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1965

SovietRxiv

Abstract

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Chemistry

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On the Microstructure and Electron-Acceptor Properties of the Sulfofluoride Group

(Presented by Academician M. I. Kabachnik, January 30, 1965)

The study of the UV spectra of benzenesulfonyl fluoride derivatives is of interest both from the standpoint of evaluating the degree of electron-acceptor character of the SO_2F group and from the standpoint of studying the microstructure of the SO_2Y group ($Y = F, Cl, Me, OH, NH_2$, etc.). The literature data are contradictory, and there is as yet no complete clarity regarding the nature of the $S \ldots O$ bond. According to (^{1}), in the SO_2 group there is not a double bond $S = O$, but only a mesomeric shift of the coordination bond toward the double bond $\overset{+}{S}—\overset{..}{O}:\overset{\ominus}{..} \leftrightarrow S = O:$, with participation of the vacant $3d$-orbitals of sulfur. The double bond $S = O$, by its character, should differ from a π-bond. Against an $S = O$ bond it was argued that there is no spectral band of the $n \to \pi^*$ transition type for the SO group and no addition reactions. However, recently a 1,4-addition reaction to $C = C—S = O$ has been described (^{2}).

It could be supposed that an increase of the positive charge on the S atom as a result of the inductive influence of the F atom ($\delta^+ S \to F^{\delta-}$) would strengthen the electron-acceptor properties of the SO_2F group in comparison with SO_2Me ($S \leftarrow CH_3$) and SO_2NH_2, and would shift the bond $S \to O$ toward $S = O$. In favor of this assumption is the shortening of the $S \ldots O$ bond in SO_2F_2 to 1.37 Å, instead of 1.50 Å in $SO_2O_2^{--}$ (^{1}).

Table 1

B	σ-*	σ_R (^{5})	λ_{max} K-band: n-H_2N—C_6H_4—B	λ_{max} K-band: n-Me_2N—C_6H_4—B
SO_2OH	0.38	0.26	232 (^{8})	256 (^{8})
SO_2NH_2	0.62	0.43	262 (^{3})	276 (^{3})
SO_2F	0.64 ***	0.46 ***	270 **	300 **
COOH	0.73	0.50	288 (^{3})	308 (^{3})
COMe	0.87	0.60	317 (^{3})	337 (^{3})
NO_2	1.27	0.64	375 (^{3})	390 (^{3})

* Taken from (^{6}), except for the value for $SO_3^{\ominus}$ (^{7}) instead of SO_3H.

Figure 1

Figure 1: Figure 1

** $\varepsilon_{\max}$ 18,900 and 26,100, respectively, at $C = 10^{-4}$ mol/l.
*** Calculated from the curves of Fig. 4.

The study of the UV spectra of derivatives of the series $A—\Phi—SO_2F$ (Φ = cyclohexylidene ring or $C_6H_5—$, $A = NMe_2, NH_2, OMe, Br, Cl, Me, H$) showed that the sulfofluoride group is a weaker acceptor than groups of type B with a double π-bond, COOH, $COCH_3$, NO_2. However, the spectral curves of benzenesulfonyl fluorides contain K-bands ($\pi \to \pi^*$ transitions), typical of compounds of the structure n-B—Φ—A (^{3,4}) (Tables 1 and 2, Figs. 1 and 2). The positions of $\lambda_{\max}$ and $\varepsilon_{\max}$ of the K-band and the similar character of the bands clearly confirm the presence of conjugation of the SO_2F group with the benzene nucleus.

Our conclusions on the presence of conjugation in the system $A\Phi SO_2F$, where $A = NH_2$ and other electron-donor groups (Fig. 2), confirm the conclusions (^{8}) on the absence in solutions of the bipolar form of sulfanilic and N,N-dimethylsulfanilic acids. According to our data, the K-bands of the system $A - \Phi - SO_2F$ are bathochromically shifted K-bands of the chromophores $A - C_6H_5$ or $C_6H_5SO_2Y$, which in turn are genetically connected with the K-band of benzene ($\lambda_{\max}$203.5, ε7000).

Recently M. A. Mostoslavskii (^{9}) pointed out a linear correlation of $\lambda_{\max}$ for two chromophores of similar microstructure upon introduction into them of identical substituents. We applied this rule in order to determine to what extent the groups SO_2F, SO_2Y are related in their action to groups containing a π-bond ($COOH$, $COMe$, NO_2). Comparison of $\lambda_{\max}$ for aniline and dimethylaniline derivatives (Fig. 3, *a*) showed the presence of a linear correlation. Small deviations from the straight line for the groups SO_2F, SO_2NH_2 may be regarded as an indication of some difference in the mechanism of their interaction with the π-electrons of the benzene nucleus from that of groups of type B with a π-bond.

Fig. 1. Influence of electron-acceptor groups on the spectrum in compounds of the type $A- -B$:
1—$Me_2N\Phi COMe$; 2—$H_2N\Phi COMe$; 3—$Me_2N\Phi COOH$; 4—$Me_2N\Phi SO_2F$; 5—$H_2N\Phi COOH$; 6—$H_2N\Phi SO_2F$

On the other hand, comparison of $\lambda_{\max}$ for benzenesulfofluorides with $\lambda_{\max}$ for benzenesulfamides and methyl phenyl sulfones shows a linear correlation (Table 2, Fig. 3, *b* and *c*). This indicates a relationship in the electronic structure of their chromophoric systems, whereas for the series of benzenesulfofluorides and p-substituted benzoic acids (Fig. 3, *d*) a linear correlation is not always observed.

Fig. 2. Absorption spectra of $A - \Phi - SO_2F$;

Figure 2

Figure 2: Figure 2

reaction scheme

Figure 3: reaction scheme

$A = 1{-}NM_{12}$; $2{-}NH_2$; $3{-}MeO$; $4{-}Br$; $5{-}Cl$; $6{-}Me$; $7{-}H$

We see the reason for this in the fact that in SO_2F and SO_2Y, even in the presence of the $S = O$ bond, we do not have conditions for coplanarity and normal conjugation. The double bond $S = O$ does not have the character of a π-bond; the groups SO_2Y have a special tetrahedral structure ([1], [10]), which prevents coplanarity of the atoms connected with S and the benzene nucleus. As a consequence of this, conjugation and displacement of the electron upon excitation by light occur without participation of the oxygen electrons of the SO group, with partial expansion of the shell up to 12 (Fig. 1, *c*) (and up to 14 electrons when two $S = O$ groups are retained (Fig. 1, *d*)). Conjugation may occur, however, even when theileswi

of the absence of a double bond in the SO group (II):

Investigation of the correlation of $\Delta\lambda^*_{\text{max}}$ of the K-bands of the H_2N B and Me_2N B series with the Hammett constants σ^- and their mesomeric components σ_R ([5,11]) by the method ([12]) (Table 1, Fig. 4) makes it possible to estimate for SO_2F the constants $\sigma \sim 0.64$ (which is close to σ^-, calculated for SO_2Me ([13,14])) and σ_R 0.46.

Table 2

λ_{max} of the absorption bands of substituted benzenesulfofluorides
A— $-SO_2F$ (Fig. 2) in dichloroethane

$C = 10^{-2}$ mol/l

A	K-band λ_{max}, mμ	K-band ε_{max}	B-band λ_{max}, mμ	B-band ε_{max}
H	220	8600	267	1300
Me	230	9800	270	1000
Cl	232	15200	270	900
Br	240	13100	270	900
MeO	245	15900	obscured	obscured
NH_2	270	20500	obscured	obscured
NMe_2*	300	22800	obscured*	obscured*

* There is also λ 223, ε 8500, analogous to the x'-band ([3]).

Fig. 3. Correlation between λ_{max} of two compounds of structure A— —B (Φ = phenylene):
a: comparison of λ_{max} $I{-}Me_2N$ B and $II{-}H_2N$ B; B = 1—H, 2—SO_3H, 3—

graphs

Figure 4: graphs

SO_2NH_2, 4—SO_2F, 5—COOH, 6—COMe, 7—NO_2;
b: comparison of λ_{max} III—A— —SO_2F and IV—A— —SO_2NH_2, A = 1—H, 2—Me, 3—Cl, 4—Br, 5—MeO, 6—NH_2, 7—NMe_2;
c: comparison of λ_{max} III and V, A— —SO_2Me; A = the same;
d: comparison of λ_{max} III and VI, A— —COOH; A = the same.

The data obtained make it possible to conclude that conjugation of the SO_2F, SO_2Y groups occurs with participation of vacant sulfur 3*d*-orbitals.

* The values of the shift of the K-band in Fig. 4 were calculated by us relative to the corresponding bands of aniline λ_{max} 230 mμ and dimethylaniline λ_{max} 250 mμ.

(I_B or II_B) through the formation of a C···S bond. The electrons of the O atom are not drawn into the chromophore system. The conjugated chromophore system terminates at the sulfur atom. In support of this conclusion one may cite the observation that the $\Delta\lambda$ effects of the SO_2F and SO_2Me groups practically coincide (n-H_2N SO_2F λ_{max} 270, n-H_2N SO_2CH_3 λ_{max} 269 [10]), despite the opposite direction of the polarizing action in the S → F and S → CH_3 bonds. The closeness of the effects of SO_2F and SO_2Me is also confirmed by the closeness of the σ found by us for n-SO_2F, 0.64, to that calculated for SO_2Me, 0.65-0.68 [13,14].

Fig. 4. Correlation of shifts of maxima ($\Delta\lambda$) with σ, σ_R for H_2N— —B; Me_2N— —B: 1 —SO_3H; 2 —SO_2NH_2; 3 —COOH; 4 —COMe; 5 —NO_2.
a —H_2N— —B, *b* —Me_2N— —B.

n-Me_2N-benzenesulfonyl fluoride was obtained by the action of an excess of CH_3I on n-$H_2NC_6H_4SO_2F$, with decomposition of the quaternary salt. From benzene: leaflets, m.p. 110.5–111°.

Found, %:	N 6.82; 6.95; F 9.15; 9.12
$C_8H_{10}FNO_2S$. Calculated, %:	N 6.89; F 9.23

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at the Moscow Pedagogical Institute
named after V. I. Lenin

Received
30 I 1965

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