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Abstract

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ON THE ELECTRONIC NATURE OF FLUORINE-CONTAINING SUBSTITUENTS

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The properties of aromatic compounds containing fluorine atoms as substituents have been well studied. The pK values of fluorine-substituted benzoic acids, anilines, and phenols, ultraviolet absorption spectra, dipole moments, and nuclear magnetic resonance spectra have been determined. The properties of trifluoromethyl derivatives of benzene have also been investigated in considerable detail. The physicochemical properties of aromatic compounds with other fluorine-containing substituents are completely unknown. We began their study by determining the pK_a of the corresponding benzoic acids. Data on acid strength are very valuable for obtaining information on the electronic nature of substituents located in the *m*- or *n*-position relative to the carboxyl group.

The pK_a values of the acids were determined by measuring the pH of half-neutralized solutions. An accurately weighed portion of the fluorine-substituted benzoic acid (to obtain a concentration of 0.01 mole/l) was dissolved in alcohol, half-neutralized with a standardized solution of sodium hydroxide free of carbonate ion, and diluted with water to a ratio of 50% alcohol and 50% water (by volume). The pH measurements were carried out with an LP-5 tube potentiometer with a glass electrode at 25°. A saturated calomel electrode was used as the reference electrode. The accuracy of the pH measurements was 0.03. To check the measurement procedure, the pK_a values of some

Table 1

Substituent	*m*-Position: pK_a	*m*-Position: $k \cdot 10^{-6}$	*m*-Position: σ_M	*n*-Position: pK_a	*n*-Position: $k \cdot 10^{-6}$	*n*-Position: σ_Π
$CF_3SO_2^*$	4,54	28,8	0,79	4,17	67,6	1,03
CF_2> CF_2 O*				4,51	30,9	0,81
NO_2	4,66 (1)	21,9	0,710 (5)	4,54 (1)	28,8	0,778 (5)
CH_3SO_2	4,78 (6)	16,6	0,645 (5)	4,68 (6)	20,9	0,72 (5)
CN	4,85 (7)	14,1	0,598 (5)	4,70 (7)	20,0	0,66 (5)
CF_3	5,11 (8)	7,7	0,428 (5)	4,94 (8)	11,2	0,54 (5)

Figure 1: Hammett plot of $\lg K$ versus σ, with substituent labels shown on the graph. Legend: —a; —b; —c.

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Substituent	*m*-Position: pK_a	*m*-Position: $k \cdot 10^{-6}$	*m*-Position: σ_M	*n*-Position: pK_a	*n*-Position: $k \cdot 10^{-6}$	*n*-Position: σ_Π
CF_3O^*	5,19	6,5	0,36	5,26	5,5	0,32
CF_2 O* O				5,20	6,3	0,36
CF_2S^*	5,21	6,2	0,35	5,17	6,8	0,38
CH_3CO	5,21 (6)	6,2	0,376 (5)	5,10 (6)	7,9	0,502 (5)
Br	5,22 (1)	6,0	0,391 (5)	5,35 (1)	4,5	0,232 (5)
$CF_3-CH{=}CH^*$				5,40	4,0	0,23
H	5,75 (1)	1,8	0			

* Substituents for which pK_a and σ-constants have been determined for the first time in the present work.

fluorine-free acids: *p*-bromo-, *p*-nitro-, and *p*-methoxybenzoic acids. The data obtained agreed with those reported in the literature ([1]). Benzoic acids with fluorine-containing substituents, which were used for determining pK , were synthesized by us and described earlier.

The results of the pK determinations are given in Table 1; for comparison, the known pK values of substituted benzoic acids in 50% aqueous ethyl alcohol are also indicated there.

Hammett ([2]) found a quantitative relationship between the nature of a substituent located in the meta or para position relative to the reaction center and the reactivity of the side chain, and expressed it by the following equation:

$$\lg \frac{k}{k_0} = \rho\sigma,$$

where k and k_0 are, respectively, the rate (or equilibrium) constants of the substituted and unsubstituted aromatic compound; σ is the substituent constant characterizing its electronic influence on the reaction center; ρ is a constant characteristic of the given reaction. Starting from the values found for the dissociation constants of benzoic acids with fluorine-containing substituents, we calculated the σ-constants of these substituents.

Fig. 1 *a* —substituents from which ρ was calculated; *b* —substituents investigated in the present work; *c* —substituents given for comparison

To find the constant ρ, six substituents were selected with accurately determined σ-constants and pK values of the corresponding benzoic acids in 50% aqueous ethyl alcohol; in addition, the data pK_a and $\sigma = 0$ for unsubstituted benzoic acid were used. For calculating ρ, only the pK values of *m*-derivatives of benzoic acid were used, since in *p*-substituted derivatives the effect of para conjugation has a strong influence on the value of the σ-constant.

Using these data by the method described in Jaffe' s review ([3]), $\rho = 1.535$ was calculated, as well as the correlation coefficient r and the standard error s. Recently Taft ([4]) came to the conclusion that, for determining ρ, one may select only those substituents whose σ-constants agree with Hammett' s data ([2]) or with the values of McDaniel and Brown ([5]) within ± 0.07 units, and with a standard error not greater than ± 0.03. The substituents selected by us, H, *m*-Br, CH_3CO, CF_3, CN, SO_2CH_3, NO_2, satisfy these conditions, since for $\rho = 1.535$, $r = 0.998$ and $s = 0.03$. In calculating ρ, σ-constant values were used for the substituents H, SO_2CH_3, CN, CF_3 obtained from the pK values in 50% alcohol, and for the substituents NO_2, Br, and $COCH_3$ from the pK values in water ([5]). On the basis of the ρ found, ⋯

calculated the σ-constants of new substituents in the meta and para positions.

The cyclic groups $O(CF_2)_2$ and CF_2O_2 were included in the *n*-series by analogy with the CH_2O_2 group, tetralin, and hydrindene ([2,3]). Table 1 includes the *m*-substituents that we used for calculating ρ, and also, for comparison, the pK_a and σ-constants of the corresponding *p*-substituents. All the substituents listed are electron-accepting or very weak electron donors. The dissociation constants of the indicated acids are greater than the dissociation constant of benzoic acid; the σ-constant values are positive. As is known, electron-donating substituents show opposite effects.

As can be seen from Table 1, the strongest electron-accepting group among the known substituents in the benzene ring is the trifluoromethylsulfonyl group. *p*-Trifluoromethylsulfonylbenzoic acid is more than twice as strong as *p*-nitrobenzoic acid.

The dependence between the σ-constant values and $\lg k$ of substituted benzoic acids in 50% aqueous ethyl alcohol is shown in Fig. 1. The inductive effect of the CF_3SO_2 group is greater than that of the nitro group, since *m*-trifluoromethylsulfonylbenzoic acid is stronger than *m*-nitrobenzoic acid. Phenyl trifluoromethyl sulfone, like nitrobenzene, is nitrated only in the meta position.

The $(CF_2)_2O$ group is electronegative, equal in strength to the nitro group.

The σ-constants of the CF_3O, CF_3S, and CF_2O_2 groups are very close to the σ-constants of halogen atoms—bromine and chlorine (for the latter $\sigma_m = 0.373$, $\sigma_p = 0.227$ ([5])).

Like the halides, the indicated groups are ortho-para directing in electrophilic substitution in the aromatic nucleus. The substituent $CF_3CH{=}CH-$ differs sharply from the CF_3 group in its influence on the benzene ring. On nitration of phenyltrifluoromethylethylene, about 50% of the *p*-isomer was isolated, whereas benzotrifluoride is nitrated only in the *m*-position. In its strength, *p*-$CF_3CH{=}CH$-benzoic acid resembles *p*-bromobenzoic acid, and not *p*-trifluoromethylbenzoic acid, of which it is the vinylog. The σ-constants for the $CF_3{-}CH{=}CH{-}$ substituent and for the bromine atom are identical and are 2.5 times smaller than the σ-constants of the trifluoromethyl group.

We also determined the pK_a in 50% aqueous ethyl alcohol of 2-trifluoromethyl-1-naphthoic acid (p$K_a = 4.25$; $k \cdot 10^{-6} = 56.2$) and of *o*-trifluoromethylbenzoic acid (p$K_a = 4.69$; $k \cdot 10^{-6} = 20.4$). The former proved to be a 2.5 times stronger acid than the latter.

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Note: Figure translations are in progress. See original paper for figures.