SULFUR-CONTAINING CARBOXYLIC ACIDS.

5.* SYNTHESIS AND STRUCTURE OF DIALKYL SULFIDES AND DIALKYL SULFOXIDES WITH VICINAL CARBOXYL OR ACYLAMINO GROUPS

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Bifunctional sulfides and sulfoxides containing carboxy, carbamoyl, or acylamino groups in the β-position are synthesized, and their IR spectra were studied. An unusual decrease in the frequencies of the carbonyl vibrations (by 20-34 cm^{-1}) was found for thiodipropionic acid, its amides, and bis(β-acylaminoethyl) sulfides by comparison with the corresponding sulfoxides. The low-frequency shift of the CO band in these carbonylsulfides was not, as expected, associated with the intramolecular S...O coordination, since the x-ray structural investigation of thiodipropionic acid and bis(2-trifluoroacetylaminoethyl) sulfide did not show short intra- and intermolecular contacts involving the sulfur atom. Both structures contain intermolecular hydrogen bonds (C=O...HO or C=O...HN).

Keywords: *derivatives of thiodipropionic acid, 2-(acylaminoethyl) sulfides, derivatives of β,β'-sulfinyldipropionic acid, 2-(acylaminoethyl) sulfoxides, x-ray structural analysis, bis(2-trifluoroacetylaminoethyl) sulfide, molecular structure.*

Intramolecular coordination (IMC) for organosulfur compounds was first found in 1961, and was mainly studied for S-heterocycles [2-4]. Only individual examples of IMC among noncyclic sulfur compounds were described for compounds containing the S atom at the C=C multiple bond [2, 5]. Examples of the coordination interaction S(II)...O are not known for saturated compounds of sulfur. On the basis of IR spectral data, we proposed the possibility of IMC in the case of some carbonyl-substituted aliphatic sulfides [6]. In order to verify this hypothesis, a series of dialkyl sulfides and dialkyl sulfoxides containing the acylamino, carboxyl, or amide groups in the β position was obtained in the present work (cf. the scheme); their IR and PMR spectra were investigated and, for two compounds, the crystal structures were determined.

Thus, β,β'-thiodipropionic acid (**1**) was obtained by the condensation of acrylic acid with sodium sulfide, and its amides (**2-4**) and the methyl ester (**5**) were obtained by the aminolysis or alcoholysis of thiodipropionyl chloride (**23**). The described synthesis of the ester (**5**) by the heating of methyl acrylate with H_2S in the presence of quaternary ammonium hydroxide [7] is less convenient. Diethyl sulfides containing acylamino groups in the vicinal position — the compounds **6-8**, as well as the N-acylated methyl(2-aminoethyl) sulfides (**9, 10**) and the thiomorpholine (**11**), were obtained by the reaction of the aminosulfides (**24-26**) with acid chlorides or anhydrides of alkanoic acids. In the acylation of bis(2-aminoethyl) sulfide (**24**) it is better to utilize Ac_2O rather than the mixture $AcCl/Et_3N$, since this facilitates the isolation of bis(2-acetylaminoethyl) sulfide **6**. The last was only obtained previously in trace amounts as a by-product in the reaction of N-acetylethyleneimine with H_2S [8]. The synthesis of the corresponding sulfides **12-22** was performed by the oxidation of the sulfides with hydrogen peroxide. The physicochemical properties of the new sulfides **4, 8-11** and the sulfoxides **15, 17, 19-22** obtained are presented in Table 1 (see scheme below).

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*For previous communication, see [1].

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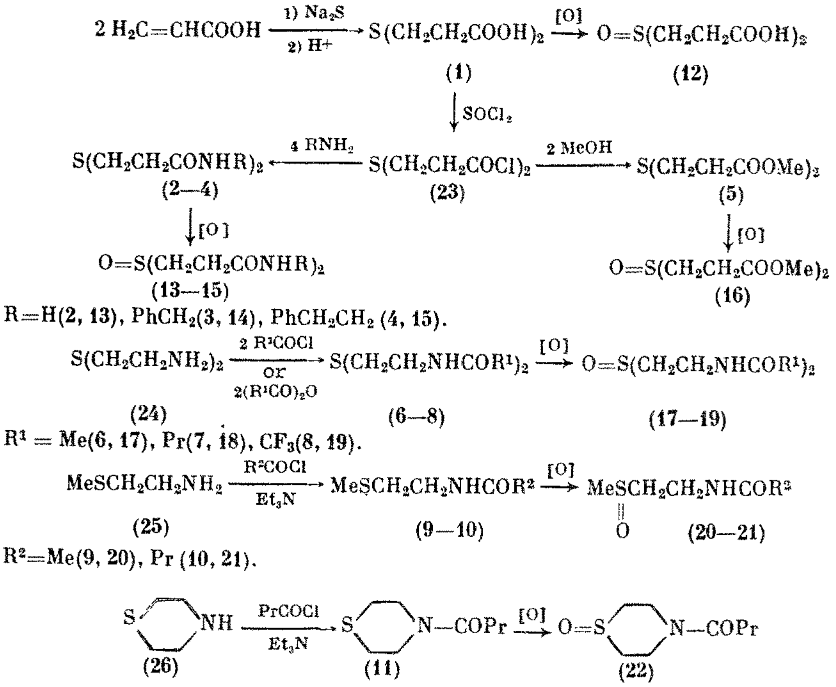
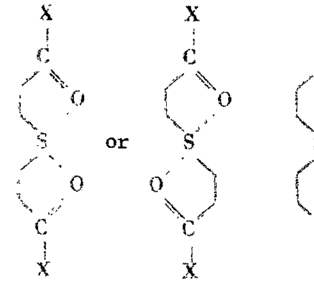


It was shown by different investigators who determined the IMC using x-ray structural analysis that the coordination interaction S(II)...O is exhibited by the low-frequency shift in the absorption of the CO group [2-4]. With the object of developing suitable models for the study of coordination bonds, we compared the IR and PMR spectra of different derivatives of sulfur-containing carboxylic acids.

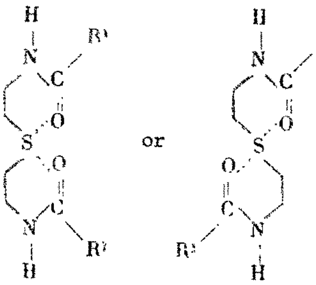
It follows from spectral data (Table 2) that, by comparison with the sulfoxide **22**, no decrease in the frequency of the carbonyl absorption is observed in the heterocyclic sulfide **11** with the fixed conformation excluding the close S...O contact. An insignificant shift in the νCO (up to 8 cm^{-1}) is shown by the unsymmetrical methyl(aminoethyl) sulfides **9-10** and the ester of thiodipropionic acid **5** by comparison with the corresponding sulfoxides **20, 21,** and **16**. The marked decrease in the carbonyl frequency (up to 34 cm^{-1}) by comparison with the sulfoxides is observed for the diethyl sulfides **1-4, 6-8** containing carboxyl, carbamoyl, or acylamino groups in the vicinal position. For the majority of the sulfoxides synthesized, the stretching vibrations of the SO bond appear in the usual [6] region (1020-1040 cm^{-1}); the decrease in the νSO for the acid **12** and the fluorine-substituted amide **19** up to 980-1000 cm^{-1} may be associated with the participation of the SO group of these compounds in the H bond.

It follows from consideration of the PMR spectra of the compounds obtained (Table 3) that when the sulfides are oxidized to the sulfoxides the methylene protons of the group adjacent to the sulfur atom become nonequivalent, and give separate multiplets, e.g., for the compounds **16, 20,** and **21**. The signal of the CH_2S groups in the heterocycle aminosulfoxide **22** is displaced to low field by ~0.15 ppm relative to the sulfide **11**. This difference is doubled ($\Delta\delta_{CH_3S}$ ~ 0.3 ppm in $CDCl_3$) for the acyclic aminosulfoxides, e.g., **17** and **21**. An analogous, but sharper, shift ($\Delta\delta_{CH_2S}$ ~ 0.6 ppm) is found for the signals of the CH_2S groups in the aminosulfoxides, e.g., **17** and **19**, in CF_3COOH by comparison with the corresponding aminosulfides **6 and 8** (see Table 3).

Therefore, the combination of the IR and PMR spectral data of the symmetrical diacylated sulfides and sulfoxides does not contradict the possible realization of the short S...O intramolecular contact according to one of the two methods for the following compounds:



X = OH(1) or NHR(2—4).



R' = Me, Pr, CF_3 (6–8).

In order to solve the problem of the IMC in these diacylsulfides, the x-ray structural investigation of β,β'-thiodipropionic acid **1*** and bis(2-trifluoroacetylaminoethyl) sulfide **8** was performed. In both structures the S atom has the angular coordination with the bond angles of 100° and 101°, respectively (Fig. 1), and does not participate in the intra- or intermolecular coordination with the carbonyl atom of O. The last forms intermolecular hydrogen bonds (IHBs). The molecules of the acid **1** are joined by the =O...H–O IHBs into infinite strips; the difference in the interatomic C_{sp^2}–O distances in the carbonyl and hydroxyl groups is regular (0.07 Å). The molecules of the amide **8** are assembled by the =O...H–N IHBs into layers; the N–C_{sp^2}–O bond angle comprises 126° and agrees with the same angle, e.g., as in N-trifluoroacetyl-1-(1-naphthyl)ethylamine [11]. The bond lengths in the molecules investigated agree well with the tabular values, particularly the S^2–C_{sp^3} bond length of 1.819 Å [12]. The distribution of the angles for C–S–C in 90 structures with the *R* factor less than 0.07, found in [9], is characterized in the range of 97-106° with the maximum of 103°, and corresponds to the values determined in this work. The S atom in **1** occurs in the particular position on the 2-axis. The torsion angles comprise 175.7° for $SC^1C^2C^3$ and 20.1° for $C^1C^2C^3O^1$ in **1**, and 180° for SC^1C^2N and 28.2° for $C^1C^2NC^3$ in **8**.

Therefore, the low-frequency shift in the absorption band of the CO group in the IR spectra of the carbonylsulfides cannot serve as a criterion for the existence of the C=O...S IMC in them, as was previously considered [2-4], and the proposition concerning this in [6] is erroneous. More suitable models for the development of the S...O IMC may be given by the *tert*-amides of thiodipropionic acid or bis(β-N-alkyl-N-acylaminoethyl) sulfides. It was found that the O atom of diacylsulfides is involved in stronger C=O...H–Y (Y = O, N) H bonds in the presence of acidic protons.

EXPERIMENTAL

The PMR spectra were obtained on the Bruker WP-200SY spectrometer (200 MHz) relative to the internal standard TMS. The IR spectra were taken using a liquid film or in tablets with KBr. The sulfides **1-3**, **7** and sulfoxides 12-14, 18 were obtained as described in [6]. Dry solvents were utilized in all experiments. The yields, constants, and the data of the elemental analysis for the new compounds **4**, **8-11**, **15**, **17**, and **19-22** are presented in Table 1. The IR spectral data for **1-22** are presented in Table 2. The PMR spectral data for **5**, **6**, **8-11**, **16**, **17**, and **19-22** are presented in Table 3. The purity of the sulfoxides was monitored titrimetrically by the reductive method, as described in [13].

Di-(2-phenylethylamide) of β,β'-Thiodipropionic Acid (4). To 6 g (0.028 mole) of the diacid chloride of β,β'-thiodipropionic acid **23** [6] in 100 ml of CH_2Cl_2 at 0°C was added 13.5 g (0.117 mole) of 2-phenylethylamine in 50 ml of CH_2Cl_2. On the following day, the precipitated residue (13.4 g) was filtered, washed with water, and dried over P_2O_5. The yield of 4.3 g of **4** was obtained; **4** had mp 138°C. The concentration of the filtrate (CH_2Cl_2) gives 5.5 g more of **4** with mp 134°C. The total yield of **4** is 9.8 g.

Dimethyl Ester of β,β'-Thiodipropionic Acid (5). To 8 g (0.037 mole) of **23** was added 100 ml of absolute MeOH, and the mixture was maintained for 1 h at 20°C prior to boiling for 2 h using a reflux condenser. Distillation gave 5.85 g (76%) of **5** with bp 66-68°C (0.02 mm) and n_D^{20} 1.4769 (see [7]).

Bis(2-acetylaminoethyl) Sulfide (6). To the solution of 8 ml (0.088 mole) of Ac_2O in 12 ml of C_6H_6 at 5-10°C was added 4.8 g (0.04 mole) of bis(2-aminoethyl) sulfide **24** [6]. The mixture was maintained for 1 h at 5°C and for 1 h at 20°C. The precipitated residue (4.5 g) was filtered off, and the mother liquor was diluted with ether. A further portion, 2.4 g, of the residue was obtained. The total yield of **6** was 6.9 g (84.5%); mp 100°C (see [8]).

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*After the work was carried out, the structure **1** was found in the Cambridge bank of structural data [9] (see [10]).

TABLE 1. Physicochemical Properties of the New Compounds

Compound	Yield, %	mp, °C; bp, °C (p, mm of Hg stem)	n_D T, °C)	Found/Calculated, %				Empirical formula
				C	H	N	S	
4	91	150–151 alcohol–water) 1 : 1	–	69.25/68.75	6.99/7.29	7.73/7.29	–	$C_{22}H_{28}N_2O_2S$
8	81	90 (alcohol–water) 1 : 1)	–	30.96/30.76	3.11/3.20	8.97/8.97	–	$C_8H_{10}F_6N_2O_2S$
9	84	120–122 (3)	1.5010(27)	44.76/45.11	8.36/8.27	–	–	$C_5H_{11}NOS$
10	72	140 (5)	1.4925(24)	–	–	8.57/8.69	19.77/19.87	$C_7H_{15}NOS$
11	83	95–97 (0.025)	1.5240(22)	55.36/55.49	8.91/9.24	–	18.95/18.49	$C_8H_{16}NOS$
15	77	177–178 (alcohol or alcohol–water) 1:1	–	66.01/66.00	6.93/7.00	7.15/7.00	–	$C_{22}H_{28}N_2O_3S$
17	84	180–181 (alcohol)	–	43.59/43.63	7.29/7.27	12.74/12.72	–	$C_8H_{16}N_2O_3S$
19	97	165–167 (alcohol)	–	29.52/29.26	3.19/3.04	8.73/8.53	–	$C_8H_{10}F_6N_2O_3S$
20	84	74–76 (alcohol–ether)	–	39.86/40.27	7.06/7.38	9.01/9.40	–	$C_5H_{11}NO_2S$
21	85	59–60; >100 (0.04)	–	47.53/47.45	8.52/8.47	7.87/7.91	18.30/18.08	$C_7H_{15}NO_2S$
22	90	93–94 (acetone–ether)	–	50.84/50.79	7.96/7.93	7.36/7.40	–	$C_8H_{18}NO_2S$

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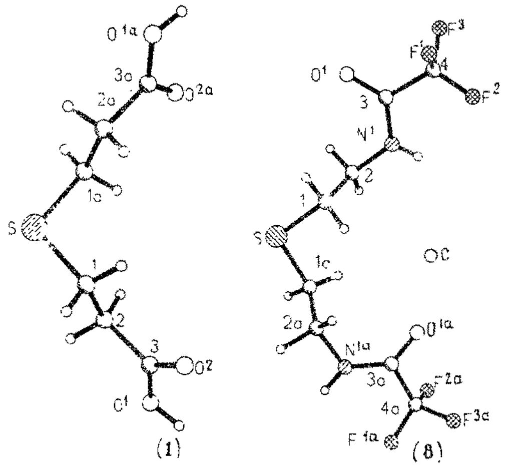
*On standing, it hardens into a low-melting white mass.

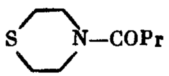


(1) (8)

Fig. 1. Configuration of molecules **1** and **8**.

Bis(2-trifluoroacetylaminoethyl) Sulfide (8). To 23.8 g (0.113 mole) of $(CF_3CO)_2O$ in 40 ml of the 1:1 mixture C_6H_6–ether was added the solution of 6.2 g (0.052 mole) of **24** in 18 ml of C_6H_6. After 2 h (20°C), the residue was filtered and washed with ether. The yield of **8** was 13.1 g.

TABLE 2. Data of the IR Spectra (ν, cm^{-1}) of the Bifunctional Sulfides **3-13** and the Sulfoxides **14-24** Corresponding to Them

Sulfide		CO	NH	Other bands	Sulfoxide	CO	NH	SO	Other bands	ΔνCO *
$S[(CH_2)_2COOH]_2$	(1)	1698	–	2500–3300 (OH) 1255 (C–O)	**12**	1730	–	980	2500–3300 (OH) 1238 (C–O)	32
$S[(CH_2)_2CONH_2]_2$	(2)	1643	3207, 3408	–	**13**	1677	3195, 3370	1038	–	34
$S[(CH_2)_2CONHCH_2Ph]_2$	(3)	1628	3260	1555–1570 (Ar+CON)	**14**	1639	3300	1020	1547–1552 (Ar+CON)	11
$S[(CH_2)_2CONH(CH_2)_2Ph]_2$	(4)	1645	3320	1545, 1560 (Ar+CON)	**15**	1670	3320	1040	1560, 1575 (Ar+CON)	25
$S[(CH_2)_2COOMe]_2$	(5)	1730	–	1180, 1210 (C–O); 1365, 1445, 2968 (Me)	**16**	1738	–	1050	1190, 1210 (C–O); 1380, 1450, 2968 (Me)	8
$S[(CH_2)_2NHCOMe]_2$	(6)	1640	3103, 3268	1570–1588 (CON) 1380, 2930, 2990 (Me)	**17**	1655	3110, 3300	1026	1558–1572 (CON); 1375, 2947, 2978 (Me)	15
$S[(CH_2)_2NHCOPr]_2$	(7)	1630–1640	3076, 3260	1555–1565 (CON) 1385, 2940–2970 (Me)	**18**	1642–1661	3100, 3300	1013	1555–1568 (CON); 1450, 2940, 2970 (Me)	12÷21
$S[(CH_2)_2NHCOCF_3]_2$	(8)	1710	3320	1580 (CON) 1170–1230 (C–F)	**19**	1730	3330	1000	1570 (CON); 1160–1240 (C–F)	20
$MeS(CH_2)_2NHCOMe$	(9)	1645–1661	3300	1540–1575 (CON); 1380, 2930, 2990 (Me)	**20**	1650–1668	3300	1030	1560–1570 (CON); 1380, 1450, 2950 (Me)	6
$MeS(CH_2)_2NHCOPr$	(10)	1646	3300	1555 (CON)	**21**	1649	3310	1030	1560 (CON); 1450 2945, 2980 (Me)	3
	(11)	1660	–	1375, 2930, 2975 (Me)	**22**	1640	–	1022	1375, 1470 (Me)	–20

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*The shift in the frequency of the sulfoxide in relation to the sulfide.

TABLE 3. Data of the PMR Spectra of the Sulfides **7**, **8**, **10-13** and Sulfoxides **18**, **19**, **21-24** (δ, ppm, *J*, Hz)

Compound	CH_3	CH_2S	CH_2C	CH_2N	NH
5[a]	3.71 s	2.81—2.87 m	2.62—2.69 m	—	—
6[a]	2.08 s	2.73 t $J_{CH_2-CH_2} = 6.5$	—	3.50 q $J_{CH_2-CH_2} = 6.5$	6.75 br.s
6[b]	2.60 s	2.95 t $J_{CH_2-CH_2} = 6.5$	—	3.84 q $J_{CH_2-CH_2} = 6.5$	8.73 narrow t
8[a]	—	2.80 t $J_{CH_2-CH_2} = 6.3$	—	3.58 q $J_{CH_2-CH_2} = 6.3$	6.71 br.s
8[b]	—	2.50 t $J_{CH_2-CH_2} = 12.9$	—	3.34 q $J_{CH_2-CH_2} = 12.9$	7.47 narrow t
9[a]	2.12 s (MeS) 2.24 s (AcN)	2.72 t $J_{CH_2-CH_2} = 8.6$	—	3.51 q $J_{CH_2-CH_2} = 8.6$	7.36 br.s
10[a]	0.94 t (Me—C), $J_{CH_3-CH_2} = 7.3$; 2.14 s (MeS)	2.65 t $J_{CH_2-CH_2} = 7.3$	2.21 t (CH_2CO) $J_{CH_2-CH_2} = 7.3$ 1.67 sextet (CH_2Me)	3.46 q $J_{CH_2-CH_2} = 7.3$	7.24 br.s
11[a]	1.02 t $J_{CH_3-CH_2} = 8.1$	2.66 narrow q (CH_2SCH_2) $J_{CH_2S-CH_2N} = 5.8$	2.36 t (CH_2CO) $J_{CH_2-CH_2} = 8.1$ 1.70 sextet (CH_2Me)	3.79 t 3.92 (CH_2NCH_2) $J_{CH_2N-CH_2S} = 5.8$	—
16[a]	3.80 s	2.86 — 3.01 m (H^A) 3.18 — 3.51 m (H^B)	2.92 q	—	—
17[a]	2.05 s	2.99 m (H^A) 3.11 m (H^B)	—	3.78 q $J_{CH_2-CH_2} = 6.5$	6.44 br.s 7.26 s
17[b]	2.42 s	3.55 $J_{CH_2-CH_2} = 6.5$	—	4.13 q $J_{CH_2-CH_2} = 6.5$	8.42 narrow t
19[b]	—	3.11 t $J_{CH_2-CH_2} = 6.35$	—	3.67 narrow q	7.84 narrow t
20[a]	2.05 s (AcN) 2.71 s (MeSO)	2.79 — 2.95 m (H^A) 3.05 — 3.37 (H^B)	—	3.70 — 3.95 m	7.11 br.s 7.34 s
21[a]	0.94 t (Me—C) $J_{CH_3-CH_2} = 8.5$ 2.65 s (MeSO)	2.79 m (H^A) 3.09 m. (H^B)	2.17 t (CH_2CO) $J_{CH_2-CH_2} = 7.3$ 1.65 sextet (CH_2Me)	3.73 m	7.14 narrow t
22[a]	1.03 t $J_{CH_3-CH_2} = 8.1$	2.60—3.07 m (CH_2SOCH_2)	2.40 narrow sextet (CH_2CO) 1.74 sextet (CH_2Me)	3.68 — 4.63 m. (CH_2NCH_2)	—

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[a] Spectrum taken in $CDCl_3$.

[b] Spectrum taken in CF_3COOH.

Methyl 2-Acetylaminoethyl Sulfide (9). To the solution of 7.4 g (0.08 mole) of methyl 2-aminoethyl sulfide **25** [14] in 50 ml of ether at 0°C was added 8.21 g (0.08 mole) of Et_3N in 70 ml of ether followed by 6.38 g (0.08 mole) of AcCl. After 12 h the residue of $Et_3N \cdot HCl$ was filtered (10.7 g). The mother liquor was concentrated, and the residue was distilled. The yield of 9 g of **9** was obtained.

Methyl-2-*n*-Butyrylaminoethyl Sulfide (10). This compound was obtained from **25**, butyryl chloride, and Et_3N by analogy with **9**.

N-(*n*-Butyryl)thiomorpholine (11). This compound was obtained from thiomorpholine **26**, butyryl chloride, and Et_3N by analogy with **9**.

Di-(2-phenylethylamine) of β,β′-Sulfinyldipropionic Acid (15). This compound was obtained from 0.014 mole of **4** in 1.8 ml of 30% H_2O_2 in the mixture of acetone (0.5 liter) and AcOH (20 ml) by analogy with **14** [6].

Dimethyl Ester of β,β′-Sulfinyldipropionic Acid (16). This compound was obtained from **5** according to [15]. The yield was ~100%; mp 65-66°C (cf. [15]).

TABLE 4. Coordinates ($\times 10^4$, or $\times 10^3$ for H) and Equivalent ($Å^2 \times 10^3$) Thermal Factors in the Structure **1**

Atom	x	y	z	U_{eq}
S	0	2108(1)	1/4	34(1)
O^1	-1344(1)	7463(3)	211(1)	49(1)
O^2	798(1)	8769(2)	790(1)	45(1)
C^1	625(2)	4415(3)	1792(1)	32(1)
C^2	-719(2)	5271(3)	1313(1)	35(1)
C^3	-341(2)	7337(3)	745(1)	30(1)
$H^{1.1}$	136(2)	352(4)	148(1)	43(4)
$H^{1.2}$	112(2)	596(4)	202(1)	41(4)
$H^{2.1}$	-116(2)	369(4)	106(1)	47(5)
$H^{2.2}$	-151(2)	609(4)	162(1)	53(5)
$H^{1.0}$	-115(3)	879(8)	-8(2)	99(9)

TABLE 5. Coordinates ($\times 10^4$, or $\times 10^3$ for H) and Equivalent ($Å^2 \times 10^3$, or $\times 10^2$ for H) Thermal Factors in the Structure of **8**

Atom	x	y	z	U_{eq}
S	582(2)	9022(2)	7294(2)	45(1)
F^1	726(8)	8436(5)	486(7)	99(3)
F^2	1116(6)	7705(8)	693(7)	119(4)
F^3	-645(7)	6849(4)	580(7)	82(2)
F^{1a}	7034(5)	10130(9)	8302(9)	140(4)
F^{2a}	7128(6)	8719(4)	7356(14)	152(5)
F^{3a}	7487(6)	10024(9)	6300(10)	144(4)
O^1	1415(4)	7678(4)	3140(7)	43(2)
O^{1a}	4953(5)	9500(4)	5627(6)	36(2)
N^1	822(6)	7823(5)	3401(7)	34(2)
N^{1a}	4440(6)	9967(5)	7829(7)	33(2)
C^1	613(7)	8962(6)	5404(8)	37(2)
C^2	795(8)	7872(6)	4914(9)	37(3)
C^3	280(7)	7720(5)	2672(9)	31(2)
C^4	103(8)	7697(6)	1082(10)	45(3)
C^{1a}	2352(7)	8981(7)	7685(9)	43(3)
C^{2a}	2987(7)	10017(6)	7582(9)	34(2)
C^{3a}	5246(7)	9692(5)	6821(9)	30(2)
C^{4a}	6732(7)	9615(6)	7238(10)	40(2)
$H^{1.1}$	32(7)	921(5)	516(8)	4(2)
$H^{1.2}$	132(7)	951(5)	511(7)	3(2)
$H^{2.1}$	142(7)	759(5)	533(7)	3(2)
$H^{2.2}$	2(7)	743(5)	526(7)	3(2)
$H^{1.6}$	153(6)	781(4)	304(6)	0(1)
H^{4a1}	234(7)	869(6)	870(8)	3(2)
H^{4a2}	280(6)	841(5)	717(8)	2(2)
H^{2a1}	288(7)	1037(6)	673(9)	4(2)
H^{2a2}	260(8)	1070(6)	833(9)	5(2)
H^{2a6}	463(7)	1011(6)	877(8)	3(2)

Bis(2-acetylaminoethyl) Sulfoxide (17). This compound was obtained from 0.02 mole of **6** and 4 ml of 20% H_2O_2 in the mixture of acetone (150 ml) and AcOH (15 ml) by analogy with **14** [6].

General Method for the Isolation of the Acylaminosulfoxides (19-22). To the solution of 0.02 mole of the sulfide **8-11** in 60 ml of AcOH was added 4 ml of 20% H_2O_2 (0.022 mole). On the following day the reaction mixture was concentrated in vacuo. The residue was crystallized or distilled; the data on the compounds are presented in Tables 1-3.

X-ray Structural Investigation. Monocrystals of the acid **1** were obtained as follows. A hot solution of 0.3 g of the substance in 15 ml of ethyl acetate was placed in a heated bath (78°C), the temperature of which was gradually lowered to 20°C. After 12 h, the precipitated crystals (0.12 g) were separated on a filter and dried in vacuo over P_2O_5. The mp was 132-133°C. Monocrystals of **8** were grown by the slow evaporation of the solution of 0.04 g of the substance in 6 ml of $CHCl_3$ (20°C, 9 days) or 0.4 g of the substance in 10 ml of the 1:2:1 mixture of AcOH–ether–petroleum ether (4°C, 6 days).

The x-ray diffraction investigation of transparent crystals of **1** and **8** was performed at −80°C on the Siemens RZ/RS automatic diffractometer using the λMoK_α, a graphite monochromator, and $\theta/2\theta$ scanning in the range 2θ = 2-45° for **1** and 3-56° for **8**. The crystals of **1** are thrombic with the space group *Pbcn; a* = 8.649(2), *b* = 5.061(1), and *c* 18.071(4) Å, *V* =

TABLE 6. Bond Lengths in the Molecules **1** and **8** (d, Å)

Bond	1	8
$S-C^1$	1.814(1)	1.825(8)
$S-C^{1a}$	1.814(1)	1.814(8)
C^1-C^2	1.512(2)	1.504(12)
C^2-C^3	1.502(2)	–
C^2-N^1	–	1.462(11)
$C^{2a}-N^{1a}$	–	1.476(9)
N^1-C^3	–	1.316(10)
$N^{1a}-C^3$	–	1.314(10)
C^3-O^1	1.226(2)	1.224(8)
C^3-O^2	1.299(2)	–
$C^{3a}-O^{1a}$	–	1.215(10)
C^3-C^4	–	1.545(12)
F^1-C^4	·	1.281(11)
F^2-C^4	–	1.319(10)
F^3-C^4	–	1.277(13)
$F^{1a}-C^{4a}$	–	1.262(10)
$F^{2a}-C^{4a}$	–	1.293(12)
$F^{3a}-C^{4a}$	–	1.235(9)

TABLE 7. Bond Angles in the Molecules **1** and **8** (φ, deg)

Angle	1	8
$C^1—S—C^{1a}$	99.9(1)	101.0(4)
$S—C^1—C^2$	111.0(1)	110.9(6)
$S—C^{1a}—C^2$	111.0(1)	112.1(6)
$C^1—C^2—C^3$	115.1(1)	-
$O^1—C^3—C^2$	113.4(1)	
$O^2—C^3—C^2$	122.7(1)	–
$O^2—C^3—O^1$	123.9(1)	-
$C^1—C^2—N^1$	-	111.0(7)
$C^{1a}—C^{2a}—N^{1a}$	–	111.7(6)
$C^2—N^1—C^3$	–	121.5(7)
$C^{2a}—N^{1a}—C^{3a}$	–	119.8(7)
$O^1—C^3—N^1$	–	125.9(8)
$O^{1a}—C^{3a}—N^{1a}$	–	127.6(7)
$N^1—C^3—C^4$	–	115.9(6)
$N^{1a}—C^{3a}—C^{4a}$	–	114.6(7)
$F^1—C^4—C^3$	–	112.0(7)
$F^2—C^4—C^3$	–	113.7(7)
$F^3—C^4—C^3$	–	109.5(7)
$F^{1a}—C^{4a}—C^{3a}$	–	114.1(7)
$F^{2a}—C^{4a}—C^{3a}$	–	113.2(6)
$F^{3a}—C^{4a}—C^{3a}$	–	110.7(7)
$F^1—C^4—F^2$	–	109.1(8)
$F^1—C^4—F^3$	–	105.0(7)
$F^2—C^4—F^3$	–	107.0(8)
$F^{1a}—C^{4a}—F^{2a}$	–	110.3(10)
$F^{1a}—C^{4a}—F^{3a}$	-	102.2(8)
$F^{2a}—C^{4a}—F^{3a}$	-	105.3(9)

791.0(3) Å^3, $Z = 4$, $d_{calc} = 1.496$ g/cm^3. The crystals of **8** are rhombic with the space group $Pna2_1$; $a = 10.015(2)$, $b = 12.987(3)$, and $c = 9.650(2)$ Å, $V = 1255.1(5)$ Å^3, $Z = 4$, $d_{calc} = 1.652$ g/cm^3. Both structures were decoded by the direct method and specified by the complete-matrix MLS in the anisotropic approximation up to $R = 0.034$, $R_W = 0.045$ from the 838 reflections of **1**, and up to $R = 0.052$, $R_W = 0.048$ from the 1008 reflections of **8** with $|F| > 4\sigma$. The atoms of H in both structures were localized in the difference synthesis, and were specified isotropically. Calculations were performed on an IBM personal computer using the SHELXTL PLUS programs.

The general form of the molecules **1** and **8** is given in Fig. 1. The coordinates and thermal parameters of the atoms, the bond lengths, and the bond angles are given in Tables 4-7.

REFERENCES

1. T. P. Vasil'eva, V. M. Bystrova, O. V. Kil'disheva, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 6, 1303 (1986).
2. A. A.Espenbetov, Candidate's Dissertation, Chemical Sciences, Institute of Heteroorganic Compounds (INÉOS), Moscow (1986), p. 67.
3. W. Walter, B. Krische, and G. Adiwidjaja, *Chem. Ber.*, **111**, No. 5, 1685 (1978).
4. W. Walter, B. Krische, and G. Adiwidjaja, *Liebigs. Ann. Chem.*, No. 1, 14 (1980).
5. A. Kucsman and I. Kapovits, *J. Mol. Struct.*, **125**, No. 3/4, 331 (1984).
6. V. V. Znamenskii, A. D. Efremov, V. M. Bystrova, and T. P. Vasil'eva, *Khim. Farm. Zh.*, No. 8, 942 (1986).
7. L. Gershbein and C. Hurd, *J. Am. Chem. Soc.*, **69**, No. 2, 241 (1947).
8. R. Kuhn, G.Quadbeck, and E. Röhm, *Chem. Ber.*, **86**, No. 4, 468 (1953).
9. *Cambridge Crystallographic Database, Release* (1989).
10. K. Prout and S. Hernandez-Casson, *Acta Cryst., (B),* **38**, No. 1, 338 (1982).
11. S. Weinstein and L. Leiserowitz, *Acta Cryst., (B)*, **36**, No. 6, 1406 (1980).
12. F. Allen, O. Kennard, D. Watson, L. Brammer, A. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2,* No. 12, S1 (1987).
13. S. Allenmark, *Acta Chem. Scand.*, **20**, No. 3, 910 (1966).
14. J. Lydon and E. Deutsch, *Inorg. Chem.*, **21**, No. 8, 3180 (1982).
15. C. Armstrong and G. Scott, *J. Chem. Soc. (B),* No. 9, 1747 (1971).