the applicability of the approach is strongly restricted to special model compounds by the required absence of non-bonded interactions and torsional strain. Most of the results[1-3,9,10] were obtained on aromatic derivatives with a substituent which can take one of two coplanar conformations. Choice of this substituent is, however, dificult since the requirements of a strong electrostatic effect and absence of direct steric effect are in some degree contradictory. A particularly suitable model was methyl 2-fluorobenzoate (*I*) since the non-bonded interactions in the conformations *ap* and *sp* may be considered equal[1,3,15]. In methyl 3-chlorobenzoate or 3-chloroacetophenone[9] the coulombic energy is already too small with respect to the experimental uncertainty (see the criticism[1]). In methyl 3-cyanobenzoate or 3-cyanoacetophenone the effect was better observable[2] but the calculations were very sensitive



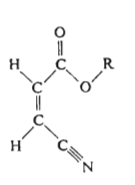
E sp



E ap



Z sp



Z ap

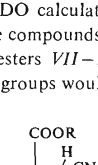
IV

V, R = CH_3
VI, R = C_2H_5

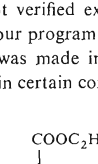
to the approximation used (point charges or point dipoles) and to the assumed charge distribution on the CN group. In this communication we have proceeded to 2-cyano-

benzoates *II* and *III*, in spite of the mentioned difficulties, since these compounds represent a logical completion of the experimental material and will enable us to compare the effect of substituents F and CN in the positions *ortho* and *meta*.

We used the same experimental approach as previously[1-3]: Dipole moments were measured in benzene solution, the integrated intensities of the carbonyl band were registered at variable temperature in decalin. The experimental populations are compared to electrostatic calculations either with the point-charges or point-dipoles approximation, further also to simple quantum chemical calculations. In the course of our investigation a closely related problem was encountered by Procházka and coworkers[16,17]: The equilibrium between stereoisomers of methyl 3-cyanopropenoate is shifted in favour of the (*Z*)-isomer *V* ($\Delta H^0 = 4$ kJ mol^{-1}), in contrast to other unsaturated esters. The advanced explanation assumed stabilizing interactions between the adjacent CO and CN groups, whether overlap or electrostatic in character[16]. If this is true, the *sp*-conformer of *V* must be also favoured against *ap*. This view was supported by CNDO calculations[17] but not verified experimentally. For this reason, we included the compounds *IV*–*VI* into our program. Finally, a comparison with saturated cyano esters *VII*–*IX* (Table I) was made in which an interaction between the functional groups would be possible in certain conformations.



VIII, R = CH_3
IX, R = C_2H_5



X

EXPERIMENTAL

Materials: Methyl 2-cyanobenzoate (*II*) m.p. 51°C; ethyl 2-cyanobenzoate (*III*) m.p. 67°C; methyl 3-cyanopropanoate (*VII*) b.p. 99–100°C at 1·0 kPa, n_{20}^{D} 1·4245; ethyl 2-cyanobicyclo-[2,2,2]octane-1-carboxylate[6] (*IX*) m.p. 51°C; ethyl 3-cyanobicyclo[2,2,2]octane-1-carboxylate[6] (*X*), b.p. 100–102°C/6 Pa. Stereoisomeric (*E*) and (*Z*)-3-methyl 3-cyanopropenoates were prepared by independent synthetic routes in order to avoid their separation[16] by preparative gas chromatography. Their configuration was checked by the values of ^3J coupling constant in ^{1}H NMR spectra which were in accord with ref.[16]. (*E*)-Methyl 3-cyanopropenoate (*IV*) was prepared from fumaric acid monomethyl ester[18], which was converted to the corresponding amide and dehydrated with phosphorus pentoxide[19], m.p. 33–34°C (ref.[16] 34°C). (*Z*)-Methyl 3-cyanopropenoate (*V*) was prepared from maleic acid monoamide in a one-pot synthesis[20] by means of methyl chloroformate, m.p. 31–32°C (ref.[16] 31°C). (*Z*)-Ethyl 3-cyanopropenoate (*VI*) was prepared in the same way as *V* by means of ethyl chloroformate[20], b.p. 39–40°C at 20 Pa, n_D^{20} 1·4512. Methyl 2-cyanobicyclo[2,2,2]octane-1-carboxylate (*VIII*) was obtained from the corresponding acid[6] with diazomethane, m.p. 34–35°C (pentane–ether); for $C_{11}H_{15}NO_2$ (193·2) calculated: 68·37% C, 7·82% H, 7·25% N; found: 68·47% C, 7·72% H, 7·09% N. The purity of all liquid products was checked by GLC.

Physical measurements: Dipole moments in benzene were measured at 25°C by the same method as in the previous communication[1]. The molar refraction was calculated from increments as previously[1,2], using appropriate exaltations for the conjugation of functional groups with the benzene nucleus or with the double bond. The experimental results are listed in Table I. Theoretical dipole moments, expected for individual conformations, were calculated on the basis of the standard bond moment scheme[21] with the following values of group moments (in 10^{-30} C m): CN (on an aromatic carbon atom) 13·34, CN (on an sp^3 carbon atom) 12·01, COOR (on an aromatic carbon atom) 5·70 at an angle of 59·5° to the C—CO bond[1,3], COOR (on an sp^3 carbon atom) 5·34 at an angle of 66° to the C—CO bond (with respect to geometrical parameters given in[22]). In the case of olefinic derivatives *IV*–*VI* both sets of groups moments were tried, corresponding to aromatic and alifatic compounds, respectively. The benzene nucleus in compounds *II* and *III* was assumed hexagonal. An alternative geometry, with angles according to the additive scheme of Domenicano[23], implies an angle of 60·05° between the bonds C—CN and C—CO, so that there is no change in the dipole moment values. The angles in the olefinic derivatives *IV*–*VI* were taken as 120°, too. In the compound *VII* the angles C—C—C of 109·5° were assumed. The geometry of bicyclo[2,2,2]octane derivatives *VIII* and *IX* was estimated assuming the D_{3h} symmetry[24]; the angles C—C—C, C—C—CO, and C—C—CN were all taken as 109·5°. The uncertainty of all these figures is without effect on the predicted dipole moments. The calculated dipole moment values are given in Table I, last column, the resulting conformer population in Table II.

The infrared absorption spectra of compounds *II*, *V*, *VI*, *VIII*, *IX*, and *X* were measured in decahydronaphthalene (53% of the *trans* isomer) in the region 1 690–1 780 cm^{-1}. Either a Perkin–Elmer model 580 instrument was used, cell thickness 1 mm, concentration 0·017 mol l^{-1} (compounds *II*, *V*, *VI*) or a Perkin–Elmer model 621 instrument, cell thickness 0·12 mm, concentration 0·15 mol l^{-1} (compounds *VIII*, *IX*, *X*). The temperature range was 302–423 K, 306–413, 301–424 for the compounds *II*, *V*, *VI*, respectively, while *VIII*, *IX* and *X* were measured at one temperature only (312 K). Correction for concentration change was carried out referring to the thermal expansibility of 2-methylene-*trans*-decahydronaphthalene[25]. In the case of compound *X* only one unresolved band was observed (ν = 1 730·2 cm^{-1}, $\frac{1}{2}A_{1/2}$ = 8·07 cm^{-1}, A = 15 077 cm^{-2} l mol^{-1}), the remaining results are listed in Table III. The population of conformers was determined as previously[1] with the assumption of equal molar absorption coefficients. The previously used procedure of band resolution was improved by smoothing out the value of $\Delta\nu_{1/2}$ for the same compound at different temperatures (quadratic interpolation), see[27]. An attempt was made to determine these coefficients by a graphical procedure[26] but acceptable values were not obtained. A more detailed discussion of this method is given elsewhere[27]. The resulting populations are listed in Table III.

Electrostatic calculations: For an equilibrium of the *ap* and *sp* conformers, and using the point-charges approximation, Eq. (*1*) acquires the form

$$2{\cdot}303\boldsymbol{R}T\log K = \frac{N_A}{4\pi\varepsilon_0}\sum_{ij} q_i q_j \left[\left(\frac{1}{r_{ij}\varepsilon_{cf}}\right)_{sp} - \left(\frac{1}{r_{ij}\varepsilon_{cf}}\right)_{ap}\right], \qquad (2)$$

where r_{ij} is the distance between the charges q_i and q_j. The effective permittivity ε_{cf} need not be generally equal for the two conformers but in a non-polar solution it equals approximately the bulk permittivity of the solvent. We used the value of ε_{cf} = 2·274 (the permittivity of benzene at 25°C) and r_{ij}'s from the standard geometry. The geometry of the ester group used by us previously[1,2] agrees very well with that determined recently by a statistical treatment of X-ray results[22]. The values of q were obtained as previously[1] by resolution of standard bond moments[21].

In the point-dipoles approximation with two dipoles, Eq. (*1*) reads:

$$2{\cdot}303\boldsymbol{R}T \log K = -\frac{N_A\mu_1\mu_2}{4\pi\varepsilon_0}\left[\left(\frac{2\cos\Theta_1\cos\Theta_2 - \sin\Theta_1\sin\Theta_2}{r^3\varepsilon_{ef}}\right)_{sp} - \left(\frac{2\cos\Theta_1\cos\Theta_2 - \sin\Theta_1\sin\Theta_2}{r^3\varepsilon_{ef}}\right)_{ap}\right] \quad (3)$$

and involves in addition to the dipoles μ_1, μ_2 and their distance r also the angles Θ_i of the vectors μ_i and r. Again the effective permittivity need not be equal for the two conformers but we used the same value as above. For μ_1 and μ_2 the group moments of CN and COOR were substituted as quoted in the preceding paragraph. The geometrical parameters r and Θ were determined

TABLE I

Dipole moment data of cyano esters *II*—*IX* (benzene, 25°C)

No	Compound	α^a β^a	P_2^0 cm^3 $R_D{}^b$ cm^3	μ (5%)^c μ (15%)^c	$\mu_{calc}{}^d$ *sp* *ap*
II	2-$NCC_6H_4COOCH_3$	12·22 −0·352	407·9 43·3	14·1 14·0	19·04 11·64
III	2-$NCC_6H_4COOC_2H_5$	11·05 −0·276	408·9 47·9	14·0 13·9	19·04 11·64
IV	(*E*)—NCCH=CHCOOCH$_3$	13·24 −0·243	306·1 27·7	12·3 12·2	11·54 (10·97)^e 11·54 (10·97)^e
V	(*Z*)-NCCH=CHCOOCH$_3$	15·25 −0·314	345·7 27·7	13·2 13·1	19·04 (17·31)^e 11·64 (9·87)^e
VI	(*Z*)-NCCH=CHCOOC$_2$H$_5$	12·65 −0·199	332·5 32·4	12·8 12·7	19·04 (17·31)^e 11·64 (9·87)^e
VII	$NCCH_2CH_2COOCH_3$	15·27 −0·268	353·9 26·6	13·3 13·2	16·94 (13·34)^f
VIII	Methyl 2-cyanobicyclo[2,2,2]-octane-1-carboxylate	10·48 −0·275	430·4 50·1	14·4 14·3	17·34^g (13·77)^h
IX	Ethyl 2-cyanobicyclo[2,2,2]-octane-1-carboxylate	10·09 −0·233	449·1 54·7	14·6 14·5	17·34^g (13·77)^h

^{a} Slopes of the plots ε *vs* w_2 and d^{-1} *vs* w_2, respectively; ^{b} calculated as given in Experimental; ^{c} all dipole moment values in 10^{-30} C m, correction for the atomic polarization 5%, or 15% of the R_D value; ^{d} calculated from group moments, see Experimental; ^{e} calculated with group moments valid for aliphatic derivatives; ^{f} free rotation around the two C—C bonds assumed; ^{g} conformation with the highest dipole moment, the O=C—O plane parallel with the C—C≡N direction; ^{h} free rotation around the C—CO bond.

from the standard geometry (as used for calculation of dipole moments) placing the point dipole in the middle of the C≡N bond and in the carbon atom of the carboxyl group, respectively. Application of Domenicano's geometry[23] would not affect the results appreciably. The results of electrostatic calculations are given in Tables II and IV. In addition to the point-charges and point-dipoles approximations we applied also the variant[9] representing the COOR group as a dipole and CN as point charges, as well as the reverse combination.

Quantum chemical calculations: The total energies of *sp* and *ap* conformers of *II*, *IV*, and *V* were calculated by the semiempirical CNDO/2 method with the standard parametrization[28]. For compound *II* the same geometry was used as previously[2], the geometry of the $COOCH_3$ group in *IV* and *V* was taken from ref.[22]. For the CH=CH—CN fragment the standard bond lengths[29] were used (in pm): C=C 134, C—H 108, C—C_{sp} 145, C≡N 116; all bond angles were taken as 120°. The standard geometry was not optimized.

DISCUSSION

When discussing the dipole moment data of Table I, it is convenient to start with (*E*)-methyl 3-cyanopropenoate (*IV*). This compound can exist in two conformations, *ap* and *sp*, but their dipole moments do not differ within the framework of the bond moment scheme as far as the bond angles of 120° are adopted. The reasonable

TABLE II

Experimental and calculated energy differences (kJ mol^{-1}) and rotamer populations of cyano esters (298 K)

Compound	ΔE_{sp-ap} (% of the *ap* rotamer)				
	μ (5%)	experiment μ (15%)	IR[a]	electrostatic calculations[b]	CNDO/2
II	2·39 (72)	2·55 (74)	2·01 (69)	1·03 (60)	8·13 (96)
III	2·46 (73)	2·72 (74)		1·03 (60)	—
V	3·91—1·21[c] (83)—(62)[c]	4·04—1·31[c] (84)—(63)[c]	0·52 (55)	1·41—1·27 (64)—(63)	10·31[d] (98)[d]
VI	4·81—1·75[c] (87)—(67)[c]	5·07—1·87[c] (88)—(68)[c]	1·08 (61)	1·41—1·27 (64)—(63)	—

[a] At 302 K; [b] point-charges approximation based on bond moments, $\varepsilon_{ef} = 2{\cdot}274$; [c] the second value calculated with group moments valid for aliphatic compounds; [d] ref.[17] gives —4·0 kJ mol^{-1} (17%) using essentially the standard geometry of ref.[29]; for compound *IV* we calculated —3·2 (22%), ref.[17] gives —5·2 (11%); the reference values in our calculation are —229 556·16 for *V ap* and —229 534·60 for *IV ap*.

agreement with experiment suggests at this stage that the „aromatic" values of group moments should be applied even to olefinic derivatives; it also allows to appreciate the reliability of further results on compounds *V* and *VI*. For aromatic derivatives *II* and *III* previous measurement[2] on methyl 4-cyanobenzoate can serve to the same purpose, the agreement with experiment was still bettJr. Now, the dipole moments of compounds *II*, *III*, *V*, and *VI* give no support fort he prevailence of *sp* rotamers. Their values can be in principle interpreted either in terms of the $ap \rightleftharpoons sp$ equilibrium or of a non-planar conformation. We hold only the former interpretation as acceptable in virtue of the results of infrared spectroscopy (Table III). In addition to the doubled carbonyl bands of all the compounds investigated, their temperature dependence observed with compounds *V* and *VI* is of particular importance. Further arguments in favour of a virtually coplanar conformation of aromatic esters were discussed previously[1], additional support was obtained from statistical treatment of X-ray results[22]. When the equilibrium model is accepted and population of rotamers calculated, there is a very good agreement between the two experimental methods for compounds *II* and *III* (Table II). This agreement is quite remarkable considering different solvents and difficulties inherent in either method: In the case of dipole moments it is the approximative character of the bond moment scheme and complex formation with benzene[3], in the case of infrared spectroscopy the very crude as-

TABLE III

Infrared spectral data of cyano esters (decahydronaphthalene, 302 K)

Value	Conformer	*II*	*V*	*VI*	*VIII*	*IX*
$\tilde{\nu}$(C=O) cm^{-1}	*ap*	1 736·6	1 738·4	1 733·8	1 735·6[c]	1 731·9[c]
	sp	1 747·2	1 748·4	1 743·4	1 743·8[c]	1 741·4[c]
$\frac{1}{2}\Delta\nu_{1/2}$ cm^{-1}	*ap*	3·51	3·58	4·18	8·22[c]	8·54[c]
	sp	2·74	2·76	3·01	4·55[c]	4·78[c]
A, cm^{-2} l mol^{-1}	*ap*	6 797	5 309	4 994	8 104[c]	8 888[c]
	sp	3 061	4 323	3 249	3 451[c]	4 101[c]
ΔH^0 [a] kJ mol^{-1}		−0·43	−1·99	−1·84	[d]	[d]
ΔG^0 [b], kJ mol^{-1}		2·01	0·52	1·08	2·1	1·9
% of the *ap* rotamer[b]		69	55	61	70[c]	68[c]

[a] Determined in the temperature range from 302 K to 413—423 K, assuming the ratio on integrated absorption coefficients α_1/α_2 to be independent of temperature; [b] at 302 K, assuming equal integrated absorption coefficients $\alpha_1 = \alpha_2$; [c] not assigned to any particular conformers; [d] measured only at 302 and 390 K, ΔH^0 uncertain.

sumption of equal molar absorption coefficients[26,27]. Note also the very good coincidence of the two methods, as obtained previously for methyl 2-fluorobenzoate (*I*) and further 2-halogenobenzoic esters[1]. However, the coincidence in Table II is much worse for the olefinic cyano esters *V* and *VI*. We are not able to decide which of the methods is in error. Most probably they deviate in opposite directions and the actual conformer populations is near to that in aromatic analogues *II*, *III*. We attempted still to recalculate the expected dipole moments of *IV*–*VI* with aliphatic group moments, not including any conjugation and/or π-electron polarization. The results are given in Table I in parentheses. While the agreement with experiment is now worse for compound *IV*, the agreement with IR spectroscopy for compounds *V*, *VI* is much better (Table II). A complete lack of conjugation is, of course, not real, but we cannot estimate the effect of geometrical and other factors according to the available evidence. Let us stress that fair agreement between the two methods does not invalidate the statement that any preference of rotamers with adjacent ester and cyano groups was not observed.

TABLE IV

Comparison of electrostatic calculations in different approximations, energy differences (kJ . . mol^{-1}) and rotamer populations (298 K, $\varepsilon_{ef} = 2{\cdot}274$)

Compound	Experiment[a]	$E_{sp} - E_{ap}$ (% of the *ap* rotamer)			
		point charges	point dipoles	combined[b]	combined[c]
Methyl 2-fluorobenzoate[1] (*I*)	1·43 (64)	1·67[d] (66)	2·46 (73)	2·46 (73)	2·03 (69)
Methyl 2-cyanobenzoate (*II*)	2·22 (71)	1·03 (60)	−8·05 (4)	−7·47 (5)	0·48 (55)
Methyl 3-fluorobenzoate	−0·55[e] (45)	0·10 (51)	−0·21 (48)	−0·22 (48)	0·12 (51)
Methyl 3-cyanobenzoate[2]	1·75 (67)	−0·11 (49)	−1·10[f] (39)	−0·99 (40)	−0·24 (48)

[a] Mean values; [b] COOR represented by a point dipole, F or CN by point charges, according to[9]; [c] COOR represented by point charges, F or CN by a point dipole; [d] differs slightly from our previous value[1] due to different charge representation of the CH_3 group (positive charges on all of hydrogen atoms); [e] calculated from the experimental dipole moment[27] of $6{\cdot}84 \cdot 10^{-30}$ C m; [f] there is an error in ref.[2]: in Table II, line 4 read −0·77, 42, −0·48, 45; an additional small difference is in the $COOCH_3$ group dipole placed previously[2] in the middle of the C=O bond, n this work on the C atom.

We searched further for any indication of attractive interaction between the two functional groups, referring to the dipole moments of compounds *VII–IX*. The dipole moment of methyl 3-cyanopropanoate (*VII*) agrees very well with that calculated for free rotation around the two C—C bonds. Since the mathematical model of completely free rotation is physically unrealistic, this finding means that several conformations are present with almost equal probabilities. This result may be due to a high entropy contribution and to the torsional strain connected with the cyclic conformation. In the derivatives of bicyclooctane, *VIII* and *IX*, these factors are absent but the results are not essentially different. The experimental dipole moments are but slightly higher than those calculated for the free rotation. It means that the conformation with the carbonyl oxygen near to the cyano group is not particularly preferred. This finding is not impaired by the fact that we are not able to decide which of the six possible conformations are actually present. According to the infrared spectra there are at least two conformers; if more, their carbonyl bands are indistinguishable. The latter possibility is not excluded since the potential energy curve for rotation around a C_{sp2}—C_{sp3} bond is usually flat. In conclusion, no experimental evidence was obtained that conformations with near CN and COOR groups should be preferred. Note that even the quantum chemical evidence[17] was not confirmed by our calculations carried out with the same semiempirical method but with different geometry, see the footnote to Table II. The calculation is evidently too sensitive to geometrical factors and the semiempirical level seems to be not sufficient. It follows that the thermodynamical instability of (*E*)-3-cyanopropenoates towards their (*Z*)-isomers cannot be explained simply by attraction[17] of CN and COOR groups, whether electrostatic or exchange in character. The thermodynamic preference of stereoisomers is itself well proven experimentally[16] and supported by CNDO calculations; in this point our calculations do not differ qualitatively from ref.[17].

The main objective of this paper was, of course, testing of the electrostatic approach in various forms. Of the four applied simple possibilities: point-charges approximation, point-dipoles approximation, and two mixed versions, only the first one was acceptable. This is evidenced by the results for compound *II*, Table IV. A more detailed comparison with various experimental results for the four cyano esters is possible form Table II. With respect to the above-mentioned problems with olefinic derivatives, attention is to be focussed to aromatic derivatives *II* and *III*. In our opinion the point-charges approximation combined with the charges calculated by the resolution of bond moments gives fair results. Although the values of energy are underestimated by a factor of two, the agreement looks better considering the percentage population of rotamers from a practical point of view and taking into account the differences between experimental methods. We can accept the conclusion that at least the essential part of energy difference between rotamers of the compounds studied is electrostatic in character.

When comparing our experimental results to CNDO/2 calculations (Table II), one must take into account that the latter relate to ΔH^0 of isolated molecules in vacuum, while the experiments and electrostatic calculations relate to a medium of relative permittivity of 2·3; the experimental values are ΔG^0 while the electrostatic calculations reproduce strictly[30] ΔH^0 but were often empirically adjusted to ΔG^0 values. According to our previous study of methyl 2-fluorobenzoate in various solvents[3] we can estimate that the resulting effect can amount to a factor of two. Even so, the CNDO calculations seem to overestimate the energy difference still by the same factor. Failure of CNDO and INDO methods for conformation around a C_{sp2}—C_{sp2} bond has been noted several times, *e.g.*[31], although our results with methyl 2-fluorobenzoate[3] were satisfactory. In any case the conclusion seems justified that the electrostatic approach works better for these special model compounds than simple semiempirical methods.

In conclusion we tried to compare several possible approximations in electrostatic calculations on four aromatic model compounds investigated to date (Table IV). Evidently the approximation with point charges is most satisfactory while combined methods seem to us both inefficient and theoretically ill-founded. Of the model compounds investigated the fluoro derivatives are more suitable than cyano derivatives. The main reason is, in our opinion, that the actual charge distribution within the cyano group is poorly represented by the bond moment scheme and by the resulting charges[2]; the failure is evident particularly with 3-cyanobenzoate. Methyl 3-fluorobenzoate as well as 3-chloro derivatives of various carbonyl compounds[9] are rather poor models since the equilibrium constants are too near to unity. Hence 2-fluorobenzoate seems to be the only one of the investigated models which satisfies all requirements. It must be stressed that our calculations were based on the principle of additivity of bond moments and on the resolution of a bond moment into two charges situated in the centres of atoms. The first step of this procedure is justified in the case of our compounds by the good agreement of experimental and additive dipole moments, the second step remains a plausible approximation. Among others our procedure neglects small fractional charges within the benzene ring, except the carbon atom adjoining to fluorine. Alternatively, charges on all atoms of the molecule can be taken into acount as calculated by a quantum chemical approach[13,32]; instead of the traditional Mulliken population analysis a more sophisticated distribution of charge was advanced recently[32]. These procedures have not yet been tested on aromatic compounds, our preliminary first attempts on the CNDO level gave bad results[2]. Nevertheless, we believe that the results obtained until now allow to conclude that conformational equilibria are relatively better represented by a simple electrostatic model than ionization equilibria. The main difference is evidently the bond breaking in the latter case which calls for considering also the transmission through bonds (*i.e.* in other terms the inhomogeneity of the space filled with the molecule).

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