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Structure and Intramolecular Hydrogen Bonds in Bis(trifluoromethylsulfonylamino)methane and *N*-[(Trifluoromethylsulfonyl)aminomethyl]acetamide

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Abstract—Bis(trifluoromethylsulfonylamino)methane in an inert medium exists as an equilibrium mixture of monomeric forms with various types of intramolecular hydrogen bonds, whose population depends on the polarity of the medium. The energetically most favorable form is a symmetrical form containing two N–H···O=S bonds. Less stable are the isomer with two N–H···F–C bonds and the unsymmetrical isomer with two different hydrogen bonds. *N*-[(Trifluoromethylsulfonyl)aminomethyl]acetamide contains one intramolecular intramolecular N–H···O=C hydrogen bond and preserves ability for self-association.

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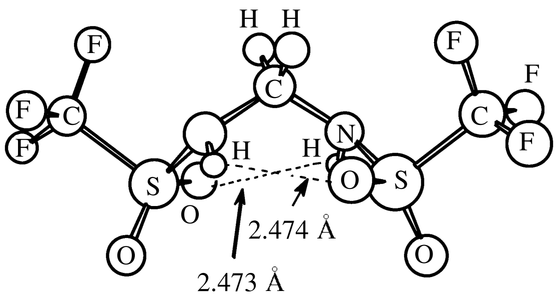
Crystalline methanesulfonamide forms cyclic dimers that combine in infinite tapes by means of strong intermolecular S=O···H–N hydrogen bonds [1]. Cyclic dimers of this compound and its *N*-methyl and *N*-benzyl derivatives are also formed in solutions and are present in equilibrium with monomers [2–4]. Perfluroalkanesulfonamides are stronger NH acids, and their self-associates even exist in the gaseous state.

The supramolecular structure of perfluroalkanesulfonamides depends on the medium. Hence trifluoromethanesulfonamides in inert solvents form cyclic and chain dimers, as well as cyclic trimers and tetramers; therewith, the relative contents of the different forms of self-associates depend on the polarity of the solvent [5, 6]. In inert solvents, *N*-methyltrifluoromethanesulfonamides exist as equilibrium mixtures of cyclic and chain dimers [7]. Proceeding with the research into the molecular and supramolecular structure of perfluoroalkanesulfonamides [5–7], in the present work we synthesized bis(trifluoromethylsulfonylamino)methane $CF_3SO_2NHCH_2NHSO_2CF_3$ (**I**), *N*,*N*-bis[(trifluoromethylsulfonyl)aminomethyl]trifluoromethanesulfonamide $CF_3SO_2N(CH_2NHSO_2CF_3)_2$ (**II**), and *N*-(trifluoromethylsulfonyl)aminomethyl]acetamide $CF_3\cdot SO_2NHCH_2NHCOCH_3$ (**III**) and studied their acidity and supramolecular structure by potentiometric titration, IR spectroscopy, dielcometry, and quantum-chemical calculations (B3LYP/6-31G*). Unlike perfluoroalkanesulfonamides we studied in [5–7], compounds **I**–**III** can form both inter- and intramolecular hydrogen bonds. The main goal of the research was to detect intramolecular hydrogen bonds and to establish their nature and effect on the supramolecular structure of the synthesized compounds.

The acidity constants of amides **I** and **III**, and, for the sake of comparison, unsubstituted compound **IV** and *N*-methyltrifluoromethanesulfonamide (**V**) in water and methanol were determined by potentiometric titration. The pK_a of amide **I** in water and of amide **II** in water and methanol could not be determined because of partial hydrolysis of these compounds under titration conditions.

R in $CF_3SO_2(NHR)$ (Comp. no.)	pK_a	
	H_2O	MeOH
$CH_2NHSO_2CF_3$ (**I**)	–	10.76
$CH_2NHCOCH_3$ (**III**)	6.25	10.11
H (**IV**)	6.33 [8]	11.06
CH_3 (**V**)	7.56 [9]	12.70

Comparison of the pK_a values in methanol shows that the acidity of amides **I** and **III** is determined not only by the electron-acceptor properties of the substituent R at the nitrogen atom of the trifluoromethanesulfonylamide group. Actually, amide **I** is less acidic by 0.65 pK_a units than amide **III**, even though the

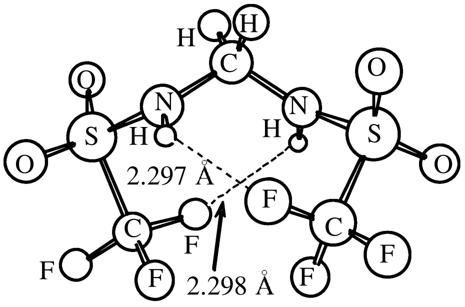


Ia

C_{2v}, 0 kJ mol^{-1}, μ 4.12 D

ν(NH) 3532 cm^{-1} (26)

ν(NH) 3532 cm^{-1} (123)

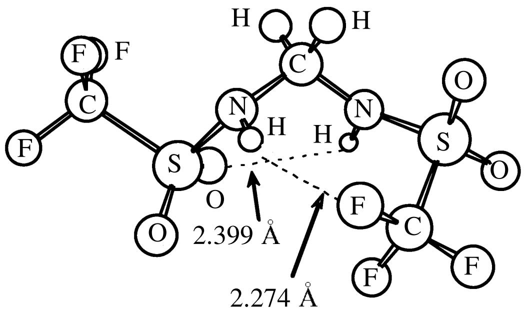


Ib

C_{2v}, 8.45 kJ mol^{-1}, μ 0.91 D

ν(NH) 3587 cm^{-1} (112)

ν(NH) 3587 cm^{-1} (17)



Ic

5.69 kJ mol^{-1}, μ 2.97 D

ν(NH) 3558 cm^{-1} (77)

ν(NH) 3557 cm^{-1} (65)

Fig. 1. Structure of compounds **Ia**–**Ic** (here and in Fig. 2, values in parentheses relate to intensities of vibration transitions).

CF_3SO_2 group is a stronger electron acceptor (σ_n 0.93) than CH_3CO (δ_n 0.50) [10]. Moreover, contrary to what might be expected, the pK_a values of amides **I** and **V** differ from each other by almost 2 pK_a units. Consequently, an important factor that can affect the structure of the amides in solution can be nonbonded interactions of different amido groups of the same molecule.

Quantum-chemical calculations showed that the potential energy surface of amide **I** contains three minima. The global minimum belongs to form **Ia** (Fig. 1), that has the highest dipole moment (μ 4.12 D) and two intramolecular N–H···O=S hydrogen bonds. The symmetry of this form is C_{2v}. Its rotation axis coincides with the bisector of the internal NCN angle. The nonbonded distance $l_{O\cdots H}$ in form **Ia** is shorter than the sum of the van der Waals radii of the O and H atoms by 0.13 Å. Form **Ib** with the same symmetry is less favored by energy (by 8.4 kJ mol^{-1}) and differs from form **Ia** by the orientation of the trifluoromethylsulfonyl group; it has a lower dipole moment (μ 0.91 D) and contains two N–H···F–C hydrogen bonds. The nonbonded distance $l_{F\cdots H}$ in form **Ib** is shorter than the sum of the van der Waals radii of the F and H atoms by 0.25 Å. Unsymmetrical form **Ic** has intermediate energy (5.69 kJ mol^{-1}) and dipole moment (2.97 D) because of the presence of two different intramolecular hydrogen bonds N–H··· O=S and N–H···F–C. The nonbonded distances $l_{O\cdots H}$ and $l_{F\cdots H}$ in form **Ic** are slightly shorter than those in forms **Ia** and **Ib**. The structures of forms **Ia**–**Ic** are shown in Fig. 1. It should be noted that their relative positions on the energy scale depend neither on the calculation method nor on the basis, kJ mol^{-1} [B3LYP/6-311++G**: 7.78 (**Ib**) and 3.77 (**Ic**); MP2/6-31G*//HF/6-31G*: 11.80 (**Ib**) and 5.52 (**Ic**)].

The geometric parameters and vibration frequencies of trifluoromethanesulfonamide and trifluoromethanesulfonic acid, calculated previously by the DFT method (B3LYP/6-31G* and B3LYP/6-31G**) fairly fitted the experimental values. A good qualitative fit of calculation to experiment was also obtained for the ν(NH) frequencies of compounds with intra- and intermolecular bonds [7, 12]. Therefore, in what follows we used calculated vibration frequencies in the analysis of the IR spectra.

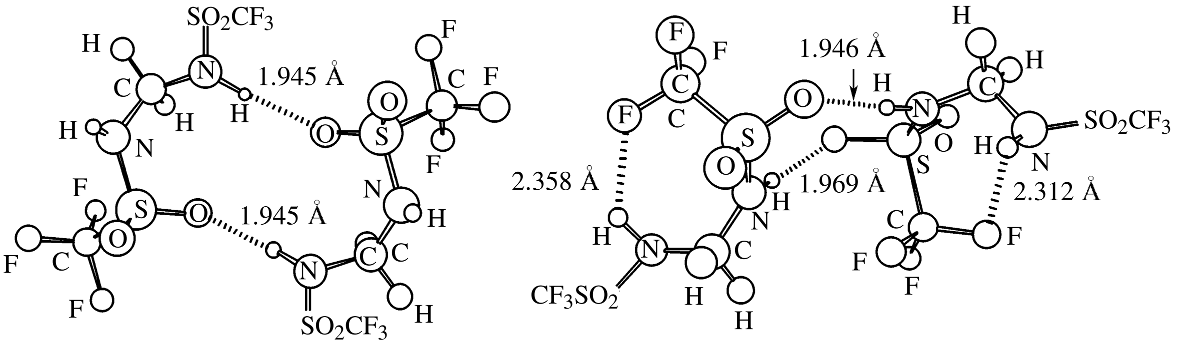
The calculated ν(NH) values of different forms of amide **I** increase in the order **Ia** < **Ic** < **Ib**. Noteworthy is the fact that the two NH vibration frequencies of unsymmetrical form **Ic** are equal to each other, whereas the nonbonded distance F···H is shorter than O···H. Moreover, even though the $l_{F\cdots H}$ distance in form **Ib** is shorter than the $l_{O\cdots H}$ distance in form **Ia**, the ν(NH) value for the first form is higher by 55 cm^{-1}. Such a variation of the vibration frequencies of the NH bonds involved in intramolecular hydrogen bonding most probably results from two effects: Definite configuration of the N–H and C–F bonds in forms **Ib** and **Ic** and varied configuration of bonds at the nitrogen atom. Below are given quantitative characteristics whose analysis provides evidence for this suggestion. The pyramidality of the nitrogen atom is characterized by the sum of its bond angles ($\Sigma\alpha_i$). The $\Sigma\alpha_i$ value for the reference compound, monomeric amide **V**, is 352°, and its ν(NH) is 3560 cm^{-1}.

	N–H···O=S			N–H···F–C		
	$l_{O\cdots H}$, Å	$\Sigma\alpha_i$, deg	ν(NH), cm^{-1}	$l_{F\cdots H}$, Å	$\Sigma\alpha_i$, deg	ν(NH), cm^{-1}
Ia	2.473	345	3532	–	–	–
Ib	–	–	–	2.297	357	3587
Ic	2.399	355	3558	2.274	345	3557

Let us examine the effect of pyramidality of the nitrogen atom. As the latter flattens, ν(NH) increases irrespective of the nature of the nonbonded contact (N–H···O=S or N–H···F–C). Therewith, in forms Ia and **Ic** this occurs, even though the $l_{O\cdots H}$ distance in **Ic** is shorter than in **Ia**. The same effect of nitrogen piramidality on ν(NH) is observed in symmetrical forms **Ia** and **Ib**. At the same time, in unsymmetrical form **Ic** both ν(NH) frequencies are equal to each other, in spite of the different nonbonded distances and pyramidalities of the nitrogen atoms. Apparently, this is explained by the fact that the formation of an intramolecular N–H···F–C bond shifts ν(NH) to larger values. Previously such a blue shift of ν(XH) was revealed in numerous experimental and theoretical studies on hydrogen bonds involving the fluorine atom (see [13, 14] and references therein). It is also explained by the repulsive interaction between the proton-donor and protonacceptor components of the H-complex, which results in contraction of the X–H bond and, as a result, increases its vibration frequency.

The calculations expected in the IR spectrum of compound **I** three equidistant ν(NH) bands belonging to forms **Ia**–**Ic**. The relative intensity of the expected bands should be independent of the concentration of the form, but, in view of the different polarities of these forms, should be strongly dependent of the ability of the medium to nonspecific solvation. Along with this theoretical prediction, we used in the analysis of the experimental IR spectrum the information on the ν(NH) band of monomeric *N*-methyltrifluoromethanesulfonamide CF_3SO_2NHMe (**V**). The calculated ν(NH) of the monomer is 3560 cm^{-1}, i.e. it almost the same as that for form **Ic**. This is explained by the similarity of the configurations of the nitrogen atoms in form **Ic** and in monomer **V** (vide supra). Furthermore, comparison of the $\Sigma\alpha_i$ and ν(NH) values for monomers **V** and **Ib** provides evidence for the possibility of the blue shift on N–H···F–C bond formation.

The IR spectra of amide I were studied in the gas phase, in the solid state, and in solvents of various polarity. The IR spectra of compound **I** (KBr, Nujol), like the spectrum of amide **V** (thin film), contain a strong single band at 3330 cm^{-1}, belonging to NH vibrations of self-associates. The gas-phase spectra of compound **I** (400–450 K) display two bands with maxima at 3500 and 3405 cm^{-1}. They are located almost symmetrically around the band of free NH groups of monomeric amide **V** in the gas phase (3445 cm^{-1} [7]). Such location of the absorption bands fits the calculation results only for forms **Ia** and **Ib** (Fig. 1). Two bands are also observed in the spectra of solutions of compound **I** in CCl_4 (3475 and 3378 cm^{-1}) and benzene (3410 and 3305 cm^{-1}). The absorption band of monomeric amide **V** in the spectra of its solutions, like in the gas-phase spectra, is located between them (3407 cm^{-1} in CCl_4 and 3327 cm^{-1} in C_6H_6) but closer to the low-frequency component. The ratio of the integral intensities of the absorption bands in the spectra of solutions of amide **I** is independent of the concentration of the solution (10^{-2}–10^{-3} M in CCl_4 and C_6H_6) and depends only slightly on temperature (297 and 338 K in C_6H_6). The calculated relative energies of the three monomeric forms of amide **I** suggest that increasing temperature should increase the intensity of the high-frequency band that belongs to the least stable form **Ib**. Furthermore, as noted above, the IR spectrum would be expected to contain the third intermediate bend from form **Ic**. The fact that the experimental spectrum did not meet these prompted us to discuss an alternative hypothesis according to which the observed



Id

μ 1.14 D
ν(NH) 3473 cm^{-1} (976)
ν(NH) 3555 cm^{-1} (79)

Ie

μ 1.14 D
ν(NH) 3448 cm^{-1} (915)
ν(NH) 3559 cm^{-1} (58)

Fig. 2. Structure of compounds **Id** and **Ie**.

bands belong to a very strong cyclic dimer of amide **I** rather than to its monomeric forms.

According to the calculations, the two cyclic dimeric forms of amide **I** (Fig. 2) are very close in energy: The energies of their formation from the most stable monomer **Ia** are 30.84 (**Id**) and 27.74 kJ mol^{-1} (**Ie**). In this case, the low-frequency band in the gas-phase spectra of amide **I** and its solutions should relate to the NH groups that close the ring in the dimer by forming N–H···O=S hydrogen bonds. The high-frequency band should then be assigned to a superposition of the bands due to free NH groups of the self-associate in form **Id** and the NH group involved in the N–H···F–C intramolecular hydrogen bonds in cyclic dimer **Ie** (Fig. 2). The calculated differences between the ν(NH) values for forms **Id** and **Ie** are 82 and 111 cm^{-1}, respectively, which is close to the gas-phase value (95 cm^{-1}).

However, there are some facts contradictory of the above assignment. First, the intensity ratio of the two observed absorption bands of amide **I** are very strongly dependent on the polarity/polarizability of the medium, measured by the Kamlet–Taft π^* parameter [15, 16]. Thus, in the spectrum of a solution of amide **I** in $CHCl_3$ (π^* 0.58), the high-frequency band (3440 cm^{-1}) is much stronger than the low-frequency band (3348 cm^{-1}), unlike what is observed in CCl_4 (π^* 0.28). In the highly polar CH_2Cl_2 (π^* 0.82), the ν(NH) range contains a single low-frequency band shifted red by 30 cm^{-1} with respect to the absorption band of free NH groups of amide **V** (3378 cm^{-1} in CH_2Cl_2). Such trends are only possible if the dimers in question decompose to give monomer **Ia** in the polar medium. However, this casts doubt on the assumption on the high strength of the dimers. Second, the spectra of solutions of amide **V** in CCl_4 and CH_2Cl_2 contain bands from both its monomers and dimers, whose intensity ratio is concentration- and temperature-dependent. It is important that the calculated energy of formation of the cyclic dimer of amide **V**, 51.71 kJ mol^{-1} [7], is much higher than those of cyclic dimers **Id** and **Ie**. Third, the IR spectra of solutions of compound **II** structurally related to amide **I** show single bands (3355 and 3320 cm^{-1}, respectively) irrespective of the polarity of the medium (CCl_4, CH_2Cl_2). Obviously, these bands belong to only one form containing two intramolecular hydrogen bonds of close strength. The spectra of the dimers of amide **II** should inevitably contain at least two absorption bands. The aforesaid suggests that the cyclic dimers of compounds **I** and **II** are unstable toward decomposition into monomers. In this case, the absence of concentration dependence of the relative intensity of bands in the spectra of CCl_4 solutions of amide **I** up to a high degree of dilution (up to 10^{-4} M). Moreover, the assumption on the presence of strong cyclic dimers does not solve the problem of the intermediate band that should also be present in their spectra. Actually, the difference of the ν(NH) frequencies that relate to the N–H···O=S fragment, for monomers **Ia** and **Ic** and dimers **Id** and **Ie** is the same (~25 cm^{-1}).

Thus, the bands observed in the spectra of solutions of amide **I** belong to their monomeric forms that are in dynamic equilibrium with each other. In a high-polarity medium, form **Ia** is preferred. In a nonpolar medium (gas, CCl_4, C_6H_6), form Ib with a low dipole moment exists along with **Ia** and **Ic**. This follows from a detailed analysis of the spectrum of compound **I** in benzene at 297 K. The two observed bands each had a well-defined asymmetry on the high-frequency branch. We could resolve both bands into two Lorentz components (Fig. 3). Two components of the high-frequency band (3406 and 3431 cm^{-1}, 297 K) relate to a specifically and a nonspecifically solvated monomeric form **Ib**. The composite nature of this band is indirectly evidenced by the lack of linear correlation between the position of its maximum in inert media and the Kamlet–Taft π^* parameter and by the high-frequency shift of this maximum with temperature (by 10 cm^{-1} from 297 to 338 K). Two components of the low-frequency band (3320 and 3301 cm^{-1}, 297 K) are associated with N–H vibrations of forms **Ic** and **Ia**, respectively. Like in the previous case, the position of the maximum is not linearly related to π^*. At the same time, the ν(NH) of amide **V** in inert media varies linearly with π^*.

$$\nu(\mathrm{NH}) = (3410 \pm 1) - (31 \pm 2)\pi^*$$
$$R\ 0.985,\ sd\ 4,\ n\ 8$$

Media	π^*	ν(NH), cm^{-1}	Media	π^*	ν(NH), cm^{-1}
Gas	–1.10	3445	CCl_4	0.28	3407
Hexane	–0.08	3412	$CHCl{=}CCl_2$	0.53	3393
Heptane	–0.02	3413	CH_2Cl_2	0.82	3380
Cyclohexane	0.00	3405	$CHCl_2CHCl_2$	0.95	3384

As follows from the aforesaid, compound **I** exists in solutions as a complex equilibrium mixture of monomeric forms. The shift of the low-frequency band in the spectra of amide **I** to lower ν(NH) values compared with amide **V** is primarily explained intramolecular N–H···O=S hydrogen bonding. The high-frequency shift of the second band is associated with intramolecular N–H···F–C hydrogen bonding.

It should be noted that the maxima of the components of the low-frequency band, belonging to forms **Ia** and **Ic**, is 23 cm^{-1} at 338 K, which almost coincides with calculation (26 cm^{-1}). By contrast, the difference in the ν(NH) of the components corresponding to forms **Ia** and **Ib**, varies from 105 (297 K) to 95 cm^{-1} (338 K) and is much higher than the calculated value (55 cm^{-1}). Roughly the same relations are observed between the mutual positions of the ν(NH) bands of monomers **V** and **Ib**. The calculated Δν(NH) of 27 cm^{-1} is much lower that experimental: 55 (gas), 68 (CCl_4), 83 (C_6H_6), and 66 cm^{-1} ($CHCl_3$). Therefore, it is not excluded that the calculation fails to reproduce sufficiently correctly the blue shift for the form of amide **I**, containing two intramolecular N–H···F–C hydrogen bonds. Furthermore, as seen from the above data, this effect is to a certain degree contributed by the solvating ability of the solvent.

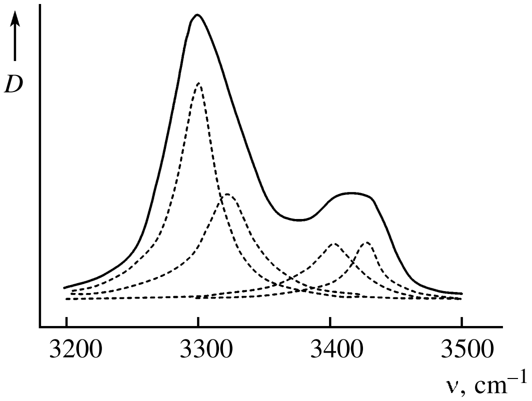
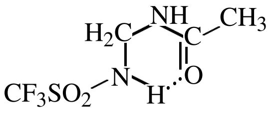
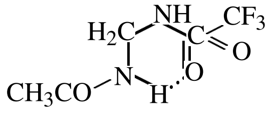


Fig. 3. N–H vibration bands in the IR spectrum of a solution of compound **I** in benzene at 338 K (solid line); components are shown by dashed lines.

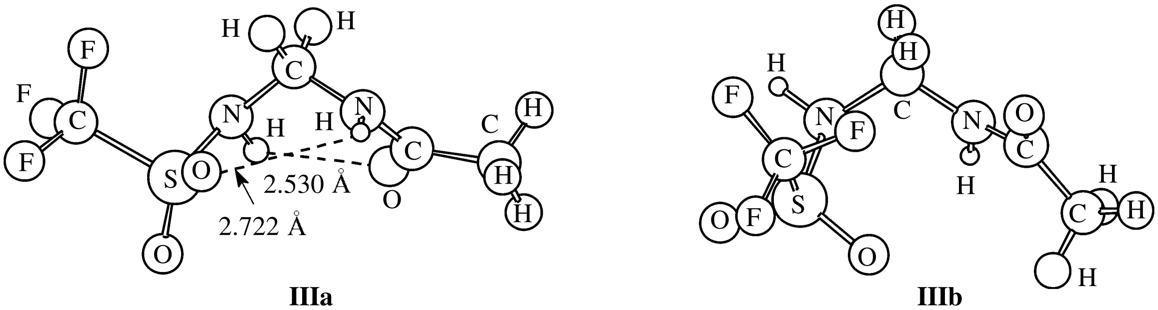
The dipole moment of amide **I** in benzene at 297 K is 2.9 D. This fact provides evidence for the existence in nonpolar media of equilibrium between monomers **Ia**–**Ic** whose calculated dipole moments vary from 1 to 4 D. As the temperature of the solution is elevated to 318 K, the μ value changes only slightly (3.1 D), which does not contradict the IR data that reveal equilibrium between the monomeric forms of amide **I**.

Amide **III** might be assumed to have two forms with intramolecular N–H···O=C and N–H···O=S hydrogen bonds (see below).





However, this assumption is not confirmed by calculations. The potential energy surface of amide **III** contains two minima: global for form **IIIa** and local for a much less stable (by 25.40 kJ mol^{-1}) form **IIIb** (Fig. 4) that lacks short contacts between electrondonor and electron-acceptor fragments. The N–H···O=C and N–H···O=S nonbonded distances in form **IIIa** are 2.530 and 2.722 Å, respectively, which provides evidence for the formation of one hydrogen bond N–H···O=C. The formation of this bond, like with amide **I**, decreases by 30– 40 cm^{-1} the ν(NH) frequency (3531 cm^{-1}) compared with the ν(NH) frequencies of the $NHSO_2CF_3$ group of form **IIIb** (3569 cm^{-1}) or amide **V** (3560 cm^{-1}). The carbonyl absorption frequency, too, shifts to 1780 and 1810 cm^{-1} (**IIIa** and **IIIb**, respectively). Free NH group of the NHCOMe groups in these forms have almost the same absorption frequencies: 3614 and 3608 cm^{-1} (**IIIa** and **IIIb**, respectively). Thus, the IR spectrum of monomer **IIIa** should contain two absorption bands separated by ~80 cm^{-1} from each other.



IIIa **IIIb**

Fig. 4. Structure of compounds **IIIa** and **IIIb**.

The IR spectra of a solid sample of compound **III** (KBr, Nujol) show absorption bands of the NH and C=O groups (3290 and 1650 cm^{-1}, respectively) involved in strong intermolecular hydrogen bonds. The spectrum of the same compound in CCl_4 (10^{-2} M and higher) contains three NH absorption bands: strong at 3300 cm^{-1} and at 3375 and 450 cm^{-1}. The carbonyl absorption region contains a broad band with well-defined maxima at 1658 and 1695 cm^{-1}. When the concentration is below 10^{-3} M, the lowest frequency NH band disappears to leave two equal intensity bands centered at 3450 (NHCOMe) and 3375 cm^{-1} ($NHSO_2CF_3$). Concurrently, the low-frequency band of the carbonyl group disappears. These changes together suggest that the equilibrium between homo-associates and monomers is shifted to the latter. The high-frequency band relates to free NH groups of compound **III**. It locates at 3450–3480 cm^{-1} characteristic of a wide range of secondary alkylamides [17]. The low-frequency shift of about 30 cm^{-1} of the NH band of the $NHSO_2$ fragment (3375 cm^{-1}) compared with amide **V** (3407 cm^{-1}) is explained by the formation of an intramolecular CO···HN hydrogen bond in form **IIIa**.

Thus, compound **I** containing two intramolecular hydrogen bonds exists in inert media as a monomer exclusively. In this respect this compound differs from amides **IV** and **V** whose monomers in analogous conditions exist in equilibrium with self-associates. Compound **III** with one intramolecular N–H···O=C bond preserves capacity for self-association.

EXPERIMENTAL

The IR spectra were measured in KBr, Nujol, and solutions on a Specord IR-75 spectrophotometer. The dielectric constants were measured on a Sh2-5 instrument (Angarsk, Design Office of Automation Joint-Stock Company) at 1 MHz. The dipole moments were calculated by the Higasi formula [18]. The acidity constants of amides **I**–**III** were determined by potentiometric titration in water and/or methanol, titrant 0.1 N NaOH in the corresponding solvent. Quantum-chemical calculations were performed using GAUSSIAN-98 [19].

Bis(trifluoromethylsulfonylamino)methane (I). Paraform, 0.6 g, was in small portions to a vigorously stirred mixture of 6 g of trifluoromethanesulfonamide and 40 ml of conc. H_2SO_4. The mixture was stirred for 1 h at room temperature and then poured into an ice-cold water. The precipitate that formed was filtered off, washed with cold water, dried, and treated with a 2 : 1 mixture of ether and hexane. The extract was filtered, and the filtrate was evaporated to obtain 2.2 g (35%) of amide **I**, mp 120°C (decomp.). ^1H NMR spectrum (CD_3CN), δ, ppm: 4.71 s (2H, CH_2), 7.76 br.s (2H, NH). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 53.22 (CH_2), 120.34 q (CF_3, J_{CF} 319.9 Hz). ^{19}F NMR spectrum (CD_3CN), δ_F, ppm: –79.31. Found, %: C 12.08; H 1.34; N 9.18; S 20.98. $C_3H_4F_6N_2O_4S_2$. Calculated, %: C 11.62; H 1.30; N 9.03; S 20.67.

***N,N*-Bis[(trifluoromethylsulfonyl)aminomethyl]-trifluoromethanesulfonamide (II)** was prepared in a similar way but at the trifluoromethanesulfonamide : Paraform ratio of 4 : 3. A suspension of trifluoromethanesulfonamide in H_2SO_4 was heated to 40°C; therewith, the amide dissolved. After Paraform was added, the reaction mixture was stirred for 4 h at 40°C and for 20 h at room temperature, and then it was treated as described above. Reaction products insoluble in hexane–ether, 1 : 2, were separated to isolate amide **II**, mp 136°C. ^1H NMR spectrum (CD_3CN), δ, ppm: 4.99 d (4H, CH_2, *J* 6.4 Hz), 7.86 br.t (2H, NH). 13C NMR spectrum (CD_3CN), δ_C, ppm: 57.89 (CH_2), 120.21 q (CF_3SO_2N, J_{CF} 321.3 Hz), 120.50 q (CF_3SO_2NH, J_{CF} 320.0 Hz). ^{19}F NMR spectrum (CD_3CN), δ_F, ppm: –76.42 (1F), –78.06 (2F). Found, %: C 13.38; H 1.31; F 35.95; N 9.35; S 20.41. $C_5H_6F_9N_3O_6S_3$. Calculated, %: C 12.74; H 1.28; F 36.28; N 8.92; S 20.41.

***N*-[(Trifluoromethylsulfonyl)aminomethyl]acetamide (III).** Acetonitrile, 2.8 ml, was added dropwise to a stirred mixture of 10 ml of 85% H_3PO_4, 3 g of trifluoromethanesulfonamide, and 1.33 g of Paraform. The mixture was heated to 65–70°C and then it self-heated to 93°C. The mixture was stirred for 4 h at 90–95°C, cooled, poured into a mixture of 100 ml of an ice-cold water and 20 ml of conc. NH_4OH. The solution was made neutral and extracted with diethyl ether (3×20 ml). The ether extract was washed with a saturated NaCl solution, dried with $MgSO_4$, the solvent was removed, and the residue was recrystallized from a 10 : 1 mixture of hexane and 2-propanol to obtain 1.6 g (36%) of compound **III**, mp 123–124°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.03 s (3H, CH_3), 4.61 m (2H, CH_2), 6.46 br.s (1H, $NHSO_2$), 7.14 br.s (1H, NHCO). ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.95 s (3H, CH_3), 4.65 m (2H, CH_2), 8.19 s (1H, $NHSO_2$), 8.76 s (1H, NHCO). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 22.47 (CH_3), 49.42 (CH_2), 120.61 q (CF_3, *J* 320.5 Hz), 171.61 (C=O). ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: –78.26. Found, %: C 22.16; H 3.08; F 25.29; N 12.52. $C_4H_7F_3N_2O_3S$. Calculated, %: C 21.82; H 3.20; F 25.89; N 12.72.

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