FLUOROSULFONYL-CONTAINING HETEROCYCLIC COMPOUNDS

VII.* ELECTRON-ACCEPTING PROPERTIES OF HEXAFLUOROTHIOACETONE DIOXIDE TRIMER

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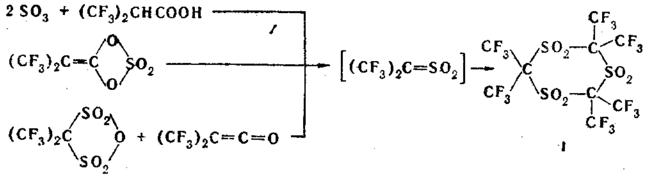
On the basis of UV and NMR spectroscopy it has been established that with ethers and tertiary amines the cyclic trimer of hexafluorothioacetone dioxide forms donor–acceptor complexes in which there is two-center coordination in the cases of 1,4-dioxane, 1-methylmorpholine, and 1,4-diethylpiperazine, and three-center coordination in the cases of 1,3,5-trioxane and hexamethylenetetramine. The reaction of the trimer with secondary amines has given amides of hexafluoro-2-H-propane-2-sulfonic acid.

The stable cyclic trisulfone (I), which is the trimer of the hypothetical hexafluorothioacetone dioxide, has been obtained by various methods and is therefore preparatively accessible [1].



I

The chemical properties of this trisulfone (I) have not been discussed previously; some of them are considered below.

The trisulfone (I) is inert to electrophilic reagents; it does not react with bis(trifluoromethyl)ketene, bromine, chlorine, sulfuryl chloride, and sulfur trioxide, even at 200°C. At the same time it reacts under relatively mild conditions with various electron-donating compounds. Thus, although solutions of the trisulfone (I) in methylene chloride, chloroform, carbon tetrachloride, and dichloroethane show no absorption in the 250–380 nm region, its solutions in di-n-butyl ether possess some absorption of light. The optical density of such solutions rises considerably in the presence of electron-donating compounds containing coordination-unsaturated oxygen or nitrogen atoms, which shows the presence of donor–acceptor interactions of these substances with the trisulfone (I).

On comparing the UV spectra of the solutions investigated (Fig. 1), it can be seen that di-n-butyl ether and 1-methylpiperidine react feebly with the trisulfone (I); 1,4-dioxane, 1-methylmorpholine, and 1,4-diethylpiperazine react more vigorously; and, finally, 1,3,5-trioxane and hexamethylenetetramine react relatively strongly. The decisive characteristic of the effectiveness of such interactions is not the electron-donating capacity of the reagent but steric factors – the number of electron-donating centers in the molecule of the reagent and their spatial correspondence with the electron-accepting centers of the molecule of the trisulfone (I), which can be represented by one, two, or even all three sulfonyl groups. The

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*For Communication VI, see [1].

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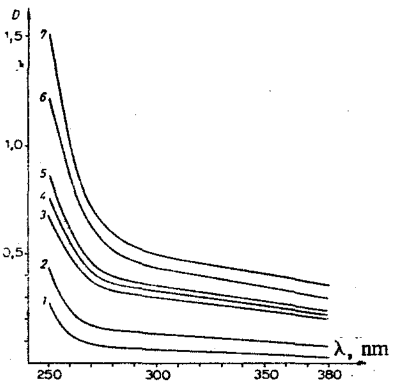
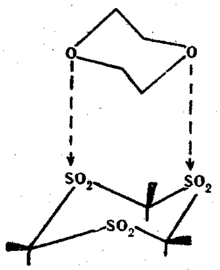
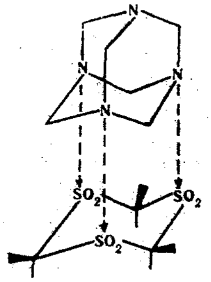


Fig. 1. UV spectra of solutions of the trisulfone (I) in di-n-butyl ether: 1) standard; 2) in the presence of 1-methylpiperidine; 3) in the presence of 1,4-dioxane; 4) in the presence of 1-methylmorpholine; 5) in the presence of 1,4-diethylpiperazine; 6) in the presence of 1,3,5-trioxane; 7) in the presence of hexamethylenetetramine.

possibility of the two-center coordination of 1,4-dioxane and of the three-center coordination of hexamethylenetetramine with the molecule of the trisulfone (I) is explained by the following considerations. The O–O interatomic distance in 1,4-dioxane ("chair" conformation) and the N–N distance in hexamethylenetetramine (structure of the adamantane type) are, respectively, 2.82 Å [2] and 2.42 Å [3]. Although the geometric parameters of the molecule of the trisulfone (I) have not been determined, they can be estimated by comparison with those for 1,3,5-trithiane. Since the degree of oxidation of the sulfur atom does not fundamentally affect the C–S interatomic distances (1.80 Å in dimethyl sulfone and 1.82 Å in dimethyl sulfide [4]), it may be considered that the distance between the SO_2 groups in the trisulfone (I) differs little from the S–S distance in 1,3,5-trithiane, which is 2.90 Å [5]. The very slight difference in the distances between the electron-donating centers in 1,4-dioxane or hexamethylenetetramine and the distance between the electron-accepting centers in the trisulfone I permit the assumption of the formation of donor–acceptor complexes of the following types:





In such complexes, inversion of the six-membered ring of the trisulfone (I) is difficult or is even impossible; consequently, in cases of multicenter coordination the "chair" conformation must be immobilized and the trifluoromethyl groups be fixed in the axial and equatorial 2,4,6-positions of the ring. It has been possible to demonstrate the latter by the ^{19}F NMR method. The spectrum of a 10% solution of the trisulfone (I) in di-n-butyl ether contains only one singlet signal ($\delta = -18.3$ ppm), which reflects some averaging of the positions of the trifluoromethyl groups as the result of ring inversion (see [1, 6]). At the same time, the spectrum of a 10% solution of the trisulfone (I) in dioxane contains two singlet signals of equal intensity (at −17.7 and −18.7 ppm); on adding 1,4-diethylpiperazine (two equivalents) to this solution, the difference in the values of this pair of chemical shifts increases slightly (−17.6 and −18.8 ppm). Similarly, two signals are found in the spectrometry of a 10% solution of the trisulfone (I) in 1,3,5-trioxane (−17.3 and −18.9 ppm) and likewise in the presence of hexamethylenetetramine (at −17.0 and −19.1 ppm). These features of the NMR spectra show the presence of two types of spatially isomeric trifluoromethyl substituents ("a") and ("e") in the fixed "chair" conformation of the trisulfone (I) when it forms a donor–acceptor complex through multicenter coordination with a polyether or a polyamine.

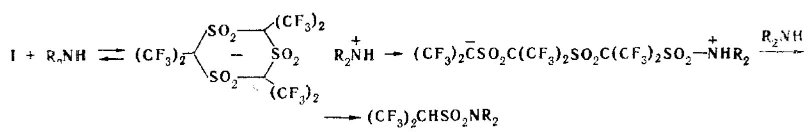
The observed differences in the values of the chemical shifts, just like the differences in the intensities of absorption in the UV region, probably reflect different levels of charge transfer in donor–acceptor coordination; it is natural that on passing from ethers to amines the strength of the coordination bond rises. This explains the following phenomenon. The optical densities of solutions of the trisulfone (I) in di-n-butyl ether, 1,4-dioxane, and 1,3,5-trioxane remain constant for several weeks; under these circumstances, the trisulfone (I) can be isolated quantitatively from these solutions by fractional distillation. If, however, 1-methylpiperidine, 1,4-diethylpiperazine, or hexamethylenetetramine was used as donor, the optical densities of such solutions fell to one half after 2-3 h, and after a day the absorption of light had fallen to zero; it was impossible to isolate the trisulfone (I) from such solutions either by fractional distillation or even by treating the solution with mineral acids. Apparently, the amine–trisulfone donor–acceptor complex originally formed changes irreversibly by the transfer of the reaction center into the anionic fragment, which leads to the decyclization of the trisulfone (I) with the subsequent cleavage of several C–S bonds. It has been possible to demonstrate this fact by preparative experiments.

TABLE 1. The Sulfonamides $(CF_3)_2CHSO_2NR_2$

Compound	NR_2	Alkalimetry			^{19}F NMR spectra	
		consumption of KOH, eqts		fluoride ion found, equivs.	chemical shift, ppm *	spin–spin coupling constants, Hz
		to phenolphthalein	to Methyl Orange			
IIa	$(CH_3)C_6H_5$	8,08	7,12	5,92	–16,6	8,1
IIb	$(CH_2)_5$	8,04	7,05	6,03	–16,5	8,0
IIc	$(CH_2CH_2)_2O$	7,96	7,06	5,99	–16,0	8,6

*The spectra of 20% solutions in ethanol were recorded; the signals were doublets.

It was found that diphenylamine, which is characterized by a low electron-donating capacity (because of steric hindrance) does not react with the trisulfone (I) even at 200°C. The more highly electron-donating N-methylaniline, piperidine, and morpholine react with the trisulfone (I) even at 0–10°C; when 2–3 equivalents of these amines were used, the corresponding amides of hexafluoro-2H-propane-2-sulfonic acid (II) were isolated with yields of 86–90%.



II a–c

The structure of the sulfonamides (II) was confirmed by their ^{19}F NMR spectra and by the results of alkaline hydrolysis.

$$(CF_3)_2CHSO_2NR_2 + 7\,\bar{O}H \rightarrow 6\,\bar{F} + CO_2 + \bar{O}OCCH_2SO_2NR_2 + 3\,H_2O$$

The behavior of the trisulfone (I) with respect to electrophilic and nucleophilic reagents that has been considered characterizes it as an electron-accepting compound, which is due to the unique compact association in its molecule of three sulfonyl and six trifluoromethyl groupings.

EXPERIMENTAL

The UV spectra were taken on a SF-4A spectrophotometer at 20°C using as standard a 0.01 M solution of the trisulfone (I) in di-n-butyl ether, to which the substances under investigation were added in a concentration of 0.05 M (Fig. 1). The ^{19}F NMR spectra were taken on a Hitachi–Perkin–Elmer model R-20 spectrometer at a field strength of 14,092 gauss, a frequency of 56.456 MHz, and a resolution of $3 \cdot 10^{-8}$ with trifluoroacetic acid as internal standard at a temperature of 34.5°C.

N-Methylhexafluoro-2H-propane-2-sulfonanilide (IIa). A solution of 3.2 g (0.03 mole) of N-methylaniline in 50 ml of ether was added to a solution of 6.4 g (0.01 mole) of the trisulfone (I) in 150 ml of dry ether. The solvent was distilled off and the residue was fractionally distilled under reduced pressure giving 2.8 g (87%) of the sulfonanilide in the form of a colorless liquid with bp 136°C (5 mm), d_4^{20} 1.6140; n_D^{20} 1.4586. Found %: C 37.6; H 3.0; F 35.2; N 4.6; S 9.6. $C_{10}H_9O_2F_6NS$. Calculated %: C 37.4; H 2.8; F 35.5; N 4.4; S 10.0.

Hexafluoro-2H-propane-2-sulfonpiperidide (IIb). A solution of 2.1 g (0.025 mole) of piperidine in 50 ml of ether was added to a solution of 6.4 g (0.01 mole) of the trisulfone (I) in 150 ml of ether. The solvent was distilled off and the residue was treated with boiling toluene (2 · 10 ml); on cooling, the extract deposited a precipitate. Recrystallization from toluene gave 2.7 g (90%) of the sulfonpiperidide; white acicular crystals with mp 58°C, bp 120°C (2 mm). Found %: C 32.4; H 3.8; F 37.9; N 4.7; S 10.8. $C_8H_{11}O_2F_6NS$. Calculated %: C 32.1; H 3.7; F 38.2; N 4.7; S 10.7.

Hexafluoro-2H-propane-2-sulfonmorpholide (IIc). Similarly, 6.4 g (0.01 mole) of the trisulfone (I) and 1.7 g (0.02 mole) of morpholine gave 2.6 g (86%) of the sulfonmorpholide in the form of white acicular crystals with mp 86°C (from benzene). Found %: C 28.1; H 3.1; F 37.6; N 4.7; S 10.4. $C_7H_9O_2F_6NS$. Calculated %: C 27.8; H 3.0; F 37.9; N 4.7; S 10.6.

Alkalimetry. A weighed sample of the compound (0.02–0.03 g) was dissolved in 10 ml of ethanol, and 20 ml of 0.1 N caustic potash solution was added to this solution. After 12–15 h, the excess of alkali was back-titrated with 0.1 N hydrochloric acid to phenolphthalein, and then to Methyl Orange. In other experiments the amount of fluoride ion in the alkaline hydrolyzate was determined by the thoriometric method. The results of the analyses are given in Table 1.

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