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Synthesis and Structure of *N*-(Diaminomethylidene)- and *N*-[Bis(cyclohexylamino)methylidene]trifluoromethanesulfonamides

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Abstract—*N*-Trifluoromethylsulfonyl-substituted guanidines $CF_3SO_2N=C(NHR)_2$ (R = H, cyclohexyl) were synthesized in nearly quantitative yield by reactions of *N*-sulfinyltrifluoromethanesulfonamide $CF_3SO_2N=S=O$ with urea and of trifluoromethanesulfonamide with *N*,*N*′-dicyclohexylcarbodiimide. *N*-[Bis(cyclohexylamino)-methylidene]trifluoromethanesulfonamide was subjected to protonation with trifluoromethanesulfonic acid and bis(trifluoromethanesulfonyl)imide, and the structure of the resulting salts and initial *N*-trifluoromethylsulfonylguanidines was studied by NMR and IR spectroscopy and DFT quantum-chemical calculations.

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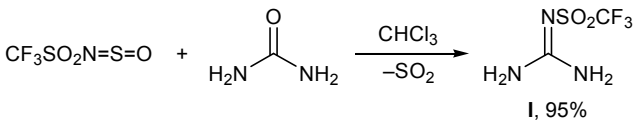
Guanidine moiety is an important structural fragment of many biologically active compounds [1]. Binding of strongly basic guanidine fragment to metals [2, 3], protonation, and hydrogen bonding play an important role in the formation of metal-complex catalysts based on guanidine derivatives and in substrate–enzyme interactions. Taking the above stated into account, development of mild and efficient procedures for the preparation of guanidine derivatives attracts considerable attention from the viewpoint of medicinal chemistry [1]. N-Trifluoromethylsulfonyl-substituted guanidines are of specific interest as guanidinylating agents due to high nucleofugality of trifluoromethylsulfonyl group. Powell et al. [4] have differentiated *guanylation* [introduction of a $–C(=NH)NH_2$ group to a nitrogen atom] from *guanidinylation* [introduction of an $–NHC(=NH)NH_2$ group to a carbon atom]. *N*-Trifluoromethylsulfonylguanidines $CF_3SO_2N=C(NH\text{-}PG)_2$ protected at both amino groups were proposed as a new class of guanidinylating agents; they were synthesized by treatment of preliminarily protected guanidine (at the NH_2 groups) with trifluoromethanesulfonic anhydride in 75–88% yield [1]. This procedure was subsequently improved by the use of $(i\text{-Pr})_2NEt$ instead of Et_3N as base; as a result, the reaction time was shortened, and the yield of the target product increased [5]. *N*-Trifluoromethylsulfonylguanidines thus obtained were used to synthesize guanidine derivatives from aliphatic and aromatic amines [1] and proline [5]. Replacement of one protecting group by a fragment ensuring immobilization of the reagent on a solid support increases the efficiency of guanidinylation [6]. An earlier procedure for the synthesis of *N*-trifluoromethylsulfonylguanidines of the general formula $TfN=C(NHAr)NMe_2$ (Tf = CF_3SO_2) was based on replacement of one trifluoromethylsulfonyl group in 2,3-bis(trifluoromethylsulfonyl)-1,1-dimethylisourea $TfN=C(OTf)N(CH_3)_2$ by amine residue via reaction with aromatic amines $ArNH_2$ [7]. A number of *N*-trifluoromethylsulfonylguanidines were synthesized by reaction of amines with *N*-[bis(methylsulfanyl)-methylidene]trifluoromethanesulfonamide $CF_3SO_2N=C(SMe)_2$ (yield 63–91%) [8] or *N*′-aryl-*N*-trifluoromethylsulfonylchloroformimidamides TfN=C(Cl)NHAr (yield 65–88%) [9].

In the present work we synthesized *N*-trifluoromethylsulfonylguanidines in nearly quantitative yield according to two novel procedures. The first of these

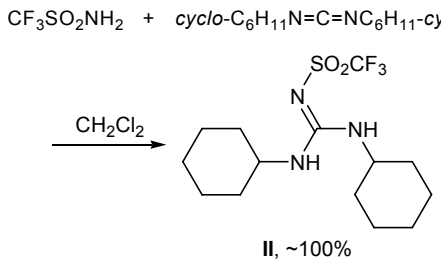
Scheme 1.



I, 95%

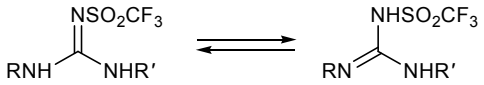
was based on the reaction of *N*-sulfinyltrifluoromethanesulfonamide $CF_3SO_2N{=}S{=}O$ with urea, which was accompanied by elimination of SO_2 molecule (Scheme 1). The second procedure implied addition of trifluoromethanesulfonamide to N=C=N cumulated bond system; as an example, the reaction with *N*,*N*′-dicyclohexylcarbodiimide was performed (Scheme 2).

Scheme 2.



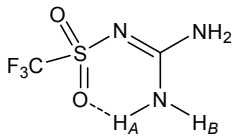
Compounds **I** and **II** thus formed were isolated as colorless high-melting crystalline substances. Provided that one or several NH groups are present in *N*-trifluoromethylsulfonylguanidine molecule, prototropic tautomerism is possible (Scheme 3).

Scheme 3.



If R, R′ = Alk or Ar, the equilibrium is displaced entirely to the left due to direct polar conjugation between the amino groups and imino group, the latter possessing a strong electron-withdrawing substituent. N-Protected *N*-trifluoromethylsulfonylguanidines, e.g., $TfN{=}C(NHBoc)_2$ (Boc = *t*-BuOCO), have similar structure [1, 5, 6]. According to the ^1H and ^{19}F NMR, IR, and X-ray diffraction data, no TfNHC(Ar)=NOH tautomers of structurally related *N*-hydroxy-*N*′-trifluoromethylsulfonylarenecarboximidamides $TfN{=}C(Ar)NHOH$ exist in the crystalline state and in solution [9]. Yagupol'skii et al. [8] were the only authors who reported on tautomeric equilibrium of $TfN{=}C(SMe)NH_2$ with TfNHC(SMe)=NH; however, this statement is quite doubtful. The ^{19}F NMR spectrum of $TfN{=}C(SMe)NH_2$ contained only one signal. It is improbable that CF_3 signals of two tautomers coincide with each other, for CF_3SO_2N groups in a single compound, differing by substituents separated by five bonds from the fluorine atom, are known to give different signals ($\Delta\delta_F > 2$ ppm [10]); structures $TfN{=}C(SMe)NH_2$ and TfNHC(SMe)=NH differ by hybridization of the nitrogen atom located much more closely to the fluorine atoms. The IR spectra do not prove the presence of the imino tautomer: the absorption band at 3220 cm^{-1} could equally arise from H-bonded NH_2 group. The presence of several NH signals in the ^1H NMR spectrum may be related to equilibrium between intramolecularly H-bonded and free amino species. Finally, the lack of tautomeric form TfNHC(Ar)=NH was shown in [11] for $TfN{=}C(Ar)NH_2$ both in crystal and in solution.

Compound **I** displayed in the ^1H NMR spectrum (DMSO-d_6) two NH signals, one narrow at δ 6.77 ppm and one broadened at δ 8.82 ppm with an intensity ratio of 1:1. Obviously, the first signal belongs to free NH_2 group, and the second, to NH_2 group involved in intramolecular hydrogen bond with fast (on the NMR time scale) exchange of H_A and H_B.



The ^1H NMR spectra of compound **II** in $CDCl_3$ and CD_2Cl_2 contained signals from methylene protons in the cyclohexane rings and four singlets at δ 7.20, 4.73, 3.87, and 3.25 ppm. In keeping with the $\{^1H\}-^{13}C$ NMR data, the first two signals correspond to H-bonded and free NH groups, respectively, and the two latter, to the NCH protons in the cyclohexyl fragments. On heating to 50°C, the NH signals coalesce with each other to give a broadened singlet at δ 5.91 ppm, while the NCH signals give rise to a narrow singlet at δ 3.57 ppm. In the ^1H NMR spectrum of compound **II** in DMSO-d_6, the NCH protons resonate as one signal at δ 3.63 ppm even at room temperature, while the NH signals become closer to each other but remain separate, δ 7.44 and 7.04 ppm. In the spectrum recorded from the same solution at 70°C, the NH signals coalesce and shift upfield to δ 3.63 ppm, and the NCH signal (δ 3.31 ppm) is overlapped by the signal of water present in the solvent. Unlike initial *N*,*N*′-dicyclohexylcarbodiimide, signals from carbon atoms in the cyclohexane rings in the ^{13}C NMR spectrum of compound **II** in $CDCl_3$ are strongly broadened, δ_C ~32 (C^2, $C^{2'}$, C^6, $C^{6'}$) and ~24 ppm (C^3, $C^{3'}$, C^5, $C^{5'}$). Thus, the NMR data indicate that *N*-trifluoromethylsulfonylguanidines **I** and **II** in solution exist in dynamic equilibrium. In order to elucidate the nature of species involved in the equilibrium, compounds **I** and **II** were studied by IR spectroscopy and quantum-chemical calculations.

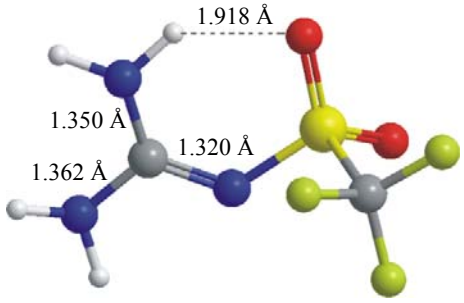


Fig. 1. Calculated structure of the molecule of *N*-(diaminomethylidene)trifluoromethanesulfonamide (**I**).

Calculation of molecule **I** at the DFT/B3LYP/6-311G** level of theory gave a structure with strong intramolecular hydrogen bond (O···H 1.918 Å) (Fig. 1). The C=NTf bond is only slightly shorter than H_2N–C, which indicates essential conjugation in the N–C=NTf fragment. Tautomeric structures TfNHC(NH_2)=NH with intramolecular hydrogen bonds involving hydrogen atoms in the amino or imino group (S=O···H–NHC and S=O···H–N=C) are characterized by considerably higher energies (by 14.4 and 15.4 kcal/mol, respectively), so that they can be discarded.

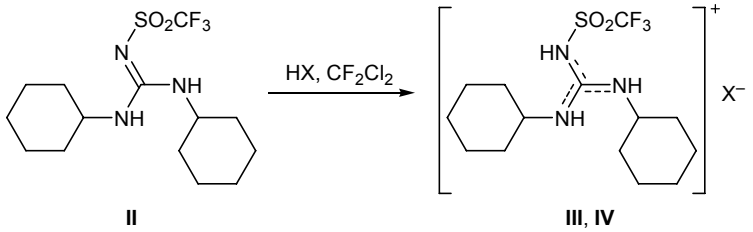
The TfN=C($NHR)_2$ tautomer of compound **II** was found to exist as four conformers which occupy minima on the potential energy surface. Their structures are shown in Fig. 2, and their relative energies are also given. All structures are highly polar (μ = 8–9 D); therefore, their relative energies should not change to an appreciable extent in going from gaseous phase to solution. The energies of conformers of the TfNHC(NHR)=NR tautomer of **II** are higher by 15–16 kcal/mol, and these structures were not considered. The length of the formally double C=NTf bond varies from 1.321 to 1.336 Å, the C–NR bond in the *syn* position to the trifluoromethylsulfonyl group ranges from 1.348 to 1.358 Å, and the *anti*-C–NR bond, from 1.352 to 1.375 Å. The C–NR bond lengths are very similar to those determined by X-ray analysis for 2,6-$Me_2C_6H_3N$=C(NHPr-*i*)$_2$ [2], whereas the C=NTf bond is shorter by 0.02–0.03 Å than C=NAr [2] as a result of conjugation in the N–C=NTf fragment. Enhancement of such conjugation, e.g., in the HONH–C(Ph)=NTf fragment [9] could make formally double C=NTf bond even longer than formally single N–C bond (1.315 and 1.307 Å, respectively, according to the X-ray diffraction data [9]).

In the IR spectrum of crystalline compound **I**, ν(NH) vibrations give rise to absorption bands with their maxima at 3481 and 3365 cm^{-1}, which are intrinsic to free NH_2 group, as well as at 3400, 3280, and 3200 cm^{-1} due to associated amino group. This assignment was made by comparison with the spectra of the same compound in solution. A solution of **I** in CCl_4 displayed only two strong ν(NH) bands at 3479 and 3366 cm^{-1} (free amino groups), which were also present in the IR spectrum of a solution of **I** in methylene chloride. Here, the low-frequency shifts to 3448 and 3336 cm^{-1} are synchronous, which indicates the absence of additional ν(NH) bands belonging to a different conformer. Thus, the results of calculations and experimental NMR and IR data show that compound **I** in solution and in the crystalline state exists as a single conformer.

The doublet absorption band at 3363/3334 cm^{-1} in the IR spectrum of crystalline compound **II** corresponds to stretching vibrations of associated NH groups. In the spectrum of a dilute solution of **II** in carbon tetrachloride we observed two strong absorption bands at 3451 and 3324 cm^{-1} with high-frequency shoulders at 3482 and 3364 cm^{-1} due to free NH groups. The intensity of the shoulders decreases in going to a solution of **II** in chloroform, and no shoulders were observed in methylene chloride (only two isolated bonds are present at 3437 and 3345 cm^{-1}). This pattern indicates the presence of two forms of molecules **II** in weakly polar medium (CCl_4, $CHCl_3$). The strong low-frequency shift of the high-frequency ν(NH) band in going from crystalline compound **II** to its solution in carbon tetrachloride (88 and 119 cm^{-1}) indicates that it belongs to NH group participating in intermolecular hydrogen bond. The position of the low-frequency ν(NH) band changes insignificantly (3364–3324 cm^{-1}), which is likely to be related to effect of the solvent; participation of the second NH group in intramolecular hydrogen bond can also be presumed. Absorption bands due to stretching vibrations of the C=N bond and bending vibrations of the NH group appear in the IR spectra of **II** at 1601 and 1582 cm^{-1} (KBr) and 1592 and 1575 cm^{-1} (CH_2Cl_2), respectively.

Compound **II** readily reacted with trifluoromethanesulfonic acid and bis(trifluoromethanesulfonyl)imide to give salts **III** and **IV** as a result of protonation of the imino nitrogen atom (Scheme 4). Salts **III** and **IV** displayed in the ^{1}H NMR spectra three NH signals: a downfield signal from proton in the NHTf group and two closely located signals from H-bonded and free NHR groups. The NCH protons in two cyclohexyl fragments resonated as one slightly

Scheme 4.

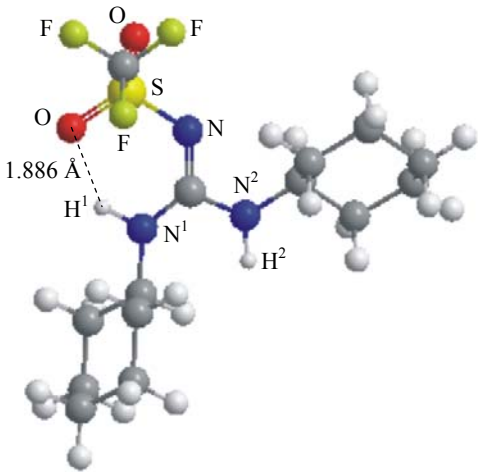


II **III**, **IV**

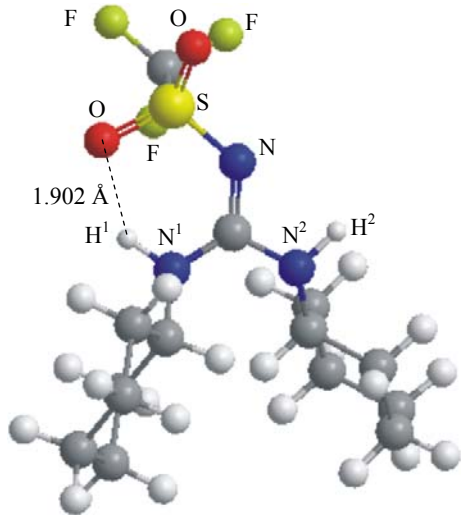
III, X = OTf; **IV**, X = Tf_2N.

broadened (**III**) or broadened signal (**IV**). We succeeded in detecting only one CF_3 signal in the ^{13}C NMR spectrum of **III**, whereas its ^{19}F NMR spectrum contained two signals with an intensity ratio of 1 : 1. In the ^{13}C and ^{19}F NMR spectra of **IV** we observed two CF_3 signals at a ratio of 1 : 2. The difference in the chemical shifts of C^1 and C^2 in the two cyclohexyl fragments was 2.7 and 1.3 ppm, respectively, i.e., the larger difference is observed for the carbon atom located more closely to the cationic center.

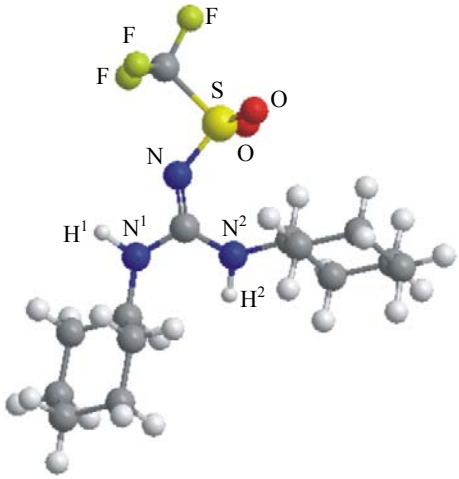
Quantum-chemical calculations of two isomeric cations in **III** and **IV**, corresponding to protonation of



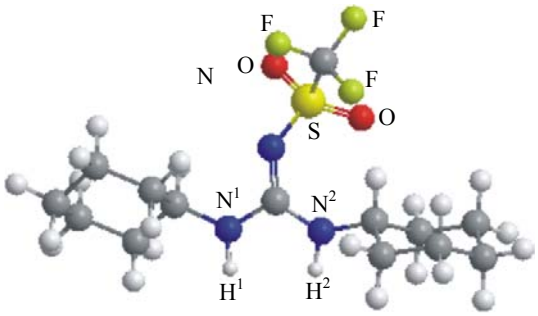
IIa, ΔE = 0 kcal/mol



IIb, ΔE = 4.9 kcal/mol



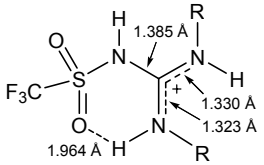
IIc, ΔE = 7.7 kcal/mol



IId, ΔE = 8.4 kcal/mol

Fig. 2. Calculated structures and relative energies of different tautomers of *N*-[bis(cyclohexylamino)methylidene]trifluoromethanesulfonamide (**II**).

the imino group in conformers **IIa** and **IIb** (Fig. 2) showed the same energy difference as that found for neutral species: $\Delta E = E(\mathbf{IIa}\text{-}H^+) - E(\mathbf{IIb}\text{-}H^+) =$ 4.7 kcal/mol; structure **IIa**-H^+ retains intramolecular hydrogen bond, but the O···H distance extends to 1.964 Å; no hydrogen bond was found in **IIb**-H^+. As might be expected, conjugation between the cationic center and NHR groups is much stronger than with the NHTf group; in addition, conjugation with the H-bonded NH group is stronger than with the free NH group, as illustrated below by the structure of the most stable conformer of **IIa**-H^+.



The IR spectra of crystalline salts **III** and **IV** and their solutions in methylene chloride revealed high-frequency shift of the ν(C=N) absorption band upon protonation of compound **IIa** (from ~1600 to ~1670 cm^{-1}). Calculation of the vibrational spectra of **IIa** and **IIa**-H^+ also predicted increase of the ν(C=N) frequency from 1649 do 1687 cm^{-1}. According to the calculations, this band corresponds to mixed vibrations of the entire $C(NH–)_3$ fragment, which are contributed mainly by ν_{as} of the N⁼⁼⁼C⁼⁼⁼N triad. In the IR spectra of crystalline samples of **III** and **IV**, ν(NH^+) vibrations give rise to broad absorption bands with their maxima at 2670 and 3130 cm^{-1}, which suggests lower degree of proton transfer in salt **IV**. The position of the ν(NH) band in the spectrum of crystalline salt **III** completely coincides with that typical of initial compound **II**, whereas the ν(NH) frequency of salt **IV** is lower by 20–40 cm^{-1}.

The synthesis of compounds **I** and **II** demonstrates two new approaches to *N*-trifluoromethylsulfonylguanidines via condensation of *N*-sulfinyltrifluoromethanesulfonamide with ureas and addition of trifluoromethanesulfonamide to cumulated N=C=N bond system.

EXPERIMENTAL

The IR spectra were recorded on a Bruker Vertex 70 spectrometer from samples prepared as KBr pellets and solutions in CCl_4, $CHCl_3$, and CH_2Cl_2. The NMR spectra were measured on a Bruker DPX-400 spectrometer at 400 (^{1}H), 100 (^{13}C), and 376 MHz (^{19}F); residual proton and carbon signals of the solvent were used as reference; the ^{19}F chemical shifts were determined relative to CCl_3F.

Quantum-chemical calculations of the structure, energy, and vibrational frequencies were performed in terms of the density functional theory with B3LYP functional and 6-311G** basis set with complete geometry optimization using Gaussian 03 software package [12].

***N*-(Diaminomethylidene)trifluoromethanesulfonamide (I).** Urea, 0.15 g (2.6 mmol), was added under vigorous stirring to a solution of 0.51 g (2.6 mmol) of *N*-sulfinyltrifluoromethanesulfonamide in 5 ml of chloroform. The mixture was heated to the boiling point (after 40 min, a solid separated from the solution) and was left overnight. The precipitate was filtered off, washed with chloroform, and dried under reduced pressure (water-jet pump). Yield 0.47 g (95%), colorless crystals, mp 158°C. IR spectrum, ν, cm^{-1}: 3481, 3400, 3365, 3280, 3206, 1725, 1698, 1618, 1580, 1399, 1386, 1328, 1197, 1152, 959, 614, 492. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.77 s (1H, NH), 8.82 br.s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 119.56 q (CF_3, J = 320.8 Hz), 155.47 (C=N). ^{19}F NMR spectrum (DMSO-d_6): δ_F –79.34 ppm. Found, %: C 12.91; H 2.42; F 29.74; N 21.99; S 16.11. $C_2H_4F_3N_3O_2S$. Calculated, %: C 12.57; H 2.11; F 29.82; N 21.98; S 16.78.

***N*-[Bis(cyclohexylamino)methylidene]trifluoromethanesulfonamide (II).** Trifluoromethanesulfonamide, 0.21 g (1.4 mmol), was added under vigorous stirring to a solution of 0.29 g (1.4 mmol) of *N*,*N*′-dicyclohexylcarbodiimide in 1 ml of methylene chloride. The mixture was stirred for 6 h at room temperature, left overnight, and evaporated under reduced pressure. Yield 0.49 g (100%), colorless crystals, mp 160°C. IR spectrum, ν, cm^{-1}: 3364, 3348, 2939, 2860, 1595, 1360, 1304, 1212, 1175, 1114, 1058, 975, 649, 599. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.10–1.46 m (10H, CH_2), 1.62 m (2H, CH_2), 1.74 m (4H, CH_2), 1.93 m (4H, CH_2), 3.25 br.s (1H, NCH), 3.87 br.s (1H, NCH), 4.73 br.s (1H, NH), 7.20 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 24.26 br (C^3, $C^{3'}$, C^5, $C^{5'}$), 25.16 (C^4, $C^{4'}$), 32.56 br (C^2, $C^{2'}$, C^6, $C^{6'}$), 50.66 (C^1, $C^{1'}$), 120.36 q (CF_3, J = 322.0 Hz), 154.41 (C=NTf). ^{19}F NMR spectrum ($CDCl_3$): δ_F –79.75 ppm. Found, %: C 47.57; H 6.73; F 17.97; N 11.58; S 9.68. $C_{14}H_{24}F_3N_3O_2S$. Calculated, %: C 47.31; H 6.81; F 16.04; N 11.82; S 9.02.

Bis(cyclohexylamino)-*N*-(trifluoromethylsulfonyl)methaniminium trifluoromethanesulfonate (III). Trifluoromethanesulfonic acid, 0.10 ml (0.18 g, 1.2 mmol), was added under vigorous stirring to a solution of 0.43 g (1.2 mmol) of compound **II** in 4 ml of methylene chloride. The mixture was stirred for 3 h at room temperature and evaporated under reduced pressure, and the residue (colorless crystals) was dried under reduced pressure. Yield 0.60 g (100%), mp 174°C. IR spectrum, ν, cm^{-1}: 3366, 3334, 3212, 3105, 2942, 2866, 1669, 1602, 1586, 1455, 1299, 1224, 1140, 1112, 1028, 640. ^1H NMR spectrum ($CDCl_3$–CD_3CN), δ, ppm: 1.24 m (10H, CH_2), 1.50 m (2H, CH_2), 1.64 m (4H, CH_2), 1.76 m (4H, CH_2), 3.46 s (2H, NCH), 6.80 s (1H, NH_{free}), 7.18 s (1H, NH_{assoc}), 10.58 s (1H, NHTf). ^{13}C NMR spectrum ($CDCl_3$–CD_3CN), δ_C, ppm: 23.32 (C^4, $C^{4'}$), 24.24 (C^3, $C^{3'}$, C^5, $C^{5'}$), 30.94 ($C^{2'}$, $C^{6'}$), 31.92 (C^2, C^6), 51.21 ($C^{1'}$), 53.75 (C^1), 119.06 q ($TfNH^+$, J = 322.4 Hz), 149.36 (C=NTf). ^{19}F NMR spectrum ($CDCl_3$–CD_3CN), δ_F, ppm: –78.78 (1F, OTf), –77.94 (1F, HNTf). Found, %: C 35.59; H 4.38; F 22.15; N 8.18; S 12.42. $C_{15}H_{25}F_6N_3O_5S_2$. Calculated, %: C 35.64; H 4.98; F 22.55; N 8.31; S 12.68.

Bis(cyclohexylamino)-*N*-(trifluoromethylsulfonyl)methaniminium bis(trifluoromethylsulfonyl)imide (IV). A solution of 0.28 g (1.0 mmol) of bis(trifluoromethanesulfonyl)imide in 3 ml of methylene chloride was added under vigorous stirring to a solution of 0.36 g (1.0 mmol) of compound **II** in 3 ml of methylene chloride. The mixture was stirred for 6 h at room temperature, left overnight, and evaporated under reduced pressure, and the residue (colorless crystals) was dried under reduced pressure. Yield 0.65 g (100%), mp 104°C. IR spectrum, ν, cm^{-1}: 3341, 3275, 3133, 2943, 2864, 1676, 1583, 1456, 1337, 1320, 1237, 1207, 1183, 1130, 1062, 942, 653, 597, 506. ^1H NMR spectrum ($CDCl_3$–CD_3CN), δ, ppm: 1.10–1.56 m (10H, CH_2), 1.64 m (2H, CH_2), 1.76 m (4H, CH_2), 1.92 m (4H, CH_2), 3.68 s (2H, NCH), 6.71 s (1H, NH_{free}), 6.94 s (1H, NH_{assoc}), 8.18 s (1H, NHTf). ^{13}C NMR spectrum ($CDCl_3$–CD_3CN), δ_C, ppm: 23.31 (C^4, $C^{4'}$), 24.29 (C^3, $C^{3'}$, C^5, $C^{5'}$), 30.84 ($C^{2'}$, $C^{6'}$), 32.15 (C^2, C^6), 51.65 ($C^{1'}$), 54.31 (C^1), 119.05 q ($TfNH^+$, J = 322.0 Hz), 119.38 q (Tf_2N^-, J = 320.9 Hz), 148.75 (C=NTf). ^{19}F NMR spectrum ($CDCl_3$–CD_3CN), δ_F, ppm: –77.39 (1F), –79.19 (2F). Found, %: C 30.70; H 3.88; F 26.02; N 8.72; S 14.44. $C_{16}H_{25}F_9N_4O_6S_3$. Calculated, %: C 30.19; H 3.96; F 26.86; N 8.80; S 15.11.

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