greatest contribution to the mass spectra, E ions predominate at 250°C, and D ions predominate at 500°C. We also note that the contribution of ions with a cyclic structure is greater in the case of block copolymers than in oligodimethylsiloxane.

The high thermal stability of polysulfone thus did not permit using mass spectrometry as a method of investigating the structure of the rigid PSN-PDMS blocks in the block copolymers in the conditions selected. Moreover, the presence of ions with m/z 59 + y•74 (D), 73 + y•74 (E), and 57 + y•73 (H), characterizing the PDMS blocks, in the spectra permits studying the deep processes of thermal destruction of the elastic phase in polysulfonepolydimethylsiloxane copolymers.

#### CONCLUSIONS

Mass spectrometry showed that the polydimethylsiloxane units in polysulfone-polydimethylsiloxane block copolymers undergo thermal decomposition with formation of a series of linear and cyclic oligodimethylsiloxanes.

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INFLUENCE OF THE REPLACEMENT OF HYDROGEN ATOMS BY FLUORINE ON THE VIBRATIONAL ENERGY OF THE NSO GROUP AND <sup>15</sup>N AND<sup>17</sup>O NMR CHEMICAL SHIFTS IN N-SULFINYLARYLAMINES

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N-Sulfinylarylamines, which have high and diverse reactivities, are widely used in organic synthesis [1-4], as well as in the chemistry of the coordination compounds of transition metals [5]. A characteristic feature of an N-sulfinylamino group bonded to an aromatic ring is its ability to display both donor and acceptor properties with respect to the ring, depending on the substituent in position 4 of the ring [6]. It would be of interest to study how the NSO group and its interaction with the aromatic ring is influenced by the replacement of hydrogen atoms in the latter by fluorine.

In the present work we studied the Raman, UV, and NMR ( $^{15}N$ ,  $^{17}O$ , and  $^{19}F$ ) spectra of the compounds C<sub>6</sub>H<sub>5</sub>NSO (I), 2-, 3-, 4-FC<sub>6</sub>H<sub>4</sub>NSO (IIa, b, c), 2,4-, 2,5-, 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSO (IIIa, b, c), and 4-XC<sub>6</sub>H<sub>4</sub>NSO (IVa-d), where X = F (a), OCH<sub>3</sub> (b), CH<sub>3</sub> (c), and CH<sub>3</sub> (d).

Consideration of the chemical shifts of nitrogen and oxygen (Table 1) shows that the introduction of the fluorine atoms into the aromatic ring of compound I results in the upfield displacement of the <sup>15</sup>N NMR signals and the downfield displacement of the <sup>17</sup>O NMR signals. This corresponds to an increase in the shielding of the nitrogen atom and the deshielding of the oxygen atom. In series of related compounds the chemical shifts of the nitrogen and oxygen atoms depends primarily on the virtual excitations in the magnetic field, which are accompanied by revolution of an electron around the nucleus, as occurs, for example, in the case of  $\sigma \leftrightarrow \pi^*$  and  $n \leftrightarrow \pi^*$  transitions. At the same time, the lower is the excitation energy and the closer is the circulation of the electron to the particular nucleus, the greater is the deshielding [7, 8]. From the data presented in Table 1 it follows that the chemical shifts of oxygen in most of the compounds studied with the exception of IIa and

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TABLE 1. Data from the NMR and UV Spectra of Compounds (I)-(VI)

	NMR data			data	
Compound	<sup>15</sup> Ν, δ, ppm	δ, ppm at 20°C	70 line- width, Hz	<sup>19</sup> F. 5. ppm (assignment of signal)	UV spectrum (λ <sub>max</sub> , nm)
(I) (IIa) (IIb) (IIc) (IIIa) (IIIb) (IIC) (IVa) (IVb) (IVc) (IVd) (V) (VI)	319,4 311,1 300,6 300,2 297,3 293,8 292,3 292,0	410 422 421 412 418 427 437 437 437 440	150 130 175 225 200 200 150 180 200	$\begin{array}{r} -48,1\\ -52,7\\ -60,5\\ -60,0({\rm F}^2), \ -53,7({\rm F}^4)\\ -46,1({\rm F}^2), \ -41,8({\rm F}^5)\\ -53,9({\rm F}^{2,6})\\ -22,2({\rm F}^{2,6}), \ -7,1({\rm F}^4),\\ -0,4({\rm F}^{3,5})*\\ -25,5({\rm F}^{2,6}), \ -7,5({\rm F}^{3,5})^{\dagger}\\ -23,9({\rm F}^{2,6}), \ -22,3({\rm F}^{3,5})^{\dagger}\\ -107,9({\rm CF}_3), \ -22,7({\rm F}^{2,3,6,6})*\\ -50,5\\ -60,8\end{array}$	315 314 312 319 324 340 346 346 346 346 356 340 338

\*Pure liquid,  $C_6F_6$  as internal reference. <sup>†</sup>Pure liquid,  $C_6F_6$  as external reference.

IIb<sup>†</sup> correlate satisfactorily with  $\lambda_{max}$  for the long-wavelength band in the UV spectrum, which undergoes a bathochromic shift upon the transition from compound II to its fluorine-containing analogs.

# $\delta^{17}O = 0.77 \lambda_{max} + 161, \quad r = 0.985, s = 2.36, n = 7.$

These findings can be explained, if we assume that the long-wavelength band in the UV spectra of the compounds studied is associated with an electronic transition between the orbital of an oxygen lone pair,  $n_0$ , lying in the plane of the  $\sigma$  skeleton ‡ and a  $\pi$ \* MO extending over the NSO group and the aromatic ring. The bathochromic shift of this band upon the transition from I, for example, to IVa is then attributed to the fact that the perfluoro effect [10] (and, similarly, the  $\pi$ -fluoro effect [11] in the case of incompletely fluorinated compounds) has no effect on the energy of  $n_0$ , which is separated from the nearest fluorine atoms by the distance of four  $\sigma$  bonds, but results in the lowering of the energy of the  $\pi$ \* MO to which the electron transition occurs. These  $n_0-\pi$ \* excitations whose energy decreases upon the transition from I to the fluorine-containing analogs, are probably the main reason for the observed deshielding of the oxygen atom.

Since the chemical shifts of the nitrogen atom do not correlate with  $\lambda_{\text{max}}$  for the longwavelength band in the UV spectrum, it may be postulated that the reason for the changes in the shielding of the <sup>15</sup>N nucleus upon the replacement of the hydrogen atoms in the molecule of N-sulfinylaniline by fluorine is different from the reason in the case of the <sup>17</sup>O nucleus. According to the theory of <sup>15</sup>N NMR [8, 12], the upfield shift may be attributed to an increase in n the electron density on the N atom, which results in a decrease in the absolute value of the paramagnetic term in the expression for the local shielding constant and thereby an increase in the shielding. Apparently, the <sup>15</sup>N NMR data presented in Table 1 are evidence that the addition of fluorine atoms to the benzene ring of N-sulfinylaniline is accompanied by an increase in the negative effective charge of the nitrogen atom.

The upfield displacement of the <sup>15</sup>N NMR signal of the nitrogen-containing aromatic compounds upon the complete replacement of the hydrogen atoms in the molecule by fluorine is a very common phenomenon [13-16]. However, examination of the data in Table 1 reveals that the <sup>15</sup>N and <sup>17</sup>O NMR spectra of the compounds studied do not show any specific perfluorination effects and that the differences between the changes in the chemical shifts of the nitrogen and oxygen atoms in N-sulfinylaniline upon the introduction of one, two, and five fluorine atoms into its molecule have only a quantitative character. At the same time, from Table 1 it follows that the influence of the relative positions of the NSO group and the fluorine atoms in the incompletely fluorinated compounds (IIa)-(IIc) and (IIIa)-(IIIc) on the <sup>15</sup>N, <sup>17</sup>O, and <sup>19</sup>F NMR chemical shifts is ambiguous and is not subject to simple interpretation.

<sup>†</sup>This is possibly due to the differences in the sequence of the MOs. <sup>‡</sup>The molecules of the N-sulfinylarylamines are found in the general case in a flat syn conformation with  $C_s$  point symmetry [9]. The NSO group is a weak acceptor [6, 17] or even a donor [18] with respect to the phenyl ring. However, as we see from Table 1, its introduction into position 4 of fluorobenzene (V) results in a 10-ppm downfield shift of the <sup>19</sup>F NMR signal. From this it follows that the NSO group already acts as a strong acceptor with respect to the 4-fluorophenyl ring. The accumulation of fluorine atoms in the aromatic ring results in changes in the direction of the mesomeric effect of the N-sulfinylamino group, which becomes a  $\pi$  donor approximately equivalent to a bromine atom with respect to the pentafluorophenyl ring in compound IVa. The latter can be evaluated from the <sup>13</sup>C NMR data on the basis of the magnitude of the difference between the relative (relative to the corresponding atoms in pentafluorobenzene) chemical shifts of the para and metal carbon atoms,  $\Delta\delta C^4 - \Delta\delta C^3$ ; the sign of this difference directly conveys the direction of the mesomeric effect of the mesomeric effect of the substituent [19]. For IVa and pentafluorobromobenzene  $\Delta\delta C^4 - \Delta\delta C^3 = -1.1$  ppm.

The replacement of the hydrogen atoms in N-sulfinylaniline by fluorine has an effect on the energy of the stretching vibrations of the NSO group. According to [9], the strong bands at 1299, 1284, and 1158 cm<sup>-1</sup> in the Raman spectrum of I are assigned to v(C-N), v(N=S), and v(S=0), respectively. When the nitrogen in IVa is replaced by the <sup>15</sup>N isotope, the bands at 1328, 1255, and 1065 cm<sup>-1</sup> in the Raman spectrum are shifted, and when the oxygen is replaced by the <sup>18</sup>O isotope, the bands at 1255, 1167, and 1065 cm<sup>-1</sup> are displaced. The greatest shift is observed in the former case for the band at 1255 and in the latter case for the band at 1167 cm<sup>-1</sup> (Table 2). A comparison of these data with the conclusions in [9] makes it possible to confidently assign the band at 1167 cm<sup>-1</sup> to a vibration with a predominant contribution from the S=O stretching vibration. The assignment of the vibrations with the participation of the nitrogen atom is complicated by their interaction with the vibrations of other fragments in the molecule.

However, in view of the data in [9], it is possible to hypothesize that the vibration at the frequency of 1328 cm<sup>-1</sup> is basically a C-N vibration, while the vibration with the frequency of 1255 cm<sup>-1</sup> is an N = S vibration. The band at 1065 cm<sup>-1</sup>, which corresponds to the bands at 1031, 1025, 1025, and 1088 cm<sup>-1</sup> in the Raman spectra of (I), (IIc), (IIIa), and (IVb), should probably be assigned to a deformation vibration involving the NSO group. The assignment of this band to  $\delta$ (C-H) in [9] seems questionable, since it is observed in the spectra of the perfluorinated analogs of (I) and undergoes an important shift on substitution of the <sup>14</sup>N isotope by <sup>15</sup>N (see Table 2).

The data reported in Table 2 suggest that the transition from (I) to (IVa) is accompanied by a slight increase in the frequency of the v(C-N) and  $v(S^2 = 0)$  vibrations and a decrease in the frequency of the  $v(N^2 = S)$  vibrations. These changes could be related to changes in the conditions of the mechanical interaction of the stretching vibrations of the N-sulfinylamine group with various vibrations of the molecule and not to changes in the force constants (bond orders) in the HSo groups.

However, a comparison of the increase in the energy of v(C-N) with the <sup>13</sup>C and <sup>15</sup>N NMR data, which points out the  $\pi$ -donor character of the NSO group in compound IVa, and the increase in the negative effective charge of the nitrogen atom upon the transition from compound I to compound IVa allow us to postulate that this transition is accompanied by redistribution of the electron density between the aryl and N-sulfinylamino groups, i.e., a decrease in the electron density in the O-S fragment and an increase in the ArN fragment, including an increase in the order of the CN bond. According to the data in [20], the effective positive charge of the sulfur atom changes to an extremely small extent upon the transition from I to IVa. In this context, it may be postulated that the principal redistribution of the electron density occurs between the ArN fragment and the oxygen atom.

In the series of compounds from IVa to IVd the substituents in position 4 of the aromatic ring influence the frequencies of the v(C-N), v(V=S), and v(S=O) stretching vibrations (see Table 2). From the data in Table 2 it also follows that the appearance of one or two fluorine atoms in the molecule of N-sulfinylaniline causes changes in the v(C-N), v(N=S), and v(S=O) frequencies, their magnitude being dependent in a complex manner on the number of fluorine atoms and their positions in the ring with respect to the NSO group.

### EXPERIMENTAL

All the NMR spectra were measured for solutions in CCl<sub>4</sub> under pulsed conditions. The <sup>17</sup>O NMR spectra were recorded with the natural content of the isotope on a Brücker CXP-300 pulse spectrometer at a frequency of 40.70 MHz. The external reference was  $D_20.0$ . The oper-

TABLE	2. V1t	orationa	I Frequei	ICLES OI	LDE NOU G	coup, c	л иг <b>*</b>	ne kaman	spectra	I OI COMPC	-(T) spund	(11)
-400	>	(UD)	-		v (N=S)			v(S=0)			Q (NSO)	
pound	NH	(O <sub>81</sub> ) N <sub>51</sub>	<u>م</u>	N <sup>51</sup>	(O <sub>81</sub> ) N <sub>51</sub>	Δv	N <sup>51</sup>	15N (18O)	Δv	N	(O81) N31	Δv
€€∰	1296 vs 1299 s 1306 vs 1310 vs	1292 m	2	1282 vs 1284 s 1294 vs	1272 S	12	1154 vs 1158 1153 s 1169 s	1154 s	4	1031 m 1034 m 1035 vs 1035 s	1030 m	4
(IIc) (IIIa)	1300 VS 1304 VS 1304	1288 s 1290 vs	12 14	1280 s 1267 vs	1270 vs 1263 w	$\frac{10}{4}$	1151 vs 1162 s 1158 s 1154 s	1161 s 1158 s	10	1025 \$ 1025 \$ 1029 \$	1014 s 1015 s	11 10
(IVa)	1328 m	1322 m (1328 m	90	1255 m	1244 w (1247 w)	<b>11</b> (8)	1167 vs	1164 s (1138 m)	3 (29)	1065 vs	1059 vs (1060 vs)	9 (2)
	1312 m 1311 m 1343 m	1305 m	2	1246 m 1243 m 1273 s	1232 m	14	1162 s 1153 vs 1129 vs	1158 s	4	1088 s 1090 w 1102 w	1081 s	2
*Data †It is	from [9 diffic	<pre>)]</pre>	determine	the post	ition of t	the ban	d due to	the overlé	aping	with thê	v(C-N) ba	.nd.

TABLE 3. Fluorine-Containing N-Sulfinylarylamines

	[		88865886
		 8	202 202 800 800 800 800 800 800 800 800
		ż	8,88,82 6,500 221 221 221 221 221 221 221 221 221 2
	alculated, 70	je.	12,10 21,71 31,54 33,78 33,78
	Ö	Ħ	2,55 2,55 1,71 1,24 1,24 1,33
		Q	45,86 45,86 41,14 41,14 34,85 37,33
		FOTILIULA	C <sub>6</sub> H <sub>4</sub> FNOS C <sub>6</sub> H <sub>4</sub> FNOS C <sub>6</sub> H <sub>5</sub> F <sub>2</sub> NOS C <sub>6</sub> H <sub>5</sub> F <sub>2</sub> NOS C <sub>7</sub> H <sub>5</sub> F <sub>2</sub> NOS C <sub>7</sub> H <sub>5</sub> F <sub>4</sub> NO <sub>2</sub> S
		<b>3</b> 2	$\begin{array}{c} 20,09\\ 20,63\\ 18,50\\ 13,54\\ 14,03\\ 14,03\\ \end{array}$
	Found, $\sigma_0$	N	9,11 9,06 8,20 5,97 6,25
		Ŀ	$\begin{array}{c} 12,37\\ 12,18\\ 21,38\\ 21,38\\ 31,84\\ 33,37\\ \end{array}$
		н	2,23 2,36 1,56 1,54 1,51
		υ	46,04 45,58 40,87 40,87 41,01 34,62 37,49
	Plaiv	'mport	922 922 932 932 932 932 932 932 932 932
	bp, °C	(p, mm Hg) mp, °C	$\begin{array}{c} 44-45 (4) \\ 64-62 (15) \\ 64-62 \\ 48-49 (4) \\ 60-61 (3) \\ 53-54 (12) \end{array}$
	Com-	punod	(ITA) (IVc)

\*Solidifies upon cooling to ~20°C.

ating conditions of the spectrometer were: pulse width, 20 µsec (90-deg pulse); time between pulses, 30 µsec; number of accumulations, 20,000-50,000. The accuracy of the measurement of the chemical shifts was  $\pm 1$  ppm. The <sup>15</sup>N NMR spectra were measured for substances 94-96% enriched with this isotope on a Bruker CXP-300 spectrometer at a frequency of 30.414 MHz. The external reference was liquid NH<sub>3</sub>. The operating conditions of the spectrometer were: pulse width, 20 µsec (90-deg pulse, 30 µsec); time between pulses, 20 µsec. The <sup>13</sup>C NMR spectra were measured on a Bruker HX-90 spectrometer at a frequency of 22.63 MHz. The internal reference was TMS. The operating conditions of the spectrometer were: pulse width, 10 µsec (90-deg pulse, 15 µsec); time between pulses, 3 µsec. The <sup>19</sup>F NMR spectra were measured on a Varian A56/60A at a frequency of 56.4 MHz. The internal reference was C<sub>6</sub>F<sub>6</sub>.

The UV spectra were recorded for solutions in n-heptane on an SF-16 spectrophotometer. The Raman spectra were obtained without a solvent on a Coderg PH-1 instrument. The source of the exciting radiation was a Spectra Physics-125 He-Ne later ( $\lambda$ exc = 6328 Å). The width of the entrance and exit slits was 4 cm<sup>-1</sup>. The mass spectrum was measured on an AEI MS-902 instrument.

Compound (I) was synthesized according to [1], (IIc) according to [6], (IIIc) according to [16], (IVa) according to [21], and (IVd) according to [20]. The remaining compounds were synthesized according to the general method in [22] from the corresponding arylamines and thionyl chloride. The boiling (melting) points and the analytical data are presented in Table 3. The compounds enriched with the <sup>15</sup>N isotope were synthesized in a similar manner.

<u>N-Sulfinylpentafluoroaniline (IVa) Enriched with the <sup>18</sup>O Isotope.</u> A mixture of 2.51 g (0.01 mole) of S,S-difluoro-N-pentafluorophenylsulfimine [21] and 1.61 g (0.01 mole) of <sup>18</sup>O-hexamethyldisiloxane, which was obtained by the hydrolysis of trimethylchlorosilane with  $H_2^{18}O$  (the enrichment with the <sup>18</sup>O isotope was 76%) according to [23], was heated for 6 h at 90°C in an Ar atmosphere in a Teflon test tube and vacuum-distilled. This yielded: a) [<sup>18</sup>O]-N-sulfinylpentafluoroaniline, yellow liquid, bp 40°C (4 mm H<sup>\chi</sup>, 0.4 g (17%) yield after four distillation cycles. For the <sup>19</sup>F NMR spectrum see Table 1. Mass spectrum: 231 ( $M_1^+$ ,  $C_6F_6NS^{18}O$ ), 229 ( $M_2^+$   $C_6F_5NS^{16}O$ ). The ratio between the intensities of the  $M_1^+$  and  $M_2^+$  peaks was 20:11, which corresponds to 65% enrichment with the <sup>18</sup>O isotope. b) Bis(pentafluorophenylthiodiimide, bp 74-75°C (4 mm Hg), mp 52°C (orange crystals), yield equal to 1.28 g. <sup>19</sup>F NMR spectrum,  $\delta$ , ppm (relative intensity): -19.8 (2), -5.8 (1), -0.2 (2) (compare [21]).

#### CONCLUSIONS

1. The replacement of the hydrogen atoms of N-sulfinylaniline by fluorine causes an increase in the shielding of the nitrogen nuclei and a decrease in the shielding of the oxygen nuclei. Apparently, the former is due to an increase in the effective negative charge of the nitrogen atom, and the latter is due to a decrease in the energy of the virtual  $n_0-\pi^*$  excitations in the magnetic field.

2. The complete replacement of the hydrogen atoms of N-sulfinylaniline by fluorine causes a small increase in the energy of the  $\nu$ (C-N) and  $\nu$ (S=O) vibrations and a decrease in the energy of the  $\nu$ (N=S) vibration.

3. A new method for the synthesis of N-sulfinylpentafluoroaniline, which makes it possible to easily introduce an <sup>18</sup>O-isotopic label into the composition of the molecule, has been found.

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INVESTIGATION OF SEVERAL α-CHLORO ETHERS BY <sup>13</sup>C AND <sup>17</sup>O NMR

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- A. V. Il'yasov, and A. N. Vereshchagin

In the series of alkyl halides and halogenated ethers, the  $\alpha$ -halo ethers are distinguished by a number of special features. The halogen atom in them has an increased mobility and a high activity in nucleophilic substitution reactions, and the C-Hal bond has a nearly ionic character [1]. The peculiarity of the electronic state of chlorine in  $\alpha$ -chloro ethers is manifested by a significant decrease in the <sup>35</sup>Cl NQR frequency  $\nu$  [2], as well as deviations of the C-O and C-Cl bond lengths from the normal values [3].  $\alpha$ -Halo ethers were not investigated sufficiently thoroughly by other physical methods.

In the present work we studied a number of  $\alpha$ -chloromethyl,  $\alpha$ -chloroethyl, and  $\alpha, \alpha$ -dichloromethyl ethers by <sup>13</sup>C and <sup>17</sup>O NMR with the natural contents of these isotopes [4, 5].

#### EXPERIMENTAL

The mono- $\alpha$ -chloro ethers were obtained by saturating a mixture of the corresponding alcohol and paraformaldehyde (in the case of the  $\alpha$ -chloromethyl ethers) or paraldehyde (in the case of the  $\alpha$ -chloroethyl ethers) with dry HCl at ~0°C [1]. The  $\alpha, \alpha$ -dichloromethyl ethers were obtained by chlorinating the alkyl formates with PCl<sub>5</sub> without a catalyst (the methyl, n-propyl, and n-butyl derivatives) or with the aid of CH<sub>3</sub>OCHCl<sub>2</sub> in the presence of HgCl<sub>2</sub> (the ethyl and isopropyl derivative) [6]. The compounds obtained were purified by vacuum distillation in an Ar atmosphere and the constants coincide with the literature values.

The <sup>13</sup>C and <sup>17</sup>O NMR spectra were recorded on a Bruker WM-250 Fourier spectrometer with a working frequency of 62.9 MHz for the <sup>13</sup>C nuclei and a working frequency of 33.9 MHz for the <sup>17</sup>O nuclei. The NMR spectra were recorded at  $\sim 25^{\circ}$ C in the case of the pure liquids in 10-mm ampuls. The stabilization was carried out relative to the external signal of the

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