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Reactions of Trifluoromethanesulfonamide with Amides and Paraformaldehyde

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Abstract—Two- and three-component condensations of paraformaldehyde with trifluoromethanesulfonamide, acetamide, trifluoroacetamide, 1*H*-benzotriazole, methanesulfonamide, and malonamide were studied. *N*-Hydroxymethyl derivatives of trifluoroacetamide and 1*H*-benzotriazole reacted with trifluoromethanesulfonamide to give *N*-(trifluoroacetylaminomethyl)- and *N*-(1*H*-benzotriazol-1-ylmethyl)-substituted derivatives of trifluoromethanesulfonamide, as well as *N*,*N*′-methylenebis(trifluoromethylsulfonamide) and *N*-(trifluoromethylsulfonylaminomethyl)trifluoroacetamide as transamination products. Three-component condensation of trifluoromethanesulfonamide with paraformaldehyde and methanesulfonamide led to the formation of 1-methylsulfonyl-3,5-bis(trifluoromethylsulfonyl)hexahydro-1,3,5-triazine, and the reaction of trifluoromethanesulfonamide with paraformaldehyde and malonamide gave 4,10-bis(trifluoromethylsulfonyl)-2,4,8,10-tetraazaspiro-[5.5]undecane-1,7-dione whose structure was proved by X-ray analysis.

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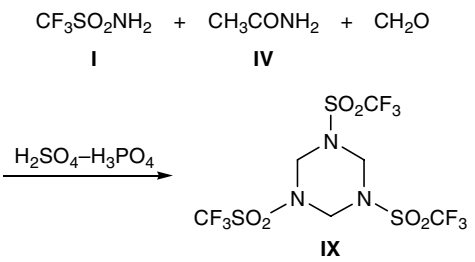
Condensations of carboxamides $RC(O)NH_2$ with formaldehyde and other aldehydes R′CHO were shown [1–3] to give *N*-(α-hydroxyalkyl)amides RC(O)NHCH(R′)OH and *N*,*N*′-alkylidenebisamides $[RC(O)NH]_2CHR'$. In the reversible reaction of acetamide with formaldehyde, *N*-(hydroxymethyl)acetamide $CH_3CONHCH_2OH$, *N*,*N*′-oxydimethylenediacetamide $(CH_3CONHCH_2)_2O$, and *N*,*N*′-methylenediacetamide $(CH_3CONH)_2CH_2$ were detected by NMR spectroscopy [1, 4]. The formation of *N*,*N*′-alkylidenediamides is catalyzed by sulfuric [2] or trifluoromethanesulfonic acid [3]. *N*-Hydroxymethyl derivatives of sulfonamides readily undergo disproportionation and polymerization [1]; however, alkane- and arenesulfonamides smoothly react with formaldehyde to give *N*-sulfonyl-substituted hexahydro-1,3,5-triazines, dihydro-1,3,5-dioxazines, and tetrahydro-1,3,5-oxadiazines [2, 5].

We previously studied the reaction of trifluoromethanesulfonamide (**I**) with paraformaldehyde and found that, depending on the conditions, it leads to the formation of a number of linear and cyclic products [6]. The major linear product is *N*,*N*′-methylenedi(trifluoromethanesulfonamide) (**II**) [6]. The three-component condensation of trifluoromethanesulfonamide with acetamide and paraformaldehyde gave a mixed analog of **II**, *N*-(trifluoromethylsulfonylaminomethyl)-acetamide (**III**) [6]. In continuation of these studies, in the present work we examined some two- and three-component condensations involving paraformaldehyde, amide **I**, and acetamide (**IV**), trifluoroacetamide (**V**), 1*H*-benzotriazole (**VI**), methanesulfonamide (**VII**), and malonamide (**VIII**).

As shown in [6], the reaction of amide **I** with paraformaldehyde is very sensitive to the temperature, reaction time, and reactant ratio. Likewise, the results of three-component condensation of amide **I** with paraformaldehyde and acetamide (or acetonitrile) strongly depended on the conditions. In 96% H_2SO_4 (acetamide) or 85% H_3PO_4 (acetonitrile) mixed condensation product **III** was obtained. When the reaction of **I** with paraformaldehyde and acetamide was performed in 92% sulfuric acid in the presence of P_2O_5 (the amount of the latter corresponded to complete binding of water present in 92% sulfuric acid; i.e., the reaction occurred in a mixture of anhydrous sulfuric and phos-

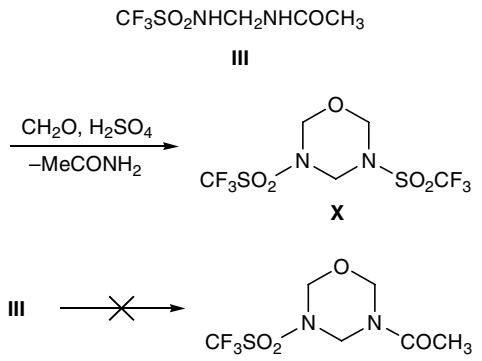
phoric acids), the major product was previously described 1,3,5-tris(trifluoromethylsulfonyl)hexahydro-1,3,5-triazine (**IX**) [6] rather than compound **III** (Scheme 1). No acetamide condensation products were detected in the reaction mixture.

Scheme 1.



Our attempt to effect cyclization of previously prepared compound **III** via reaction with paraformaldehyde resulted in the formation of known symmetric compound **X** instead of expected unsymmetrically substituted oxadiazine (Scheme 2). Obviously, the reaction involves transamination with liberation of acetamide.

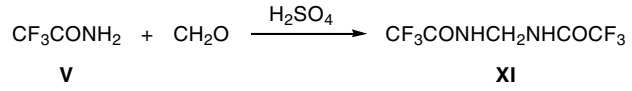
Scheme 2.



Hydroxymethylation of amides is very sensitive to the hydroxymethylating agent [1]. *N*,*N*′-Methylenediacetamide $(CH_3CONH)_2CH_2$ cannot be obtained by reaction of acetamide with trioxane, chlorodimethyl ether, or bis(chloromethyl) ether; it is formed only when urotropin is used as source of CH_2O [7]. Amidomethylation of arenes with urotropin in trifluoroacetic acid is accompanied by side formation of acid decomposition products such as trifluoroacetamide (**V**) and *N*,*N*′-methylenedi(trifluoroacetamide) [8].

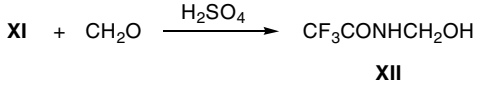
With a view to compare the behavior of sulfonamides and carboxamides in the hydroxymethylation processes, trifluoroacetamide (**V**) was brought into reaction with paraformaldehyde at a ratio of 2:1 in concentrated sulfuric acid. Unlike compound **I** [6], trifluoroacetamide with paraformaldehyde did not produce cyclic compounds like **IX** or **X**, and the only identified and isolated product was *N*,*N*′-methylenedi(trifluoroacetamide) (**XI**) (Scheme 3).

Scheme 3.



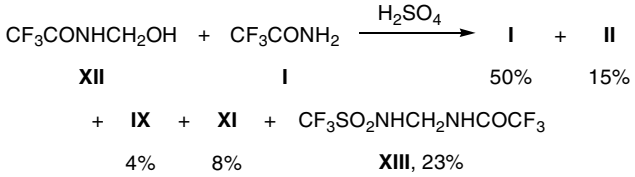
We failed to effect cyclization of compound **XI** by reaction with paraformaldehyde in sulfuric acid; instead, *N*-hydroxymethyltrifluoroacetamide (**XII**) was obtained (Scheme 4). The yield of **XII** was poor (the conversion was only ~50% in 3 h), but it can be readily separated from unreacted initial bis-amide **XI** and purified by sublimation.

Scheme 4.



The synthesis of compound **XII** via hydroxymethylation of trifluoroacetamide was reported in [1, 9]; it was also used as amidomethylating agent [9–13]; however, we found no published spectral parameters of this compound. We examined the reaction of *N*-hydroxymethyltrifluoroacetamide (**XII**) with trifluoromethanesulfonamide (**I**) with a view to obtain *N*-(trifluoromethylsulfonylaminomethyl)trifluoroacetamide (**XIII**). According to the NMR data, this reaction led to a mixture of products (Scheme 5).

Scheme 5.

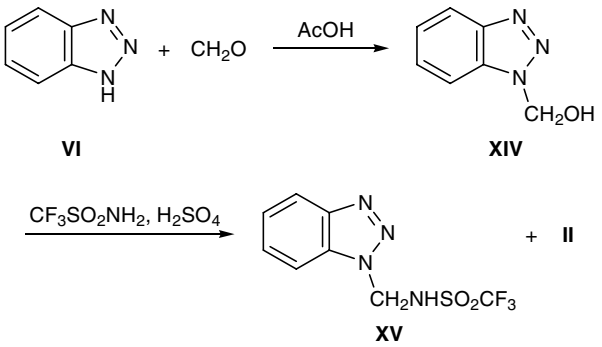


Unreacted sulfonamide **I** and a part of bis-sulfonamide **II** were removed by washing the product mixture with water. In keeping with the relative signal intensities in the ^1H ad ^{19}F NMR spectra, the residue contained ~60% of target product **XIII**, ~30% of **XI**, ~5% of **IX**, and ~5% of **II**. Compounds **I**, **II**, **IX**, and **XI** were identified in the product mixture by comparing the ^1H, ^{13}C, and ^{19}F NMR signals with those of authentic samples obtained in [6] and in the present work. *N*-(Trifluoromethylsulfonylaminomethyl)trifluoroacetamide (**XIII**) was identified on the basis of almost complete coincidence of the ^1H and ^{13}C signals

from the methylene group with the corresponding signals of its closest analog, *N*-(trifluoromethylsulfonylaminomethyl)acetamide (**III**) [6]. The chemical shifts of the methylene carbon atoms in compounds **II**, **IX**, **XI**, **XIII**, and **III** are quite characteristic (δ_C 53.22, 61.9, 45.3, 49.3, and 49.4 ppm, respectively [6]); therefore, the assignment based thereon seems to be reliable.

It is known that three-component reaction of 1*H*-benzotriazole with sulfonamides and aldehydes leads to 1-(organylsulfonylaminoalkylidene)benzotriazoles [14]. For example, 1-(methylsulfonylaminomethyl)-1*H*-benzotriazole was obtained by reaction of methanesulfonamide with formaldehyde and 1*H*-benzotriazole or by condensation of methanesulfonamide with 1-hydroxymethyl-1*H*-benzotriazole [14]. We have found that 1-hydroxymethyl-1*H*-benzotriazole (**XIV**) reacts with trifluoromethanesulfonamide in a similar way to give mixed condensation product (**XV**). According to the ^{1}H NMR data, more than 30% of *N*,*N*′-methylenebis(trifluoromethanesulfonamide) (**II**) is also formed (Scheme 6).

Scheme 6.



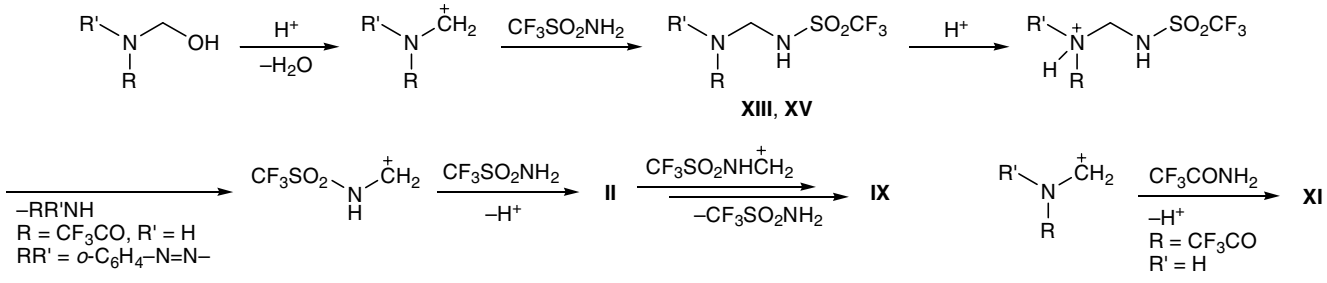
The formation of compound **II** can be avoided by carrying out one-pot three-component condensation of 1*H*-benzotriazole with paraformaldehyde and trifluoromethanesulfonamide (**I**) on slight heating; in this case, a small amount of compound **IX** was formed, and the major product was *N*-(1*H*-benzotriazol-1-ylmethyl)trifluoromethanesulfonamide (**XV**). Hexahydrotriazine **IX** is readily separated from compound **XV** by recrystallization from methanol, where the latter is readily soluble. Like other N-substituted trifluoromethanesulfonamides, *N*-(1*H*-benzotriazol-1-ylmethyl)trifluoromethanesulfonamide (**XV**) is a strong NH acid. Its pK_a value in methanol is equal to 11.08, i.e., it is almost similar to that of trifluoromethanesulfonamide itself (pK_a 11.06 [15]).

The formation of compound **II** in addition to **XIII** and **XV** in the reactions shown in Schemes 5 and 6, as well as of compounds **IX** and **XI** in the first of these, seems to be surprising, for the reaction mixtures contained no free formaldehyde. Obviously, both reactions include partial transamination of initially formed compounds **XIII** and **XV**, as shown in Scheme 7. Unlike the reaction with *N*-hydroxymethyltrifluoroacetamide (Scheme 5), no symmetric product like $(RR'N)_2CH_2$ (analogous to **XI**) was formed in the reaction with 1-hydroxymethyl-1*H*-benzotriazole. The reason is that 1*H*-benzotriazole liberated during the process (Scheme 7) gives a salt with concentrated sulfuric acid and is thus excluded from further reacting.

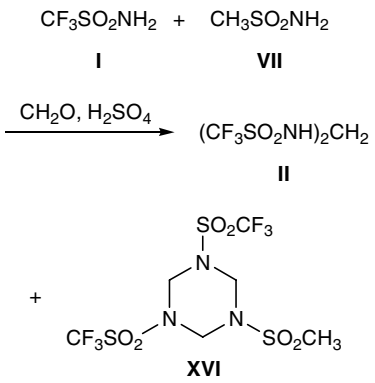
Mixed cyclic condensation product, 1-methylsulfonyl-3,5-bis(trifluoromethylsulfonyl)hexahydro-1,3,5-triazine (**XVI**, a close analog of **IX**), was formed together with linear product **II** in the reaction of an equimolar mixture of trifluoromethanesulfonamide (**I**) and methanesulfonamide (**VII**) with paraformaldehyde in concentrated sulfuric acid (Scheme 8). The ratio of compounds **II** and **XVI** before separation was ~5:1. Compound **II** was washed off from the product mixture with diethyl ether–hexane (2:1), and column chromatography of the residue gave individual compound **XVI**.

The structure of **XVI** is confirmed by the presence in its ^{13}C NMR spectrum of a signal at δ_C 41 ppm from the CH_3SO_2 group, a quartet at δ_C 120 ppm from the CF_3 carbon atom, and two closely located methylene

Scheme 7.



Scheme 8.



carbon signals at δ_C 61.2 and 61.9 ppm with an intensity ratio of 2:1. The ^{1}H NMR spectrum recorded at room temperature contained two signals: a singlet from the methylsulfonyl group at δ 3.1 ppm and a very broad singlet at δ 5.3 ppm from the methylene protons, their intensity ratio being 1:2. Temperature variation leads to splitting of the latter signal into separate signals from axial and equatorial protons in the six-membered ring; thise data indicate that heteroring **XVI** (like compound **IX**) is conformationally labile [16].

Unexpectedly, in the three-component condensation of malonamide (**VIII**) with trifluoromethanesulfonamide (**I**) and paraformaldehyde we isolated a high-melting substance which showed in the ^{1}H NMR spectrum a singlet at δ 8.8 ppm from NH proton and two *AB* quartets at δ 4.0 and 4.8 ppm. The ^{13}C NMR spectrum contained two signals at δ_C 50–56 ppm from methylene carbon atoms, a quartet signal from CF_3 group, and a signal at δ_C 165 from amide carbonyl carbon atom. In the IR spectrum of this compound we observed a carbonyl absorption band at 1680 cm^{-1}, i.e., at a frequency typical of linear amides. On the basis of the above data, the product was assumed to have a cyclic structure containing C(O)NH and CF_3SO_2N fragments. Its structure was finally proved by X-ray analysis as 4,10-bis(trifluoromethylsulfonyl)-2,4,8,10-tetraazaspiro[5.5]undecane-1,7-dione (**XVII**); obviously, it was formed via three-component condensation involving not only both amide groups of initial malonamide but also its activated methylene group as shown in Scheme 9.

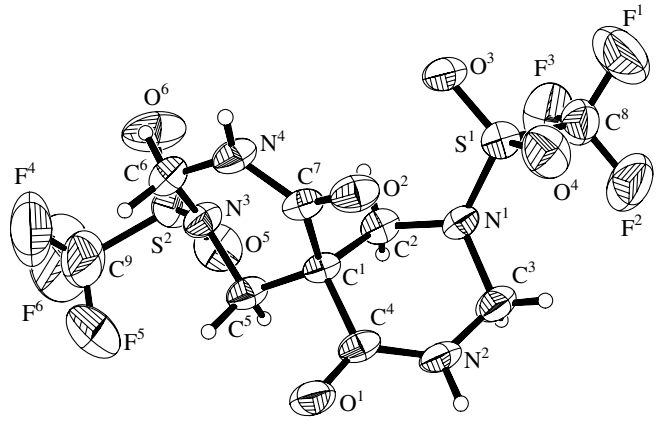
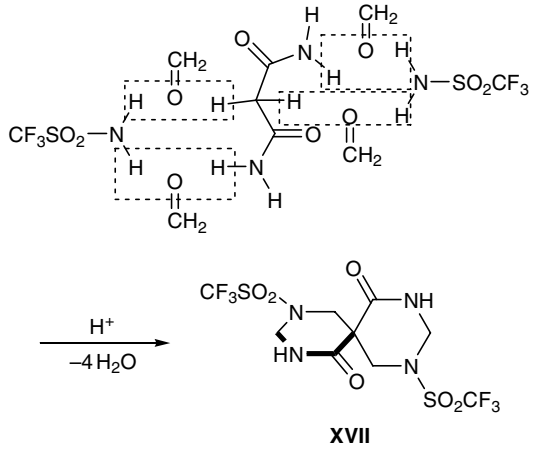


Fig. 1. Structure of the molecule of 4,10-bis(trifluoromethylsulfonyl)-2,4,8,10-tetraazaspiro[5.5]undecane-1,7-dione (**XVII**) according to the X-ray diffraction data.

Scheme 9.



According to the X-ray diffraction data (Fig. 1; Tables 1, 2), the interatomic distances and bond angles in molecule **XVII** correspond to standard values. Both spiro-fused heterorings adopt almost similar unsymmetrical *chair* conformations. The C^1, C^2, C^3, and N^2 atoms in the $C^1C^2C^3N^1N^2$ ring lie in one plane within 0.08 Å, while the N^1 and C^4 atoms deviate from that plane in opposite directions by 0.66 and 0.12 Å, respectively. In the second ring, the C^1, C^6, C^7, and N^3 atoms lie in one plane within 0.09 Å, and the N^4 and C^5 deviate from that plane by 0.26 and 0.66 Å, respectively (in opposite directions). Molecules **XVII** in crystal are linked through intermolecular hydrogen bonds NH···O involving both NH groups and carbonyl oxygen atoms; as a result, chains along the [010] axis are formed (Fig. 2, Table 2).

EXPERIMENTAL

The NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400, 100, and 376 MHz for ^{1}H, ^{13}C, and ^{19}F, respectively; the chemical shifts were measured relative to hexamethyldisiloxane (internal reference; ^{1}H, ^{13}C) or CCl_3F (^{19}F). The progress of

Table 1. Bond lengths *d* and bond angles φ in the molecule of 4,10-bis(trifluoromethylsulfonyl)-2,4,8,10-tetraazaspiro[5.5]-undecane-1,7-dione (**XVII**)

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
S^1–O^4	1.413(2)	O^1–C^4	1.224(3)	S^2–C^9	1.830(5)	N^3–C^5	1.476(3)
S^1–O^3	1.420(2)	O^2–C^7	1.228(3)	F^1–C^8	1.315(4)	N^4–C^7	1.339(4)
S^1–N^1	1.593(2)	N^1–C^2	1.461(4)	F^2–C^8	1.308(4)	N^4–C^6	1.445(4)
S^1–C^8	1.834(3)	N^1–C^3	1.464(4)	F^3–C^8	1.292(4)	C^1–C^5	1.524(4)
S^2–O^6	1.405(3)	N^2–C^4	1.318(4)	F^4–C^9	1.284(6)	C^1–C^7	1.526(3)
S^2–O^5	1.416(3)	N^2–C^3	1.437(4)	F^5–C^9	1.308(7)	C^1–C^4	1.528(4)
S^2–N^3	1.600(2)	N^3–C^6	1.446(4)	F^6–C^9	1.276(6)	C^1–C^2	1.547(4)
Angle	φ, deg	Angle	φ, deg	Angle	φ, deg	Angle	φ, deg
$O^4S^1O^3$	121.79(15)	$C^7C^1C^2$	107.5(2)	$C^2N^1C^3$	112.9(2)	$F^3C^8F^2$	108.9(3)
$O^4S^1N^1$	112.74(13)	$C^4C^1C^2$	111.8(2)	$C^2N^1S^1$	123.81(18)	$F^3C^8F^1$	109.5(3)
$O^3S^1N^1$	108.57(13)	$N^1C^2C^1$	109.7(2)	$C^3N^1S^1$	121.1(2)	$F^2C^8F^1$	107.7(3)
$O^4S^1C^8$	103.94(16)	$N^2C^3N^1$	110.2(2)	$C^4N^2C^3$	128.2(2)	$F^3C^8S^1$	111.4(2)
$O^3S^1C^8$	105.39(15)	$O^1C^4N^2$	123.5(3)	$C^6N^3C^5$	113.1(2)	$F^2C^8S^1$	109.9(2)
$N^1S^1C^8$	102.17(15)	$O^1C^4C^1$	118.1(3)	$C^6N^3S^2$	122.39(19)	$F^1C^8S^1$	109.4(3)
$O^6S^2O^5$	123.06(18)	$N^2C^4C^1$	118.4(2)	$C^5N^3S^2$	121.36(18)	$F^6C^9F^4$	110.0(5)
$O^6S^2N^3$	108.69(15)	$N^3C^5C^1$	107.8(2)	$C^7N^4C^6$	125.8(2)	$F^6C^9F^5$	106.8(5)
$O^5S^2N^3$	109.27(14)	$N^4C^6N^3$	108.5(2)	$C^5C^1C^7$	112.2(2)	$F^4C^9F^5$	109.4(6)
$O^6S^2C^9$	105.1(2)	$O^2C^7N^4$	122.8(2)	$C^5C^1C^4$	108.4(2)	$F^6C^9S^2$	110.9(5)
$O^5S^2C^9$	104.4(2)	$O^2C^7C^1$	119.8(2)	$C^7C^1C^4$	106.17(19)	$F^4C^9S^2$	110.7(4)
$N^3S^2C^9$	104.7(2)	$N^4C^7C^1$	117.2(2)	$C^5C^1C^2$	110.7(2)	$F^5C^9S^2$	109.0(3)

Table 2. Hydrogen bonds in the crystal structure of 4,10-bis(trifluoromethylsulfonyl)-2,4,8,10-tetraazaspiro[5.5]undecane-1,7-dione (**XVII**)

D–H···A	*d*(D–H), Å	*d*(H···A), Å	*d*(D···A), Å	∠DHA, deg	Symmetry operation
N^2–H(N^2)···O^1	0.87	1.95	2.802(3)	166.6	$1-x, 1-y, -z$
N^4–H(N^4)···O^2	0.86	2.26	2.964(3)	139.7	$1-x, -y, -z$

reactions was monitored by TLC on silica gel 60 F-254 plates (hexane–diethyl ether, 1:2).

X-Ray analysis of a 0.24×0.14×0.10-mm single crystal of compound **XVII** was performed on an Enraf–Nonius CAD4 diffractometer (MoK_α irradiation, β-filter, θ/2θ scanning). No correction for absorption was introduced. The set of experimental reflections was treated with account taken of the Lorentz factor and polarization. The structure was solved by the direct method and was refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms and isotropic approximation for hydrogen atoms. $C_9H_{10}F_6N_4O_6S_2$; colorless prisms (from methanol); monoclinic crystal system, space group $P2_1/c$; unit cell parameters: a = 12.743(3), b = 11.572(2), c = 11.626(2) Å; β = 103.12(3)°; V = 1669.6(6) Å^3; Z = 4; ρ = 1.784 g/cm^3. Final divergence factors: R = 0.045, R_w = 0.115 [from 3271 reflections with $I > 2\sigma(I)$].

***N,N′*-Methylenebis(trifluoroacetamide) (XI).** Trifluoroacetamide, 1.5 g, was dissolved in 15 ml of concentrated sulfuric acid, and 0.2 g of paraformaldehyde was added in small portions under stirring. The mixture was stirred for 3 h at room temperature, poured onto ice, and extracted with diethyl ether. The extract was dried over $MgSO_4$, the solvent was distilled off, and the residue was dried under reduced pressure and purified by recrystallization from ethanol. Yield 1.05 g (68%), mp 196–198°C (sublimes above 180°C [8]). ^{1}H NMR spectrum (CD_3CN), δ, ppm:

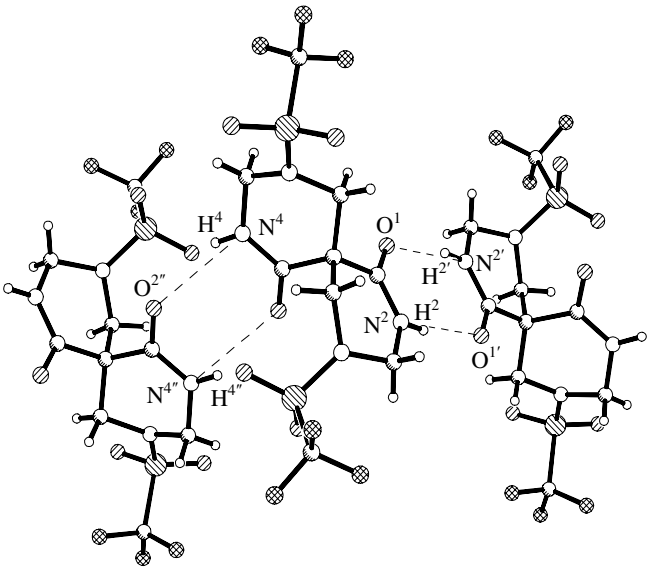


Fig. 2. Intermolecular hydrogen bonds in the crystal structure of 4,10-bis(trifluoromethylsulfonyl)-2,4,8,10-tetraazaspiro[5.5]undecane-1,7-dione (**XVII**).

4.77 m (2H, CH_2), 8.15 br.s (2H, NH). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 45.31 (CH_2), 115.74 q (CF_3, J_{CF} = 287.8 Hz), 158.20 q (CO, J_{CF} = 37.7 Hz). ^{19}F NMR spectrum (CD_3CN): δ_F –76.77 ppm. Found, %: C 25.24; H 1.72; N 11.90. $C_5H_4F_6N_2O_2$. Calculated, %: C 25.22; H 1.69; N 11.77.

2,2,2-Trifluoro-*N*-(hydroxymethyl)acetamide (XII). Paraformaldehyde, 0.73 g (0.024 mol), was dissolved in 10 ml of concentrated sulfuric acid, 1 g (4.2 mmol) of *N*,*N*′-methylenebis(trifluoroacetamide) was added in small portions under vigorous stirring, and the mixture was stirred for 3 h at room temperature and poured into an ice–salt mixture. The precipitate of initial *N*,*N*′-methylenebis(trifluoroacetamide), 0.25 g, was filtered off, and the filtrate was extracted with three portions of diethyl ether, neutralized with $NaHCO_3$, and extracted with three portions of ethyl acetate. The organic extracts were dried over $MgSO_4$ and evaporated to isolate 0.3 g of *N*,*N*′-methylenebis(trifluoroacetamide) from the ether extract and 0.25 g of amide **XII** from ethyl acetate. The latter was purified by vacuum sublimation. Yield 50% (on the reacted initial compound), mp 102–104°C; published data [2]: mp 105°C. ^1H NMR spectrum (CD_3CN), δ, ppm: 4.05 t (1H, OH), 4.72 t (2H, CH_2), 8.15 br.s (1H, NH). In the spectra recorded at 60°C, the OH and NH signals were located in a stronger field, at δ 3.86 and 7.99 ppm, respectively, while the position of the CH_2 signal almost did not change (δ 4.76 ppm). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 64.42 (CH_2), 117.10 q (CF_3, J_{CF} = 286.1 Hz), 158.26 q (CO, J_{CF} = 36.8 Hz). ^{19}F NMR spectrum (CD_3CN): δ_F –77.14 ppm. Found, %: C 25.89; H 2.82; N 10.24. $C_3H_4F_3NO_2$. Calculated, %: C 25.19; H 2.82; N 9.79.

Reaction of 2,2,2-trifluoro-*N*-(hydroxymethyl)-acetamide with trifluoromethanesulfonamide. Trifluoromethanesulfonamide, 0.42 g (2.8 mmol), was dissolved in 15 ml of concentrated sulfuric acid on heating to 32°C, 0.4 g (2.8 mmol) of compound **XII** was added in small portions under vigorous stirring, and the mixture was stirred for 1 h at room temperature and left overnight. It was then stirred for 1.5 h at 40°C and for 1 h at 60–65°C, cooled, poured into an ice–salt mixture, and extracted with diethyl ether (3×30 ml). The extract was dried over magnesium sulfate, the solvent was removed, and the solid residue (0.55 g) was dried under reduced pressure. After removal of initial trifluoromethanesulfonamide by washing with water, the residue (0.15 g) contained (according to the NMR data) ~5% of **II**, ~10% of **IX**, ~25% of **XI**, and ~60% of **XIII.**

2,2,2-Trifluoro-*N*-(trifluoromethylsulfonylaminomethyl)acetamide (XIII). ^1H NMR spectrum (CD_3CN), δ, ppm: 4.71 t (2H, CH_2, J = 6.2 Hz), 7.67 s (1H, $NHSO_2$), 8.40 s (1H, NHCO). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 49.26 (CH_2), 116.73 q (**C**F_3CO, J_{CF} = 287.0 Hz), 120.47 q (CF_3SO_2, J_{CF} = 319.9 Hz), 158.37 q (CO, J_{CF} = 37.8 Hz). ^{19}F NMR spectrum (CD_3CN): δ_F, ppm: –79.36 s (CF_3SO_2), –76.99 s (CF_3CO).

***N*-(1*H*-1,2,3-Benzotriazol-1-ylmethyl)trifluoromethanesulfonamide (XV).** *a*. A suspension of 2.5 g of trifluoromethanesulfonamide and 2 g of 1-hydroxymethyl-1*H*-benzotriazole (**XIV**) (prepared by the procedure described in [17]) in 20 ml of concentrated sulfuric acid was stirred until it became thick, an additional 10 ml of concentrated sulfuric acid was added, and the mixture was stirred for 2 h. The mixture was then poured into a saturated solution of NaCl containing ice and extracted with diethyl ether (3×30 ml), the extract was dried over magnesium sulfate, and the solvent was distilled off under reduced pressure. The residue was washed with hexane–diethyl ether to remove *N*,*N*′-methylenebis(trifluoromethanesulfonamide) and recrystallized from ethanol.

b. Paraformaldehyde, 1.3 g, was added in small portions under stirring to a suspension of 5 g of benzotriazole and 6.3 g of trifluoromethanesulfonamide in 50 ml of concentrated sulfuric acid, the mixture was stirred for 3 h at 70°C, cooled, and poured onto ice,

and the precipitate was filtered off and recrystallized from ethanol. Yield 10.5 g (90%), mp 164–166°C. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 6.10 d (2H, CH_2, J = 6.2 Hz), 7.48 d.d.d (1H, 7-H, J = 8.2, 7.2, 0.8 Hz), 7.64 d.d.d (1H, 8-H, J = 8.0, 7.4, 0.7 Hz), 7.83 d (1H, 9-H, J = 8.5 Hz), 8.07 d (1H, 6-H, J = 8.3 Hz), 8.22 br.s (1H, NH). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 55.73 (CH_2), 111.11 (C^6), 120.30 q (CF_3, J_{CF} = 319.9 Hz), 120.46 (C^9), 125.59 (C^8), 129.20 (C^7), 133.18 (C^5), 147.34 (C^4). ^{19}F NMR spectrum (CD_3CN): δ_F –79.35 ppm. Found, %: C 33.71; H 2.34; F 20.94; N 19.04; S 12.03. $C_8H_7F_3N_4O_2S$. Calculated, %: C 34.29; H 2.52; F 20.34; N 19.99; S 11.44. The concentration of nitrogen is slightly lower than the theoretical value due to the presence of a small impurity of trifluoromethanesulfonamide (~5%, according to the ^{1}H NMR data) which we failed to separate.

Reaction of trifluoromethanesulfonamide with methanesulfonamide and paraformaldehyde. Trifluoromethanesulfonamide, 3 g (0.02 mol), and methanesulfonamide, 1.9 g (0.02 mol), were added under stirring to 40 ml of concentrated sulfuric acid, the mixture was heated to 40°C, 0.6 g (0.02 mol) of paraformaldehyde was added over a period of 3 h, and the mixture was stirred for 3 h. The mixture thickened and was poured onto ice, and the precipitate was filtered off, washed with a saturated solution of NaCl and water, and dried under reduced pressure. The filtrate was saturated with sodium chloride and extracted with diethyl ether, the extract was dried over $MgSO_4$ and evaporated, and the residue was dried under reduced pressure. The residue was combined with the above precipitate and treated with diethyl ether–hexane (2:1) to remove compound **II**. The residue was subjected to column chromatography on silica gel using solvent mixtures with increasing polarity (hexane–diethyl ether–acetone, 2:1:1; hexane–diethyl ether–acetone, 1:2:1; acetone; methanol) to isolate 0.5 g of 1-methylsulfonyl-3,5-bis(trifluoromethylsulfonyl)hexahydro-1,3,5-triazine (**XVI**), mp 204°C. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 3.14 s (3H, CH_3), 5.30 very broad s (6H, CH_2). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 41.42 (CH_3), 61.24 (C^2, C^6), 61.86 (C^4), 120.18 q (CF_3, J_{CF} = 320.3 Hz). ^{19}F NMR spectrum (CD_3CN): δ_F –77.99 ppm. Found, %: C 17.09; H 2.14; F 27.00; N 9.79; S 22.54. $C_6H_9F_6N_3O_6S_3$. Calculated, %: C 16.78; H 2.11; F 26.55; N 9.79; S 22.41.

Reaction of trifluoromethanesulfonamide with malonamide and paraformaldehyde. Malonamide, 2 g, was dissolved in 50 ml of concentrated sulfuric acid, 8.76 g of trifluoromethanesulfonamide was added, and the mixture was heated to about ~60°C until it became homogeneous. The solution was cooled to 45°C, 2.36 g of paraformaldehyde was added in small portions under vigorous stirring, and the mixture was heated to 80–90°C, stirred for 5 h at that temperature, and poured into ice water. The precipitate, 4.8 g, was filtered off, dried in air, and treated with diethyl ether–hexane (1:2). From the organic solution we isolated 2.52 g of *N*,*N*′-methylenebis(trifluoromethanesulfonamide) (**II**) which was identical to an authentic sample [6]. The undissolved material was 4,10-bis(trifluoromethylsulfonyl)-2,4,8,10-tetraazaspiro[5.5]undecane-1,7-dione (**XVII**). Yield 2.27 g, mp 240–242°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.95 d (1H, H_A in $COCH_2CO$), 4.14 d (1H, H_B in $COCH_2CO$, J_{AB} = 13.3 Hz), 4.76 d (1H, $H_{A'}$ in NCH_2N), 4.85 d (1H, $H_{B'}$ in NCH_2N, J_{AB} = 11.0 Hz), 8.79 s (1H, NH); the $H_{A'}$ proton showed a weak coupling (J = 1.0 Hz) with the NH proton. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 49.35 br.s (C_{spiro}), 56.11 (NCN), 119.28 q (CF_3, J_{CF} = 322.3 Hz), 165.58 (CO). ^{19}F NMR spectrum (CD_3CN): δ_F –76.41 ppm. Found, %: C 24.00; H 2.28; F 25.02; N 12.22; S 14.94. $C_9H_{10}F_6N_4O_6S_2$. Calculated, %: C 24.11; H 2.25; F 25.43; N 12.50; S 14.30.

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