3,3,3-Trifluoro-*N*´-(3-trifluoromethylphenyl)-1,2-propanediamine and its *N*-mono- and *N,N*-dicarboxyethyl derivatives: synthesis, protolytic and complexation properties

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3,3,3-Trifluoro-*N*´-(3-trifluoromethylphenyl)-1,2-propanediamine (**5**) was synthesized by the reaction of 2-diazo-1,1,1-trifluoro-3-nitropropane or 3,3,3-trifluoro-1-nitropropene with 3-aminobenzotrifluoride followed by the reduction of the nitro group. The Michael 1,4-addition of diamine **5** to acrylic acid occurs only at the N(1) atom and affords *N*-mono- or *N*,*N*-dicarboxyethyl derivatives **6** and **7**, depending on the reactant ratio. Protolytic equilibria **5—7** in aqueous solutions were studied by pH-potentiometry and UV spectroscopy. Only the aliphatic amino group can be protonated in an aqueous solution, while the aromatic amino group remains unprotonated even in 12 *M* HCl. The stability constants of transition metal (Cu^{2+}, Ni^{2+}, Zn^{2+}) complexes with ligands **5—7** were determined by pH-potentiometric titration. The stability of the complexes and selectivity of the ligands toward Cu^{2+} ions increase with an increase in the number of *N*-carboxyethyl groups.

Key words: 3,3,3-trifluoro-*N*´-(3-trifluoromethylphenyl)-1,2-propanediamine, 3-[2-(3-trifluoromethylphenylamino)-3,3,3-trifluoropropylamino]propionic acid, 3,3-[2-(3-trifluoromethylphenylamino)-3,3,3-trifluoropropylamino]dipropionic acid, carboxyethylation, protolytic equilibria, complexation, transition metal ions, selectivity.

Structural fragments of 1,2-ethylenediamine and β-alanine with aryl and alkyl substituents at the nitrogen atoms are constituents of many compounds with a wide spectrum of biological activity.[1—3] For example, β-alanine derivatives can enhance inhibition processes in the central nervous system, being agonists of γ-aminobutyric and glycine receptors and, thus, potential anticonvulsive preparations in treating epilepsy.[2] A pharmacophore based on *N*-substituted β-alanine containing the amine and carboxylate acceptors and the lipophilic fragment was proposed as a result of the simulation and pharmacological studies.[2] The introduction of an additional lipophilic trifluoromethyl group into both the aromatic ring and ethylene chain favors absorption and transport of the medicine in biological systems and, therefore, improves the pharmacological properties of a candidate molecule.[4]

In analytical chemistry, carboxymethylated derivatives of 1,2-ethylenediamine are used as chelating agents. However, they are poorly selective toward metal ions with similar properties. As shown previously,[5—7] the ligands containing the β-alaninate group are more selective toward Cu^{2+} ions than the glycinate analogs. For instance, the high selectivity of *N*-phenyliminobis-3-propionic acid[6,7] and its derivatives[7] toward Cu^{2+} ions is caused by all the energy and spatial factors leading to a decrease in the stability of the complexes with the metal ions and a simultaneous increase in the differentiating ability toward Cu^{2+} ions, which form the most stable complexes. Therefore, it can be expected that ligands containing simultaneously the β-alaninate group, aromatic and aliphatic amino groups, and trifluoromethyl substituent with unique electronic and steric features would manifest interesting complexation properties.

In the present work, we synthesized 3,3,3-trifluoro-*N*´-(3-trifluoromethylphenyl)-1,2-propanediamine and its *N*-mono- and *N,N*-dicarboxyethyl derivatives contain-

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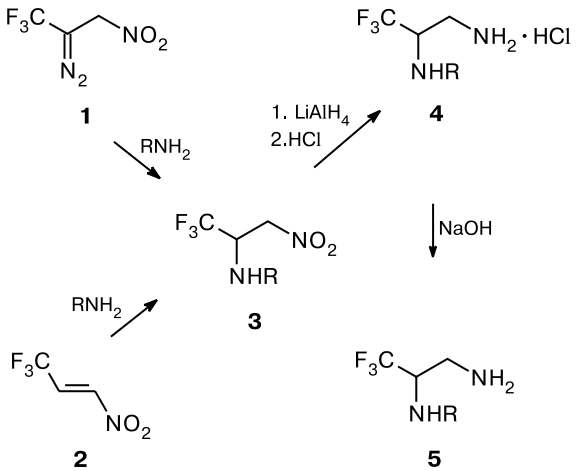
ing trifluoromethyl groups in both the ethylene fragment and aryl substituent at the N(2) nitrogen atom and studied their protolytic and complexation properties.

Results and Discussion

Synthesis of 3,3,3-trifluoro-N′-(3-trifluoromethylphenyl)-1,2-propanediamine and its derivatives. The starting compounds for the synthesis of several fluoro-containing 1,2-diamines, including CF_3-substituted derivatives, can be the corresponding β-nitroenamines[8] or β-nitrodiazoalkanes,[9] which are prepared from available nitriles of fluorocarboxylic acids. A simple and convenient procedure for the synthesis of the ethylenediamine derivatives is the method based on the Michael addition of amines to nitroalkenes followed by the reduction of the nitro group in the reaction products.[10] At the same time, no data were reported on the use of this method for the synthesis of fluoroalkyl-substituted 1,2-diamines. In the present work, we studied two alternative methods for the synthesis of 1-trifluoromethyl-1,2-ethylenediamines, using compound **5** as an example, from 2-diazo-1,1,1-trifluoro-3-nitropropane[11] (**1**) or *E*-3,3,3-trifluoro-1-nitropropene[12] (**2**), which is a synthetic analog of diazo compound **1** [13,14] (Scheme 1).

Scheme 1

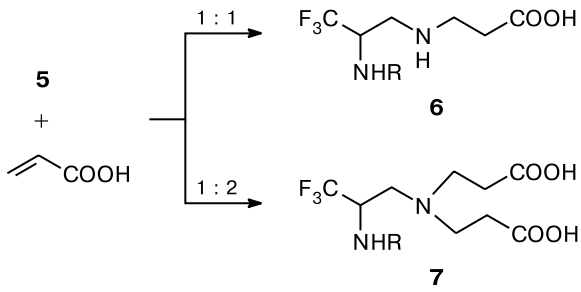


R = 3-$CF_3C_6H_4$

The reaction of compound **1** or **2** with 3-aminobenzotrifluoride in benzene at 60 °C affords β-nitroamine **3** in 82 and 84% yields, respectively. The reduction of the nitro group in nitroamine **3** by the action of $LiAlH_4$ in THF followed by the treatment with dry HCl produces diamine hydrochloride **4**, from which diamine **5** was obtained by the treatment with an aqueous solution of NaOH. The ^1H NMR spectrum of compound **4** contains a singlet of the NH_3^+ group at 8.35 ppm and a doublet of the proton of the arylamino group (δ_{NH} = 6.83 ppm, ^3J = 9.8 Hz), which indicates that only the N(1) nitrogen atom is protonated.

The carboxyethylation of compound **5** with acrylic acid affords *N*-mono- or *N*,*N*-dicarboxyethyl derivatives **6** or **7**, depending on the ratio of reactants (Scheme 2). No addition to the N(2) nitrogen atom occurs even in excess carboxyethylating agent because of its low nucleophilicity.

Scheme 2



Protolytic equilibria. The completely deprotonated forms of compounds **5**—**7** are organic bases of moderate strength and capable of adding protons to the aliphatic and aromatic amino groups and to one (compound **6**) or two (compound **7**) carboxylate groups. The general and stepwise protonation constants obtained from the pH-potentiometric titration data are given in Table 1 in comparison with the constants of the related compounds: 1,2-ethylenediamine (En),[15] *N*-phenylethylenediamine (PhEn),[16] and 3,3,3-trifluoropropane-1,2-diamine (**8**).

The protonation constants of the aromatic amino group in compounds **5**—**7** were not determined from the potentiometric data, because the condition necessary for

Table 1. Protonation constants $\beta_H = \frac{[H_nL]}{[H]^n[L]}$ and $K_H = \frac{[H_nL]}{[H][H_{n-1}L]}$ for selected *N*- and *C*-substituted ethylenediamines (T = 25 °C, I = 0.1 *M* KNO_3)

Ligand L	*n*	logβ_H	logK_H
5	1	7.69±0.02	7.69
6	1	7.76±0.02	7.76
	2	11.05±0.02	3.29
7	1	7.33±0.02	7.33
	2	11.18±0.03	3.85
	3	13.95±0.05	2.77
8	1	7.91±0.01	7.91
	2	9.87±0.02	1.96
PhEn[16]	1	9.59	9.59
	2	9.5	–0.1
En[15]	1	9.89	9.89
	2	16.97	7.08

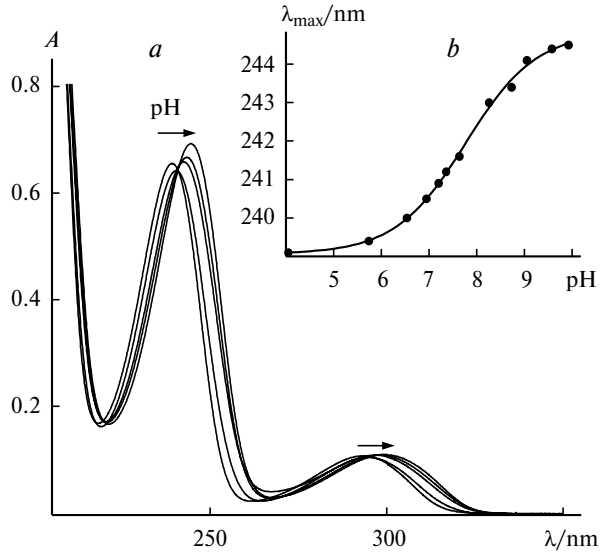
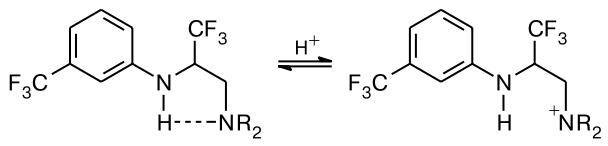


Fig. 1. Electronic absorption spectra of an aqueous solution of diamine **5** at different pH ($C = 5 \cdot 10^{-5}$ mol L^{-1}).

this procedure $C_L > 1/K_H$ (see Ref. 17) is not fulfilled due to the low protonation constant and insufficient solubility of the compounds in water.

Additional information on the protonation of the aromatic amino group can be obtained from analysis of the electronic spectra in the UV region where the benzene chromophore absorbs. The absorption spectra of aqueous solutions of compound **5** at different acidities of the solution are presented in Fig. 1. The spectra of solutions of compounds **6** and **7** are similar and differ insignificantly by the position of maxima of the absorption bands. In the whole studied acidity interval (from 12 *M* HCl to 1 *M* KOH), no protonation of the aromatic amino group and related changes in the spectral curves (hypochromism and hypsochromic shift of absorption bands)[18] are observed, which indicates a very low basicity of the N(2) nitrogen atom ($\log K_H < -1$). Nevertheless, slight hypsochromic shifts of the absorption bands of $^1B_{1u}$ 245 nm and $^1B_{2u}$ 300 nm are observed in the region of protonation of the aliphatic amino group (pH = 9—6, Fig. 1, *b*), which is probably related to the cleavage of the intramolecular hydrogen bond (Scheme 3).

Scheme 3



R = H, $(CH_2)_2COOH$

The low basicity of the aromatic amino group is unambiguously related to the strong electron-withdrawing effect of the *N*′-(3-trifluoromethyl)phenyl and *C*-trifluoromethyl substituents in the ethylenediamine fragment of compounds **5—7**. This effect can be analyzed by comparison of the protonation constants of the pairs of compounds En—PhEn and En—**8** (see Table 1), which differ by the presence of the *N*-phenyl or *C*-trifluoromethyl substituent, respectively. The introduction of the phenyl substituent into En only insignificantly decreases the first constant of protonation of the aliphatic amino group $\Delta\log K_{1H}$(En—PhEn) = 0.3 and decreases substantially the basicity of the nitrogen atom, which is directly conjugated with the benzene ring ($\Delta\log K_{2H}$(En—PhEn) = 7.2). By contrast, the introduction of the *C*-trifluoromethyl substituent into En decreases the basicity of both amino groups to a great extent: $\Delta\log K_H$(En—**8**) = 2.0 and 5.1 for N(1) and N(2), respectively. The summation of these two effects enhanced by the presence of one more trifluoromethyl substituent in the benzene ring results in a very low basicity of the aromatic amino group.

Complexation with transition metal ions. The composition and stability constants of the complexes formed by ligands **5—7** with Cu^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} ions were determined by pH-potentiometric titration of solutions containing the ligand and metal nitrate in different mole ratios, an equimolar amount of nitric acid, and a supporting electrolyte (0.1 *M* KNO_3). In all cases, points of the titration curves lying in the interval of pH 2—7 before the onset of hydrolysis of cations were used to calculate the stability constants of the complexes. Different models including the formation of complex species $[M_pH_qL_r]$ were tested. The results that describe best of all the experimental data are given in Table 2. For several systems including Cd^{2+} and Zn^{2+} (see Table 2), the titration curves before the onset of cation hydrolysis coincide with similar titra-

Table 2. Stability constants $\beta_{pqr} = \dfrac{[M_pH_qL_r]}{[M]^p[H]^q[L]^r}$ of 3,3,3-trifluoro-*N*′-(3-trifluoromethylphenyl)-1,2-propanediamine and its *N*-mono- and *N,N*-dicarboxyethyl derivatives (T = 25 °C, I = 0.1 *M* KNO_3)*

Ligand L	M	*p*	*q*	*r*	Complex	$\log\beta_{pqr}$
5	Cu	1	0	1	CuL	3.77±0.12
	Ni	1	0	1	NiL	1.9±0.2
	Zn	1	0	1	ZnL	1.7±0.2
6	Cu	1	0	1	CuL	5.84±0.02
		1	0	2	CuL_2	10.36±0.03
	Ni	1	0	1	NiL	3.07±0.03
		1	0	2	NiL_2	5.15±0.10
7	Cu	1	0	1	CuL	7.60±0.04
	Ni	1	0	1	NiL	4.42±0.04
	Zn	1	0	1	ZnL	2.90±0.03

* Since the stability constants of the Cd (L = **5**, **6**, **7**) and Ni (L = **6**) complexes are low, they cannot be determined by pH-metry.

tion curves of the ligands within the error of pH measurements (±0.01), which does not allow one to calculate the complexation constants from these potentiometric data.

The stability constants of the complexes formed by diamine **5** are low (see Table 2). Since the basicity of the N(2) nitrogen atom is very low, it seems probable that compound **5** behaves as a monodentate ligand coordinating the central metal ion through the aliphatic amino group. Only the stability constants of the ML complexes were calculated because of low stability, although the formation of other, less stable complexes ML_n is quite probable.

N-Mono- or *N*,*N*-dicarboxyethyl derivatives **6** and **7** form more stable complexes than the starting diamine **5** due to closure of one or two six-membered β-alaninate chelate rings. Ligand **6** forms complexes ML and ML_2, whereas ligand **7** forms only complexes ML; no formation of protonated complexes was observed.

For all the ligands under study, the stability series of the complexes coincides with the Irwing—Williams series: $Cu^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+}$. The difference between logarithms of constants of the complexes, which are most similar in stability, can be used as a measure of selectivity of the ligand toward a certain metal ion. For instance, the selectivity of the ligands toward the Cu^{2+} ions compared to the Ni^{2+} ions increases in the series **5**, **6**, **7** ($\Delta\log\beta_{Cu/Ni}$ = 1.87 (**5**), 2.77 (**6**), and 3.18 (**7**)). Both the stability of the complexes that formed and selectivity of the ligands toward the Cu^{2+} ions increase with an increase in the number of the *N*-carboxyethyl groups.

Thus, the method for the synthesis of trifluoromethyl-substituted 1,2-ethylenediamines was proposed and demonstrated for 3,3,3-trifluoro-*N*′-(3-trifluoromethylphenyl)-1,2-propanediamine (**5**). The introduction of trifluoromethyl groups in both the ethylene chain and *N*′-phenyl substituent decreases the nucleophilicity of the secondary amino group to such an extent that diamine **5** is carboxyethylated with acrylic acid only at the N(1) nitrogen atom and, hence, mono- or diaddition products can be obtained depending on the ratio of reactants. The study of protolytic equilibria in aqueous solutions of compounds **5—7** compared to the fluorinated and non-fluorinated analogs showed that only the combined effect of the *C*-trifluoromethyl and *N*′-(3-trifluoromethyl)phenyl substituents in 1,2-ethylenediamine resulted in such a low basicity of the N(2) amino group. Selectivity of ligand **7** toward Cu^{2+} ions and sufficient stability of the complexes that formed provide possibilities of using this ligand as a copper-selective complexing agent.

Experimental

NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 and 376 MHz for ^1H and ^{19}F, respectively) using Me_4Si (^1H) and C_6F_6 (^{19}F) as internal standards. IR spectra were measured on a Perkin—Elmer Spectrum-BX II FT-IR spectrometer in KBr pellets or in thin layer. UV spectra of aqueous solutions of **5—7** were obtained on a Shimadzu UV-3101PC spectrophotometer at 25.0±0.1 °C with an increment of 0.1 nm.

pH-Potentiometric titration was carried out using an earlier described procedure[19] with a 0.1 *M* carbonate-free solution of KOH as titrant, ionic strength I = 0.1 *M* KNO_3, and T = 25.0±0.1 °C. The acidic ionization constants of **5—7** were determined by the titration of 10^{-3} *M* aqueous solutions containing an equimolar amount of nitric acid; no additional acid was introduced in the case of dihydrochloride **8**. To determine complexation constants, 10^{-3} *M* solutions of **5—7** were titrated, varying the concentration of $M(NO_3)_2$ (M = Cu, Ni, Zn, Cd) in the range of metal to ligand ratios from 2 : 1 to 1 : 3. All calculations were performed using the SUPERQUAD program.[20]

Diazo compound **1** (see Ref. 11) and nitroalkene **2** (see Ref. 12) were synthesized according to earlier described methods.

3-Nitro-2-(3-trifluoromethylphenyl)amino-1,1,1-trifluoropropane (3). Method *A*. A solution of diazo compound **1** (2.62 g, 15.5 mmol) in benzene (20 mL) was added dropwise with stirring for 20 min to a solution of 3-aminobenzotrifluoride (2.50 g, 15.5 mmol) in benzene (20 mL) heated to 60 °C. Then the mixture was stirred for 6 h at 60 °C and cooled to ~20 °C. The solvent was removed *in vacuo*, and the residue was recrystallized from hexane. The yield was 3.84 g (82%).

Method *B*. A mixture of nitroalkene **2** (2.68 g, 19.0 mmol) and 3-aminobenzotrifluoride (3.06 g, 19.0 mmol) in benzene (40 mL) was stirred for 6 h at 60 °C and then treated according to method *A*. The yield was 4.82 g (84%), m.p. 81—82 °C. Found (%): C, 39.81; H, 2.65; N, 9.30. $C_{10}H_8F_6N_2O_2$. Calculated (%): C, 39.75; H, 2.67; N, 9.27. IR, ν/cm^{-1}: 3393 (NH); 1621, 1601 (Ar); 1569, 1385 (NO_2). ^1H NMR ($CDCl_3$), δ: 4.11 (d, 1 H, NH, J = 10.7 Hz); 4.61, 4.81 (both dd, 1 H each, CH_2NO_2, ^2J = 13.5 Hz, ^3J = 8.8, 4.4 Hz); 4.92 (ddqd, 1 H, CH—CF_3, ^3J = 10.7, 8.8, 6.5, 4.4 Hz); 6.93 (dd, 1 H, H(6), J = 8.2, 2.4 Hz); 6.97 (dd, 1 H, H(2), J = 2.4, 1.7 Hz); 7.14 (ddq, 1 H, H(4), J = 7.8, 1.7, 1.8 Hz); 7.36 (dd, 1 H, H(5), J = 8.2, 7.8 Hz). ^{19}F NMR ($CDCl_3$), δ_F: 87.06 (d, CF_3, J = 6.5 Hz); 98.76 (t, CF_3—Ar, J = 0.8 Hz).

3,3,3-Trifluoro-*N*′-(3-trifluoromethylphenyl)-1,2-propanediamine hydrochloride (4). A solution of β-nitroamine **3** (4.50 g, 14.9 mmol) in anhydrous THF (50 mL) was added dropwise with stirring and cooling to 0 °C for 30 min to a suspension of $LiAlH_4$ (2.83 g, 74.5 mmol) in anhydrous THF (100 mL). Then the mixture was refluxed with stirring for 4 h and cooled to 0 °C. Water (2.83 g), a 10% solution of NaOH (2.83 g), and H_2O (8.49 g) were successively added. The mixture was stirred for 15 min and filtered. The solvent was removed *in vacuo*. The residue was dissolved in anhydrous benzene (40 mL), and the solution was cooled to 10 °C. Dry HCl was bubbled through the solution to saturation. A precipitate that formed was filtered off, dried *in vacuo*, and dissolved in ethyl acetate (15 mL). Hexane (15 mL) was added, and a precipitate was filtered off and dried *in vacuo*. The yield was 2.94 g (64%), m.p. 168—169 °C (subl.). Found (%): C, 38.82; H, 3.69; N, 8.89. $C_{10}H_{11}F_6N_2 \cdot HCl$. Calculated (%): C, 38.91; H, 3.59; N, 9.08. IR, ν/cm^{-1}: 3312, 3257 (NH); 2987, 2911 (NH_3^+), 1619 (Ar). ^1H NMR (DMSO-d_6), δ: 3.07, 3.30 (both m, 1 H each, CH_2); 4.81 (m, 1 H, CH—CF_3); 6.83 (d, 1 H, N<u>H</u>—Ar, J = 9.8 Hz); 6.99 (dm, 1 H, H(4), J = 8.6 Hz); 7.06 (dd, 1 H, H(6), J = 8.6, 2.3 Hz); 7.08 (m, 1 H, H(2)); 7.38 (dd, 1 H, H(5), J = 8.6, 7.8 Hz); 8.35 (br.s, 3 H,

NH_3^+). ^{19}F NMR ($CDCl_3$), δ_F: 88.64 (d, CF_3, J = 6.9 Hz); 101.19 (s, CF_3—Ar).

3,3,3-Trifluoro-*N*´-(3-trifluoromethylphenyl)-1,2-propanediamine (5). A solution of hydrochloride **4** (5.25 g, 17.0 mmol) in H_2O (35 mL) was treated with a 10% solution of NaOH to alkaline pH and extracted with CH_2Cl_2 (2×20 mL). The solvent was distilled off, and the residue was distilled *in vacuo*. The yield was 4.21 g (91%), b.p. 98—99 °C (4 Torr). IR, ν/cm^{-1}: 3308 (NH); 1618, 1601 (Ar). ^1H NMR ($CDCl_3$), δ: 1.26 (br.s, 2 H, NH_2); 3.04 (ddq, 1 H, C<u>H</u>H—$CHCF_3$, ^2J = 13.5 Hz, ^3J = 4.8 Hz, $^4J_{H,F}$ = 1.0 Hz); 3.18 (dd, 1 H, CH<u>H</u>—$CHCF_3$, ^2J = 13.5 Hz, ^3J = 4.7 Hz); 3.89 (dqdd, 1 H, HC—CF_3, J = 9.0, 7.3, 4.8, 4.7 Hz); 4.82 (d, 1 H, N<u>H</u>—Ar, J = 9.0 Hz); 6.86 (dd, 1 H, H(6), J = 8.2, 2.3 Hz); 6.92 (dd, 1 H, H(2), J = 2.3, 1.8 Hz); 7.01 (ddq, 1 H, H(4), J = 7.7, 1.8, 0.8 Hz); 7.28 (dd, 1 H, H(5), J = 8.2, 7.7 Hz). ^{19}F NMR ($CDCl_3$), δ_F: 87.90 (dd, CF_3, ^3J = 7.3 Hz, $^4J_{H,F}$ = 1.0 Hz); 98.90 (t, CF_3—Ar, J = 0.8 Hz).

3-[2-(3-Trifluoromethylphenylamino)-3,3,3-trifluoropropylamino]propionic acid (6). A mixture of diamine **5** (0.95 g, 3.5 mmol) and acrylic acid (0.25 g, 3.5 mmol) in 1,2-dichloroethane (10 mL) was refluxed for 6 h and cooled to room temperature. A precipitate that formed was filtered off and recrystallized from acetonitrile. The yield was 0.50 g (43%), m.p. 191—192 °C. Found (%): C, 45.39; H, 4.11; N, 8.01. $C_{13}H_{14}F_6N_2O_2$. Calculated (%): C, 45.36; H, 4.10; N, 8.14. IR, ν/cm^{-1}: 3340, 3332 (NH); 1649 (CO); 1619 (Ar). ^1H NMR (DMSO-d_6), δ: 2.33 (t, 2 H, $CH_2C\underline{H}_2COOH$, J = 6.7 Hz); 2.75 (td, 2 H, $C\underline{H}_2CH_2COOH$, J = 6.7, 1.7 Hz); 2.82, 2.91 (both dd, 1 H each, $C\underline{H}_2NH$, ^2J = 12.5 Hz, ^3J = 8.7, 3.7 Hz); 4.47 (m, 1 H, HC—CF_3); 6.43 (d, 1 H, N<u>H</u>—Ar, J = 9.0 Hz); 6.90 (d, 1 H, H(6), J = 7.6 Hz), 7.03 — 7.05 (m, 2 H, H(2), H(4)); 7.31 (t, 1 H, H(5), J = 7.9 Hz). ^{19}F NMR (DMSO-d_6), δ_F: 89.23 (d, CF_3, ^3J = 7.4 Hz); 101.25 (s, CF_3—Ar).

3,3-[2-(3-Trifluoromethylphenylamino)-3,3,3-trifluoropropylimino]dipropionic acid (7). A mixture of diamine **5** (2.65 g, 9.7 mmol) and acrylic acid (1.75 g, 24.3 mmol) in 1,2-dichloroethane (40 mL) was refluxed for 6 h and cooled to room temperature. A precipitate was filtered off and recrystallized from 1,2-dichloroethane. The yield was 2.25 g (67%), m.p. 145—146 °C. Found (%): C, 46.02; H, 4.33; N, 6.66. $C_{16}H_{18}F_6N_2O_4$. Calculated (%): C, 45.16; H, 4.36; N, 6.73. IR, ν/cm^{-1}: 3322 (NH); 1663 (CO); 1620, 1604 (Ar). ^1H NMR (DMSO-d_6), δ: 2.24—2.29 (m, 4 H, $CH_2C\underline{H}_2COOH$); 2.66—2.89 (m, 6 H, CH_2N, $C\underline{H}_2CH_2COOH$); 4.48 (m, 1 H, HC—CF_3); 6.33 (d, 1 H, N<u>H</u>—Ar, J = 9.0 Hz); 6.89 (d, 1 H, H(6), J = 7.8 Hz); 7.00—7.07 (m, 2 H, H(2), H(4)); 7.30 (t, 1 H, H(5), J = 7.8 Hz); 12.08 (br.s, 2 H, COOH). ^{19}F NMR (DMSO-d_6), δ_F: 89.24 (d, CF_3, ^3J = 7.5 Hz); 101.31 (s, CF_3—Ar).

3,3,3-Trifluoropropane-1,2-diamine hydrochloride (8) was obtained by the treatment of a benzene solution of the corresponding diamine[8] with anhydrous HCl followed by recrystallization from an ethyl acetate—hexane (1 : 3) system. IR, ν/cm^{-1}: 2948 (NH_3^+). ^1H NMR (DMSO-d_6), δ: 3.38, 3.35 (both dd, 1 H each, CH_2, ^2J = 14.6 Hz, ^3J = 6.6, 4.7 Hz); 4.65 (dqd, 1 H, HC—CF_3, ^3J = 7.7, 6.6, 4.7 Hz); 9.13 (br.s, 6 H, 2 NH_3^+). ^{19}F NMR (DMSO-d_6), δ_F: 91.04 (d, CF_3, ^3J = 7.7 Hz).

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