SovietRxiv

Soviet-era science, translated into English

PHYSICAL CHEMISTRY

L. M. Yagupol' skii, V. F. Bystrov, and E. Z. Utyanskaya

1960

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196001.06526

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

L. M. Yagupol' skii, V. F. Bystrov, and E. Z. Utyanskaya

STUDY OF THE CHEMICAL SHIFTS OF MAGNETIC RESONANCE OF F^{19} NUCLEI IN FLUOROBENZENES WITH FLUORINE-CONTAINING SUBSTITUENTS

(Presented by Academician V. N. Kondrat' ev, 1 VI 1960)

In recent years a large number of aromatic compounds with various substituents containing fluorine have been synthesized. Their physicochemical properties have hardly been studied. The purpose of the present work is to elucidate the influence of fluorine-containing substituents on the distribution of electron density in the benzene ring and to establish the connection between the structure of these compounds and their reactivity by means of the method of nuclear magnetic resonance (NMR).

The chemical shifts of fluorine in the ring of monosubstituted fluorobenzenes were measured relative to the resonance line of fluorine in unsubstituted fluorobenzene and are determined by the formula

$$\delta = \frac{H_X - H_{C_6H_5F}}{H_{C_6H_5F}} \cdot 10^6, \tag{1}$$

where H_X and $H_{C_6H_5F}$ are the resonance values of the external magnetic field for the F^{19} nuclei, respectively, in substituted and unsubstituted fluorobenzene. The resolving power of the apparatus was $\sim 1 \cdot 10^{-6}$; the accuracy of measurement of the chemical shifts was $\pm 0.3 \cdot 10^{-6}$. The samples were pure liquids. The measurements were made with an external standard. The effective volume of the sample under study was ~ 80 mm^3, that of the standard ~ 20 mm^3. No correction for the diamagnetic susceptibility of the sample was introduced. The strength of the constant magnetic field was 4530 gauss. The NMR apparatus and the measurement procedure have been described in detail previously ([1]). The results of measurements of the chemical shifts of fluorine in the benzene ring are given in Table 1.

Table 1

Chemical shifts of fluorine in the benzene ring

SovietRxiv

Substituent X	o	m	p	3,4
SO_2CF_3	−8.7	−4.7	−15.1	
SCF_3	−7.8	−2.3	−4.7	
OCF_3	+17.4	−2.3	+2.8	
$CH{=}CH{-}CF_2$			−2.4	
$CF_2\langle^{O}_{O}$				+3.9
$O\langle^{CF_2}_{CF_2}$				−8.6

The redistribution of electron density in the benzene ring caused by the substituent affects both the chemical shift of fluorine in substituted fluorobenzenes ([2]) and the reactivity of benzene derivatives ([3]). The general quantitative relation between the nature of the substituent situated in the meta- or para-position relative to the reaction center and the reactivity of the side chain is expressed by the well-known Hammett equation ([3])

$$\lg \frac{k}{k_0} = \sigma\rho, \tag{2}$$

where k and k_0 are rate (or equilibrium) constants for the reactions of substituted and unsubstituted benzene derivatives; ρ is a constant depending on the type and conditions of the reaction and on the nature of the side chain; σ is a constant depending only on the nature and position of the substituent. In work ([2]), an approximate empirical relationship was established between the chemical shift δ and the Hammett σ-constant:

$$\delta_{\mathrm{m}} = -5.92\sigma_{\mathrm{m}}, \tag{3}$$

$$\delta_{\mathrm{p}} = -17.9\sigma_{\mathrm{p}} + 4.84. \tag{4}$$

The development of the theory of the chemical reactivity of benzene derivatives ([4]) led to the establishment of new, more precise quantitative relationships between the δ and σ quantities ([5]). Taft showed that the influence of a substituent on the reactivity of meta- and para-benzene derivatives can be represented as the sum of independent contributions from the inductive effect and the conjugation effect,

$$\sigma_{\mathrm{p}} = \sigma_{\mathrm{i}} + \sigma_{\mathrm{c}}, \tag{5}$$

$$\sigma_{\mathrm{m}} = \sigma_{\mathrm{i}} + \alpha\sigma_{\mathrm{c}}, \tag{6}$$

SovietRxiv

where α is a constant depending on the type of reaction ([6]). The quantitative relationship between the σ and δ values is given in the following form ([5]):

$$\delta_{\mathrm{m}} = -5.83\sigma_{\mathrm{i}} + 0.20, \tag{7}$$

$$\delta_{\mathrm{p}} = -5.83\sigma_{\mathrm{i}} - 18.80\sigma_{\mathrm{c}} + 0.80. \tag{8}$$

However, for strong electron-acceptor groups (for example, CN, NO_2, $COCH_3$) the σ_{p} values calculated from equations (7), (8), and (5) from chemical-shift data have values greater than the normal σ_{p}-constants ([5,6]). It has recently been shown that the normal σ_{p}-constant is applicable only in the case when there is no direct conjugation, or it is small, between the para substituent and the functional group ([6,7]). In the presence of such conjugation one should expect a continuous series of σ_{p}-constants for each substituent, since the deviation of an individual value from the normal σ_{p}-constant depends on the magnitude of the para-conjugation effect.

It was shown that equation (7) is valid for all previously investigated groups without exception ([5,6]). Using this equation we calculated the values

Table 2

Substituent	σ_{i}	σ_{p} from pK_a	σ_{c} eq. (5)	σ_{m} eq. (6)	σ_{m} from pK_a	δ_{c} (ppm)	σ_{m} eq. (3)	σ_{p} eq. (4)
OCF_3	0.43	0.32	−0.11	0.38	0.36	−0.24	0.39	0.11
OCH_3	0.25([6])	−0.27([8])	−0.52	0.10	0.12([8])	–	–	–
SCF_3	0.43	0.38	−0.05	0.41	0.35	0.16	0.39	0.53
SCH_3	0.27([6])	0.01([8])	−0.26	0.16	0.15([8])	–	–	–
CF_3	0.41([6])	0.54([8])	0.13	0.46	0.43([8])	0.19*	0.35*	0.56*
CH_3	−0.05([6])	−0.17([8])	−0.12	−0.08	−0.07([8])	–	–	–
SO_2CF_3	0.84	1.03	0.19	0.92	0.79	0.58	0.79	1.12
SO_2CH_3	0.58([6])	0.72([8])	0.14	0.64	0.65([8])	–	–	–
$CH{=}CH{-}CF_3$		0.23	–	–	–	–	–	0.40
$CF_2\langle^{O}_{O}$	–	0.36	–	–	–	–	–	0.05
$O\langle^{CF_2}_{CF_2}$	–	0.81	–	–	–	–	–	0.75

* In the calculation the values $\delta_{\mathrm{m}} = -2.1$ and $\delta_{\mathrm{p}} = -5.1$ ([6]) were used.

σ_i for the substituents investigated in this work (Table 2), and the values of the σ_p constants obtained by equation (2) from the pK_a values of substituted benzoic acids ([10]), for which it may be assumed that para-conjugation between

SovietRxiv

the carboxyl group and the substituents under study is small, are also given there. The corresponding σ_c values calculated from equation (5) are also given in Table 2. Substituents with positive σ_c are meta-directing in electrophilic substitution reactions in the aromatic nucleus, while those with negative σ_c are ortho-para-directing ([4]). Indeed, upon nitration of benzene derivatives with the substituents CF_3 and SO_2CF_3, only meta nitro compounds are formed; with SCF_3, 65% para and 35% ortho; and with OCF_3, 90% para nitro products are formed. The σ_m values calculated from equation (6) agree, with accuracy generally good for the Hammett rule, with the σ_m values obtained from the dissociation constants of the corresponding benzoic acids. For benzoic acids with the substituents CH_3 and OCH_3, the pK_a values were determined in aqueous medium ($\alpha = 0.29$([6])), and with the other substituents in 50% aqueous alcohol ($\alpha = 0.42$([6])). Table 2 gives the σ_c values (n.m.r.) calculated from equations (7) and (8). The larger value of σ_c (n.m.r.) as compared with σ_c for the groups SO_2CF_3, CF_3, and SCF_3 is apparently connected with the greater magnitude of the para-conjugation effect of these substituents with F than with the COOH group. The para-conjugation of the OCF_3 group with F is apparently smaller than with the COOH group. Table 2 also gives the values of σ_m and σ_p calculated from equations (3) and (4).

Table 2 gives, for comparison, the values of the σ-constants of analogous substituents not containing fluorine. In all cases the introduction of fluorine increases the inductive effect of the corresponding substituent. Conju-

Table 3

Substituent	SO_2NH_2	NO_2	SO_2CF_3	CN	$CF_2=CF_2$	COOH	CF_3	SCF_3	CH=CH	Br	CF_3	Cl	OCF_3	CF_2H	FO	SCH_3	CH_3	OCH_3
δ_p	−15.4	10.8		−9.6	−8.6	−6.6	−5.1	−4.7	−2.4	1.2	2.3	2.4	2.8	3.9	6.4	—	5.5	11.4
σ_p	1.03	0.78	0.72	0.66	0.81	0.50	0.54	0.38	0.23	0.23	0.23	0.23	0.32	0.36	0.06	0.01	−0.17	−0.27
λ_{max} (I), mμ (in alcohol)	476	475	445	—	450	447	430	432	455	—	420	420	419	420	—	419	408	407

Table 4

Substituent	SO_2NH_2	CF_3	NO_2	SO_2CH_3	CN	CF_3	F	Cl	Br	J	SCF_3	OCF_3	SCH_3	OCH_3	CH_3
δ_m	−4.7	−3.3	—	−3.0	−2.8	−3.1	−2.1	−2.4	−2.6	−2.3	−2.3	—	−1.3	+0.9	
σ_m	0.79	0.71	0.65	0.56	0.43	0.34	0.37	0.39	0.35	0.35	0.36	0.15	0.12	−0.07	

the binding of the substituent with the ring upon replacement of hydrogen by fluorine in the OCH_3 and SCH_3 groups ($\sigma_c < 0$) is considerably decreased,

SovietRxiv

whereas in the SO_2CH_3 group ($\sigma_c > 0$) it is somewhat increased as a result of withdrawal of electrons by the fluorine atoms from the oxygen and sulfur atoms. The conjugation effects of the CH_3 and CF_3 groups are close in magnitude but opposite in sign. Apparently, in the present case the fluorine atom has the same tendency to attract an electron by the mechanism of σ–σ conjugation as the hydrogen atom has to donate it.

To compare the influence of the substituents investigated in the present work and those studied earlier on the benzene ring, in Tables 3 and 4 we compared the chemical shifts of fluorine in the ring, δ_m and δ_p ([2,6]), and the σ-constants ([8]) of these substituents. The groups are arranged in decreasing order of their electron-acceptor properties. It is evident from Tables 3 and 4 that the SO_2CF_3 group is the strongest of the electron-acceptor substituents known at present. In their influence on the benzene ring the substituents OCF_3, SCF_3, and CH=CH –CF_3 are similar to halogens; the CF_3 group is close to $COCH_3$ and CN;

$$\begin{matrix} O\diagdown \\ O\diagup \end{matrix}CF_2 \quad \text{to } OCF_3 \quad \text{and} \quad \begin{matrix} CF_2\diagdown \\ CF_2\diagup \end{matrix}O \quad \text{to } CF_3.$$

The group CH=CH–CF_3 (the vinylene homolog of benzotrifluoride) possesses a smaller electron-acceptor strength than the CF_3 group. A corresponding analogy is observed for CH=CH–COOH and the COOH group.

From Table 3 one may note a correspondence between the wavelength corresponding to the absorption maximum in the visible spectrum of dimethylaminoazobenzene derivatives with a substituent in the 4′-position (I) ([9]), and the chemical shift of fluorine in the corresponding para-fluorobenzenes (II).

$$(CH_3)_2N—C_6H_4—N=N—C_6H_4—R \qquad F—C_6H_4—R$$

(I) (II)

This correspondence is evidently explained by electron displacements of the same type, which determine the chemical shift of fluorine in the para position and the displacement of the maximum of the absorption band in the visible spectrum.

Institute of Organic Chemistry
Academy of Sciences of the Ukrainian SSR

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
25 V 1960

SovietRxiv

CITED LITERATURE

1. V. F. Bystrov, L. L. Dekabrun, Yu. N. Kil' yanov, A. U. Stepanyants, E. Z. Utyanskaya, *Pribory i tekhn. eksperim.*, No. 1 (1961).

2. H. S. Gutowsky, D. W. McCall, B. R. McGarvey, L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952).

3. L. P. Hammett, *Physical Organic Chemistry*, 1940; H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

4. R. W. Taft, in M. S. Newman, *Steric Effects in Organic Chemistry*, 1959, ch. 13.

5. R. W. Taft, *J. Am. Chem. Soc.*, **79**, 1045 (1957).

6. R. W. Taft, I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343, 5352 (1959).

7. H. Van Bekkum, P. E. Verkade, B. M. Wepster, *Rec. Trav. chim.*, **78**, 815 (1959).

8. D. H. McDaniel, H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

9. L. M. Yagupol' skii, M. S. Marinenko, *ZhOKh*, **27**, 1395 (1957); I. N. Zhmurova, *ZhOKh*, **27**, 2704 (1957); E. Savicki, *J. Org. Chem.*, **22**, 915 (1957); L. M. Yagupol' skii, L. N. Yagupol' skaya, *DAN*, **134**, No. 6 (1960).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.