ELECTROSTATIC EFFECTS ON CONFORMATIONAL EQUILIBRIA. SOLVENT DEPENDENCE

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The conformational equilibrium $E \rightleftarrows Z$ of methyl 2-fluorobenzoate was determined from the intensity of the carbonyl bands in 17 aprotic solvents of different polarity. The estimated values of ΔG^0 depend linearly on the reciprocal permittivity of the solvent as expected according to the electrostatic theory in combination with common cavity models. If a small correction is admitted for the unequal absorption coefficients of the two rotamers and/or for the steric effect of fluorine, the results agree very well with electrostatic calculations; the values extrapolated to vacuum agree also reasonably with CNDO/2, INDO and PCILO, but not with STO-3G calculations. On the whole, the electrostatic theory seems to work better with conformational equilibria than with proton transfer reactions. This conclusion does not depend on the solvent used or on any particular cavity model.

The present series of papers is concerned with electrostatic effects on conformational[1,2] and ionization[3-5] equilibria with the intention to compare these two fields of application and to apply the results from one field in the other. Of the two, the theory of ionization equilibria is much more developed[6]. If a dipolar substituent is involved, its effect on the relative dissociation constant K/K^0 is expressed by the basic equation[7,8]

$$2{\cdot}303RT \log (K/K^0) = \frac{Ne\mu \cos \Theta}{r^2 \varepsilon_{ef}}, \qquad (1)$$

where μ is the substituent dipole situated at the distance r and at the angle Θ with respect to the ionizable proton. The effective permittivity ε_{ef} has an intermediate value between ε_e of the solvent and ε_i of the molecule itself[8-10]. In order to apply Eq. (*1*) to a conformational equilibrium (K), one of the rotating moieties of the molecule must be considered as a point dipole (point-dipoles approximation), the other as a system of fractional charges z_i (point-charges approximation) replacing the unit charge e; several expressions like (*1*) are to be summed up over all charges and subtracted for the two respective conformations. This approximation[11] is rather unnatural as there is no evident reason why one moiety should be represented differently than the other. Whatever approximation is used, Eq. (*1*) must be modified with respect to the laws of electrostatics. In a general form it can be written as a function of the charges and/or dipoles, and of the geometrical parameters (r, Θ):

$$2{\cdot}303RT\log K = Nf(\mu_i, z_i, r_i, \Theta_i, \varepsilon_{ef})\,. \tag{2}$$

TABLE I

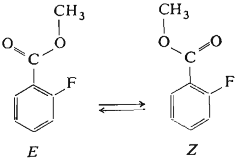
Conformer Population of Methyl 2-Fluorobenzoate in Various Solvents and the Pertinent Spectral Data (312 K)

No	Solvent	ε[a]	ν(C=O)[b] cm^{-1}		B_E[c]	B_Z[c]	$N_E = B_E : (B_E + B_Z)$ %	$\Delta G^0 \pm s$[d] kJ mol^{-1}
			E	*Z*				
1	Hexane	1·89	1 729·3[e]	1 747·5[e]	700	398	63·8	1·47 ± 0·03
2	Cyclohexane	2·01	1 727·9	1 746·1	695	411	62·9	1·37 ± 0·03
3	Dioxan	2·21	1 721·4	1 737·0	686	629	52·1	0·22 ± 0·05
4	Decalin	2·21	1 727·2	1 745·3	711	437	61·9[f]	1·26 ± 0·03
5	Tetrachloromethane	2·23	1 723·6[g]	1 740·9[g]	861	532	61·8	1·25 ± 0·06
6	Benzene	2·27	1 722·1	1 737·6	750	583	56·3[h]	0·65 ± 0·05
7	Tetrachloroethylene	2·30	1 724·6	1 742·3	767	466	62·2	1·29 ± 0·04
8	Dibutyl ether	3·06	1 726·5	1 743·7	716	494	59·1	0·96 ± 0·04
9	Chlorobenzene	5·62	1 721·3	1 735·7	661	733	47·4	—0·27 ± 0·06
10	1-Bromobutane	6·9	1 723·9	1 738·9	689	686	50·1	0·01 ± 0·07
11	Dichloromethane	8·93	1 719·1	1 731·0	845	864	49·4	—0·03 ± 0·21
12	(*Z*)-1,2-Dichloroethylene	9·20	1 720·2	1 731·9	765	840	47·7	—0·24 ± 0·17
13	1,3-Dibromopropane	9·29	1 719·8	1 732·7	676	812	45·4	—0·48 ± 0·11
14	Acetonitrile	36·0	1 721·8[j]	1 733·4[j]	604	700	46·3	—0·38 ± 0·08
15	Nitromethane	38·6	1 721·0	1 732·3	657	709	48·1	—0·20 ± 0·11
16	Sulfolane	44	1 718·7	1 729·8	716	737	49·3	—0·07 ± 0·19
17	Dimethyl sulfoxide	46·7	1 718·2	1 729·6	731	720	50·4	0·04 ± 0·09

[a] Relative permittivity (ε of vacuum = 1); [b] the relative accuracy is given by a standard deviations of 0·1 cm^{-1}, or usually less, as obtained from the band separation; [c] integrated absorption intensities of the *E* and *Z* form, respectively; their standard deviation varies from 0·5 to 2%; [d] the standard deviation expresses the inaccuracy of the band separation procedure; [e] ref.[15] gives 1 731 and 1 749 cm^{-1} for ν_E and ν_Z, respectively; [f] previously[1] we found 63% at 298 K; [g] ref.[16] gives 1 726 and 1 741 cm^{-1} for ν_E and ν_Z, respectively; [h] from dipole moment data we estimated[1] 64—66% at 298 K; [j] ref.[15] gives 1 723 and 1 733 cm^{-1} for ν_E and ν_Z, respectively.

Eq. (*1*) has been experimentally tested in several efficient ways. In particular the dependence on μ or on $\mu \cos \Theta/r^2$ was followed for varying substituents[4], further the dependence on $\cos \Theta/r^2$ or on $\cos \Theta/r^2\varepsilon_{ef}$ for a constant substituent at different positions[3,4], or the dependence on ε_{ef} for varying solvents[12,13]. In the case of conformational equilibria these possibilities are more restricted since systems with a variable dipolar substituent are difficult to realize. Therefore, Eq. (*2*) has been mostly tested only by comparing simply the left-hand and right-hand sides[1,2,11,14]. Nevertheless, one important possibility remains, *viz.* the dependence on solvent which is the object of the present paper. Hitherto, the conformational equilibria have been studied in solvents of low polarity, assuming ε_i, ε_e, and ε_{ef} all equal. In this way the difficulties with estimating ε_{ef} are obviated since the mathematical models in use[8-10], representing the molecule as a regular-shaped cavity in the solvent, are elaborated only for pole-dipole or pole-pole interactions, not for several charges or two dipoles. In this paper we are using polar solvents, too, and hence we shall focus our attention on conclusions which can be reached without the exact knowledge of ε_{ef}.

As a model compound, we chose methyl 2-fluorobenzoate investigated previously by us in decahydronaphthalene solution[1] and before that by Eglinton and co-authors[15,16] in four solvents but only in a qualitative manner. There is a good evidence that this compound exists in two virtually planar conformers, *E* and *Z*, the torsional energies of which and approximately also the non-bonded interactions are equal. On this condition the equilibrium $E \rightleftharpoons Z$ is dominated by the electrostatic effect. In general, the choice of similar models is rather difficult since the above preconditions (equal non-bonded and torsional energies) are sometimes contradictory to the requirement of strong electrostatic interactions.* Our experimental approach was based, like previously[1], on intensity measurements of the carbonyl band. The results were compared with the electrostatic theory and in addition with some quantum chemical calculations.



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* In an alternative approach the electrostatic effects were studied on a single conformation the dihedral angle of which was controlled by the balance of coulombic and torsional forces[34].

EXPERIMENTAL AND RESULT

Materials: Methyl 2-fluorobenzoate was prepared previously[1]. Decalin contained[1] 53% of *trans*-decahydronaphthalene.

Spectral measurements: The IR absorption spectra were recorded in the region 1550 to 1800 cm^{-1} in 0.12M solutions at 312 ± 1 K. A Perkin-Elmer 621 instrument and 0.1 mm cells were used. The band separation was carried out as previously[1]; in more polar solvents the bands are broader and the precision decreases. In Table I are given the percentage of the E rotamer and ΔG^0 of the conformational equilibrium, both calculated with the assumption of equal molar absorption coeffcients of the two forms. The error is expressed by the standard deviation as given by computer fitting.

Calculations: The previous electrostatic calculations[1] in the point-charges approximation were complemented by the point-dipoles approximation with the dipole values of 5.7 and $4{\cdot}9 \,.\, 10^{-30}$ Cm for the $COOCH_3$ group and C—F bond, respectively. In the quantum chemical calculations standard parametrization was used, see ref.[17-20] for EHT, CNDO/2 — INDO, PCILO, and STO-3G, respectively. The standard geometry[21] agreed well with an X-ray analysis of 2-fluorobenzoic acid[22] and was not optimized. The results are listed in Table II.

DISCUSSION

The change of electrostatic energy connected with the process $E \rightleftharpoons Z$ is expressed generally by Eq. (*2*). If the point-charges approximation is used this equation acquires the particular form

$$\Delta E_{elst} = N \sum_{ij} q_i q_j \left[\left(\frac{1}{r_{ij}\varepsilon_{ef}} \right)_Z - \left(\frac{1}{r_{ij}\varepsilon_{ef}} \right)_E \right], \qquad (3)$$

where the distances r_{ij} between two charges differ generally in the two conformations. With the point-dipoles approximation the equation reads:

$$\Delta E_{elst} = - N\mu_1\mu_2 \left[\left(\frac{2 \cos \Theta_1 \cos \Theta_2 - \sin \Theta_1 \sin \Theta_2}{r^3 \varepsilon_{ef}} \right)_Z - \right.$$
$$\left. - \left(\frac{2 \cos \Theta_1 \cos \Theta_2 - \sin \Theta_1 \sin \Theta_2}{r^3 \varepsilon_{ef}} \right)_E \right] \qquad (4)$$

and involves in addition to the dipoles $\mu_1\mu_2$ and their distance r still the angles Θ of the vectors μ and r. The effective permittivity ε_{ef} can acquire different values in the two equations and also in the two conformations. As mentioned, there is no theory predicting ε_{ef} and hence ΔE_{elst} for a more complex charge distribution like in our case. For a simple distribution, however, ε_{ef} has been always expressed[8-10] as a function of the solvent bulk permittivity ε_e and of further parameters proper to the solute molecule (the internal permittivity ε_i, dimensions of the molecule, location of charges and/or dipoles). For a constant molecule, ΔE_{elst} should be always a single-valued fucntion of ε_e, nearly linear with respect to ε_e^{-1}.

In Fig. 1 our experimental values of ΔG^0 are plotted against the reciprocal value of the solvent permittivity. The graph consists of two regions differing in the accuracy of individual points and of the linear relationship as well. Nevertheless, the linearity is fulfilled reasonably with respect to the experimental uncertainty. There are only three notable exceptions: the solvents benzene, chlorobenzene, and dioxan. For the remaining 14 points the correlation coefficient is 0·963 and the standard deviation 0·21 kJ mol^{-1}. A general theory of solvent effects on reactivity[23,24] distinguishes specific interactions like hydrogen bonds, acid-base equilibria, charge-transfer complexes, and non-specific interactions controlled by the solvent polarity and polarizability. Among the solvents used in this study, the non-specific interactions are almost excluded except just the three mentioned. In the case of benzene and chlorobenzene the charge-transfer, although weak, may be perceptible in relation to the scale of the graph. The abnormal behaviour of dioxan is known from the electronic spectroscopy[25] and the explanations in terms of its local dipoles[25] or varying conformations[26] were advanced. A possible effect of solvent polarizability on our ΔG^0 values was searched for by a multiple regression with the variables $(\varepsilon - 1)/$

TABLE II

Principal Quantum Chemical Characteristics of Methyl 2-Fluorobenzoate

Method	ΔH^0 (Z—E) kJ mol^{-1}	Rotational barrier $\Delta H^{\neq}$ kJ mol^{-1}	μ 10^{-30} Cm E	μ 10^{-30} Cm Z
Expt. extrapolated[a]	~3·7			
CNDO/2	3·16	—1·60	5·57	10·07
INDO	3·73	—1·94	6·07	10·71
EHT	—0·02	12·49	(4·67)[b]	(9·27)[b]
PCILO[c]	4·24	14·62	—	—
STO-3G	—1·86	13·21	2·87	6·70
Elst. calculation[a]				
(point charges)	3·79	—	—	—
(point dipoles)	5·59	—	—	—
Bond moments	—	—	5·40	10·61

[a] For the limiting value $\varepsilon_{ef} = 1$; [b] dipole moments $\mu = 0{\cdot}3\mu_{EHT}$, ref.[33]; [c] the benzene nucleus is represented as an average of the two Kekule structures, ref.[2].

$/(2\varepsilon + 1)$ and $(n^2 - 1)/(n^2 + 2)$, representing as usual[24] the polarity and polarizability terms, respectively. It turned out that the latter term was insignificant at any level. In correlating some ionization equilibria[24] the polarizability term was found significant in two examples of four. In general, it should be important for ions and for strongly polar molecules or transition states. In the above examples, however, its occurrence can be hardly rationalized and it may even be a mathematical artifact compensating for some imperfections of the model. (For instance it is difficult to understand that the dependence on polarity and on polarizability could have opposite signs[24].) The correlation of our data with the Kirkwood function[27] $(\varepsilon - 1)/$ $/(2\varepsilon + 1)$ alone is but slightly worse ($r = 0.958$, $s = 0.24$ kJ mol^{-1}) than with ε^{-1}. Generally, the function $(\varepsilon - 1)/(2\varepsilon + 1)$ is believed to hold for dipolar molecules in a polar solvent, while ε^{-1} for reactions involving ions[23]. An experimental decision in a concrete case is almost impossible since the two functions are rather closely correlated[28], particularly for $\varepsilon > 8$.

In an alternative approach, the reactivities or spectral data are correlated with a single solvent parameter, which is either physico-chemical (the internal pressure[29] $\delta = (\Delta H_{\text{vap}}/V)^{1/2}$) or empirical in character (the most successful were[23] the E_T values). The plot of our data against E_T (Fig. 2) lacks some points the E_T values for which are not available. Nevertheless, the general pattern is similar to Fig. 1. The polar solvents are more differentiated but the fit is not better. The same three solvents deviate in Fig. 2 as in Fig. 1; hence the E_T values are also unable to account for specific interactions of this kind. A plot against the internal pressure δ (not shown) is also incomplete and reveals more scattering, so that it is difficult to say which points deviate; in addition to the already mentioned three solvents it could be particularly dimethyl sulfoxide. This result is not surprising since the correlation with δ should apply strictly to non-polar solutes in little polar solvents[29].

We conclude that benzene, chlorobenzene, and dioxan show specific interactions and must be eliminated from any correlation; if this is done, the results agree qualitatively with the electrostatic theory since they are correlated with ε_e^{-1} better than with any other quantity. In order to reach more quantitative conclusions, we must first notice that in polar solvents the apparent population of the E conformer drops under 50%. This fact is incompatible with Eq. (*3*) or (*4*) whatever the value of ε_{ef} may be, but at least two different explanations can be provided: Either the molar absorption coefficients of the conformers E and Z are not equal, or there is some difference in the non-bonded interaction (steric strain). The opinion was already offered[16] that the effective size of the ether oxygen in E is larger than that of the carbonyl oxygen in Z. Certainly one of these effects or both together can be responsible for the small observed shift. In any case we may introduce an *ad hoc* correction of 0·4 kJ . . mol^{-1} and attempt to estimate ΔG^0 as it would be controlled by the pure electrostatic effect (the broken straight line in Fig. 1). The corrected values are in excellent agreement with the estimate[1] from dipole moments in benzene solution (Fig. 1).

This would indicate the different absorption coefficients to be the more important source of observed anomalies, *i.e.* of the small systematic shift on the one hand and of the large deviation in benzene on the other. We attempted to estimate roughly the possible steric effect by comparing the conformational equilibria for different 2-halogenobenzoates[1] (F, Cl, Br, I) in relation to the steric constants[30] of the respective halogens. One can infer that the steric effect in the fluoro derivative, if present, should probably not exceed 0·15 kJ mol^{-1}.

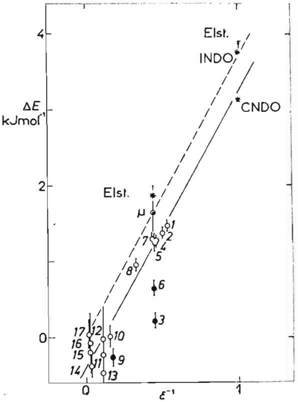

FIG. 1

Experimental and Calculated Energy Difference between Conformers of Methyl 2-Fluorobenzoate as a Function of Solvent Permittivity

○ Experimental ΔG^0_{312} in solvents without specific interaction, ● with specific interactions (from carbonyl band intensites — error ±2*s* indicated); ⊙ experimental ΔG^0_{298} in benzene from dipole moments[1]; * and ⤒ calculated by the electrostatical approach and by quantum chemical methods. Full straight line obtained by regression, broken line drawn through the origin of coordinates.

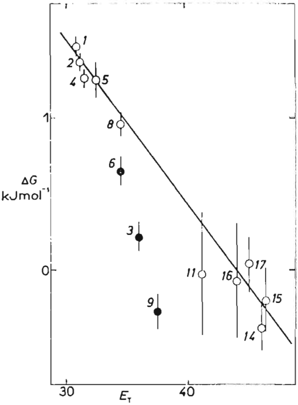

FIG. 2

Experimental Gibbs Energy Differences between Conformers of Methyl 2-Fluorobenzoate Plotted Against Solvent Parameter E_T

The same symbols are used as in Fig. 1.

The broken straight line in Fig. 1 thus represents the pure electrostatic energy and can be confronted with the calculation. This comparison is not possible in the whole range since the values of ε_{ef} are not available. At three points, however, a trivial solution or at least a limiting value can be obtained: *1*) If $\varepsilon_e = \varepsilon_i$ (approximately for benzene solvent) then ε_{ef} is also equal; the respective value[1] is shown by an asterisk in Fig. 1. *2*) For $\varepsilon_e = \infty$, ε_{ef} is not infinite but rather large and in the coordinate-ε^{-1} virtually zero; this corresponds to the zero intercept of the broken line. *3*) If $\varepsilon_e = 1$, then ε_{ef} is certainly greater but the value calculated with $\varepsilon_{ef} = 1$ can be taken as an upper limit. In all three points the corrected experimental data match quite well the calculation. Note that the calculated values have been obtained with the point-charges approximation, while the point-dipoles approximation seems to work worse in this case (Table II). We intend to return to this point in a subsequent paper in connection with further model compounds.

The corrected and extrapolated experimental values can be further compared to quantum chemical calculations (Table II). While there is a reasonable agreement with CNDO/2, INDO, and PCILO, the *ab initio* method on the STO-3G level failed completely, predicting even the prevalence of the *Z* conformer. Also the dipole moment values calculated by this method seem to be less reliable than the others. It is true that the geometrical parameters were not optimized but they are certaintly realistic and the STO-3G method is believed to be suitable for an experimental geometry. Hence its failure is not understandable. Note the quite opposite picture concerning the rotation barriers: here the predictions of STO-3G, PCILO, and even of EHT are reasonable while CNDO/2 and INDO overestimate as usually the non-bonded interactions and predict in this case the existence of only one, nonplanar conformation. The latter result could be possibly somewhat improved by optimizing the geometrical parameters irrespective of their experimental values. Evidently we cannot rely on any simple quantum chemical method with conformational problems of this kind. Note still that the essential agreement of quantum chemical and electrostatic calculations reveals – independently of the experiments – that the model in use is warranted, *i.e.* that other effects than electrostatic are negligible.

Summarizing the results, we can state that the electrostatic theory in its simple form as expressed by Eq. (*3*) is in principle adequate for the equilibrium under study. A more accurate proof is difficult to obtain for any conformational equilibrium owing to large experimental errors and difficulties with choosing a proper model compound. Even so, it is in our opinion obvious that the theory reproduces correctly in particular the solvent effect which is just a difficult point in the case of ionization equilibria[12,13]. One difference between these two applications consists certainly in the choice of solvents. We think, however, that the heart of the problem is the variable bond energy of the bond being broken in the ionization process. To elucidate this point, further data are still needed concerning ionization equilibria in various solvents and in the gas phase.

The carbonyl stretching frequencies of the E and Z conformers (Table I) are known with a good relative precision and offer the possibility to express the solvent effects by the Buckingham equation[31]. The original form of this equation

$$\nu = A + B\frac{\varepsilon - 1}{2\varepsilon + 1} + C\frac{n^2 - 1}{2n^2 + 1} \tag{5}$$

has been recently complemented[32] by a cross-term:

$$\nu = A + B\frac{\varepsilon - 1}{2\varepsilon + 1} + C\frac{n^2 - 1}{2n^2 + 1} + D\frac{\varepsilon - 1}{2\varepsilon + 1}\cdot\frac{n^2 - 1}{2n^2 + 1} \tag{6}$$

Our data do not fit either form well. Without the cross term and if we drop the ill-behaved solvents benzene, chlorobenzene, and dioxan, we get with Eq. (*5*) the correlation coefficients of 0·941 and 0·961, and standard deviations 1·36 and 2·00 cm^{-1} for ν_E and ν_Z, respectively. The term C is little significant, particularly with ν_Z. The most deviating solvents are tetrachloromethane, dichloromethane and 1-bromobutane. With the cross-term added, the correlation is not better, the standard deviations even worse (1·41 and 2·10 cm^{-1}, respectively). The coefficients B—D are obtained with a great uncertainty; this is due particularly to a close correlation between the first and third variable ($r_{13} = 0{\cdot}961$). A more significant correlation would be perhaps possible if special solvents were included, varying sufficiently in the refractive index, such as tribromomethane or diiodomethane used in ref.[32]. In our opinion the original Buckingham equation is generally not well documented, the less is its extension. Maybe the cross-term can sometimes substitute the first term but both together are superfluous.

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