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DIFFERENT ELECTRONIC EFFECT OF THE "Z" AND "E" FORM OF THE FORMAMIDO GROUP AS REFLECTED BY TAFT´S SUBSTITUENTS CONSTANTS

Z. Arnold*, V. Krchňák
Institute of Organic Chemistry and Biochemistry
Czechoslovak Academy of Sciences, 166 10 Prague 6
and P. Trška
Department of Organic Chemistry, Institute of Organic Technology, 166 18 Prague 6

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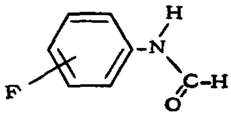
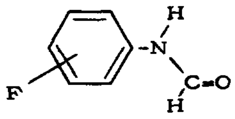
The formamido group is known[1] to occur in most compounds in both Z and E form. To obtain information on the electronic effect of this conformationally heterogenous group we have recently measured the ^{19}F NMR chemical shifts[2] of m- and p-fluoroformanilide. The data observed in three solvents of different type, C_6D_6, CD_3OD and CD_3CN are presented in Table 1. The characteristic feature of all these spectra is the presence of two well separated signals which coalesce at about 70°C. The relative intensities of these signals are solvent-dependent and their ratio in benzene was found identical with that of Z and E conformers (61 : 39) as determined under the same conditions by means of ^1H NMR spectroscopy (see also ref.[3]). The two ^{19}F signals thus identify the two forms given above. Moreover, the difference between the two chemical shifts can be regarded as a measure of the difference between the electronic effects of the two forms of the formamido group. If we now accept the validity of the Taft correlations[4] between the observed ^{19}F chemical shifts and empirical reactivity parameters, σ_I and σ_R°, we get the figures given in the right part of Table 1.

form Z



form E



The results of our present study will now be summarized

i) from the two forms of the formamido group which can be identified by ^{19}F spectroscopy in fluoroformanilides the form E exhibits stronger electronic effect than the form Z.

ii) the observed difference between the electronic effect of the two forms can to a greater extent be ascribed to the operation of the inductive effect while the resonance effect seems to be less important. iii) the calculated values of the σ_I and σ_R^o constants are, of course, dependent on the applied correlation equation and so far no other relevant data for confrontation are available. iiii) when considering the important role of the inductive effect in the two forms which are identical with respect to the atom sequence and differ only in respect of their geometry it can be inferred that an explanation of the observed data in terms of the electrostatic field theory might be possible. We feel, however, that before some more definite conclusions as to this and other aspects of the present problem can be reached, more material, both experimental and theoretical, has to be accumulated.

Table 1. The ^{19}F NMR Chemical Shifts of m- and p-Fluoroformanilide and the Calculated σ Constants of the Z and E Form of the Formamido Group [a,b,c]

Solvent	Form	δ_m	δ_p	σ_I	σ_R^o	σ^o
C_6D_6	Z	-1.467	4.931	0.29	-0.22	0.07
	E	-1.849	5.271	0.34	-0.24	0.10
CD_3OD	Z	-1.435	4.633	0.29	-0.21	0.08
	E	-2.009	4.963	0.37	-0.24	0.13
CD_3CN	Z	-1.397	5.154	0.28	-0.22	0.06
	E	-1.700	5.505	0.32	-0.24	0.08

[a] The symbols δ_m and δ_p are used in this Table for ^{19}F NMR shifts given in p.p.m. relative to fluorobenzene as internal standard. Negative values refer to downfield, positive to upfield shifts. [b] Spectra were recorded with Varian XL-100-15 apparatus at 94.1 MHz, with noise decoupling. The conditions of the measurements were essentially identical with those used by Taft[2]. [c] The calculation was carried out using the equations[2] :

$$\sigma_I = (0.6 - \delta_m)/7.1 \; ; \qquad \sigma_R^o = (\delta_m - \delta_p)/29.5 \; ; \qquad \sigma^o = \sigma_I + \sigma_R^o$$

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1. W.E.Stewart,T.H.S.Siddall III: Chem.Rev. 70, 517 (1970).
2. R.W.Taft,E.Price,I.R.Fox,I.C.Lewis,K.K.Andersen,G.T.Davis: J.Amer.Chem.Soc. 85, 709, 3146 (1963) and papers quoted therein.
3. R.E.Carter: Acta Chim.Scand. 22, 2643 (1968).
4. We are aware that some of Taft's conclusions have been criticized (W.Adcock, M.J.S.Dewar,B.D.Gupta: J.Amer.Chem.Soc. 95, 7353 (1973) and papers quoted therein) but as a matter of fact no material inconsistent with the correlation derived by him - at least in the fluorobenzene series - has been presented.