Synthesis of new organic super acids—*N*-(trifluoromethylsulfonyl)-imino derivatives of trifluoromethanesulfonic acid and bis(trifluoromethylsulfonyl)imide

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Salts of *N*-trifluoromethylsulfonyl derivatives of trifluoromethyl- and phenylsulfonimidoyl imides have been synthesized by two different routes. Both methods are one-pot reactions, that run in mild conditions with good yields. Two novel organic super acids: bis[*N*-(trifluoromethylsulfonyl)trifluoromethanesulfonimidoyl]imide and *N*,*N*′-bis(trifluoromethyl-sulfonyl)diimino trifluoromethanesulfonic acid were prepared and the structure of their potassium salts was obtained by single-crystal X-ray diffraction.

Introduction

According to data on the gas-phase acidity of a significant variety of OH-, NH- and CH-acids, bis(perfluoroakylsulfonyl)imides (PFSI) are among the strongest acids known to date[1] and their derivatives are widely used as electrolytes in lithium batteries and as ionic liquids,[2] Lewis acid catalysts[3] and intermediates of bioactive molecules.[4] They are stable in both H-form and anionic form. However, one can not state that PFSI meet all the requirements for such applications at present and in the coming years. The main restrictions are acidity, charge delocalization and solubility. An elongation of the perfluoroalkyl fragment only slightly increases the acidity in comparison to that of the CF₃-derivative, but it also induces a rigidity of the molecule, decreasing conductivity with an increase of local viscosity. Long perfluoroalkyl chains are both hydrophobic and lipophobic, making solubility increasingly difficult in organic and aqueous solvents. A substitution of perfluoroalkyl fragments in simple imides by unfluorinated or partialy fluorinated groups yields in a substantial decreasing of the acidity and solubility.

Another approach to the improvement in previously named properties of PFSI consists of substitution of one or more oxygen atoms by a more electron-withdrawing group (=NTf). Such substitution in PFSIs or their salts leads one to expect that compounds of this sort should have an advantage over PFSI in; high acidity in protonated form or high degree of dissociation of their salts; a considerable extension of the anionic charge delocalization; and the availability of one or two chiral centres at sulfur, so that such compounds are attractive for use as novel chiral Lewis acids in catalytic asymmetric reactions.

The development of chiral acid catalysts has been a relatively unexplored area in organic synthesis, although PFSIs were used to induce enantiomeric selectivity for preparation of optically active compounds or for induction of stereoselectivity in polymerization reactions.[5]

In the course of our quest for new organic acids, we have developed an interestingly simple yet efficient method for the synthesis of sulfoximidoyl fluorides PhS(O)(NSO₂CF₃)F **1**[6] and CF₃S(O)(NSO₂CF₃)F **2**.[7] This last compound is a novel reagent, acting as a synthon for the introduction of super attractive groups. In this paper we present methods of synthesis of PFSI analogies in which a NSO₂CF₃ group substitutes one or two oxygen atoms.
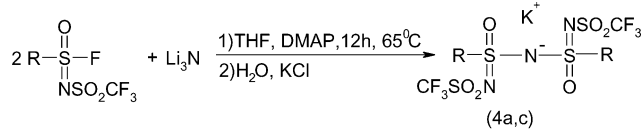
Results and discussion

There are a number of methods available at present for the synthesis of various PFSI. Des Marteau *et al.* reported the multistep reactions using liquid NH₃ and trimethyldisilazane.[8,9] One-pot synthesis by the reaction of perfluoroalkanesulfonyl fluoride with liquid NH₃, in the presence of triethylamine (TEA) as a base, at −40 °C was successfully employed.[10] An easy one-pot synthesis of symmetric PFSI from perfluoroalkylhalogenides and Li₃N was developed.[11] A new one-pot synthesis of PFSI through the reaction of perfluoroalkanesulonyl halides with acetamide derivatives, in the presence of K₂CO₃ as a base was described recently.[12]

We have examined this method with *N*-(trifluoromethylsulfonyl) trifluormethylsulfoximidoyl fluoride **2**. The reaction with trifluoroacetamide in the presence of K₂CO₃ resulted in the production of the half-sulfonylated intermediate [CF₃S(O)-(NSO₂CF₃)–N–C(O)CF₃]⁻ K⁺, without giving the bis[*N*-(trifluoromethylsulfonyl)trifluoromethanesulfoximidoyl] imide. It is possible that the observed result can be ascribed to steric hindrance or lack of nucleophilcity of the intermediate anion.

We report here two one-pot syntheses of symmetric and asymmetric imides containing such electron-withdrawing sulfoximidoyl groups, through the reaction of sulfoximidoyl fluorides with Li₃N or through the condensation of different sulfoximidoyl fluorides with sulfoximidoyl amides, in the presence of pyridine as a base.

Refluxing one mole of Li₃N with two moles of *N*-(trifluoromethylsulfonyl)arylsulfonimidoyl fluoride **1**, in THF, in the presence of dimethylaminopyridine as catalyst, and following treatment with KCl, yielded potassium salt of bis[*N*-(trifluoromethylsulfonyl)arylsulfonimidoyl] imide **4a** (80%) (Scheme 1).

Under the same conditions, the reaction with *N*-(trifluoromethylsulfonyl)trifluoromethane-sulfonimidoyl fluoride **2** gives mainly decomposition and reduction products. Modifications of reaction conditions or solvent did not lead to any better results. The bis[*N*-(trifluoromethylsulfonyl)trifluoromethanesulfonimidoyl] imide **4c** forms (by ¹⁹F NMR data)

2 R—S(=O)(NSO₂CF₃)—F + Li₃N →[1)THF, DMAP,12h, 65°C / 2)H₂O, KCl] R—S(=O)(CF₃SO₂N)—N—S(=O)(NSO₂CF₃)—R K⁺

(4a,c)

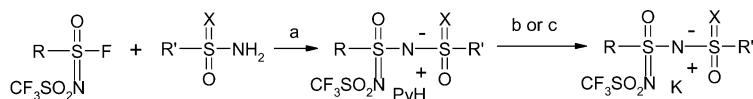R= Ph (4a) (80%), CF₃ (4c) (15%)

Scheme 1

in yields of 15–20%, but its isolation was unsuccessful. This result was an impact for the generation of another synthetic approach. We have found that fluoride **2** reacts with different amides in the presence of pyridine in methylene chloride solution under very mild conditions (several hours at rt) with nearly quantitative yields of pyridinium salts of imides. Coupling of this sort requires more harsh conditions for fluoride **1** (long heating in an excess of pyridine as solvent), with just the same yields of 80–90%, whereas morpholinesulfonyl fluoride and diethylaminosulfonyl chloride do not react with amides even upon very harsh conditions and a stronger base as a catalyst (Scheme 2).

Pyridinium salts of imides appear as light-brown oils and to be quite stable, but cannot be distilled under a high vacuum without decomposition. They were all transformed into relevant potassium salts **4a–e** by the action of K₂CO₃ in methylene chloride or by passing through an ion-exchange resin (Dowex 50 WX8-200) in potassium form; the latter method is favored in so far as it offers the prospect of separation from byproducts. Several examples are given in the Table 1. Potassium salts of

imides **44** are the mixtures of diastereoisomers. The crystal structures of salts **4c** and **4d** have been determined†.

The crystal structure of the salts have been determined by the single crystal X-ray investigation (Fig. 1–4). The main bond lengths and angles in anions **4c** and **4d** are virtually the same. In both anions the N–S distances in CF₃SO₂N fragments (average N–S 1.594 Å) are longer than in CF₃SON fragments (average N–S 1.555 Å) and the C–S distances in CF₃SO₂ moieties are shorter than in CF₃SO (average C–S bonds 1.822 and 1.858 Å, respectively), reflecting the different electron-withdrawing properties of these groups. In the coordination sphere of potassium atoms of the structure **4c** there are nine heteroatoms—six oxygen atoms with the K...O distances in the range of 2.670–2.912(5) Å and three fluorine atoms of trifluoromethyl groups with the K...F distances in the range of 3.048–3.342(7) Å. In the crystal structure of **4d**, two potassium atoms K(1) and K(2) occupy special positions on the two-fold axis, with the anions in a median position. Coordinationally surrounding the atom K(1) are eight oxygen atoms with the K...O distances in the range of 2.736–3.183(7) Å. For the atom K(2) the coordination number is also eight—there are two nitrogen atoms with the K...N distances of 3.079 Å and six oxygen atoms with the K...O distances in the range of 2.766–3.147(10) Å.
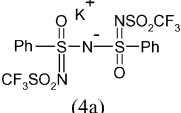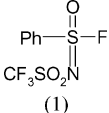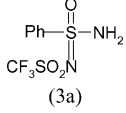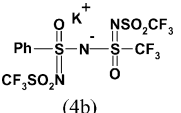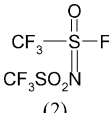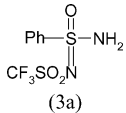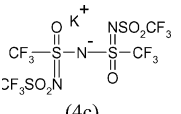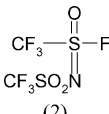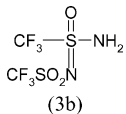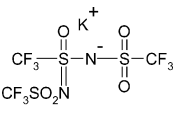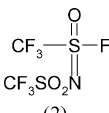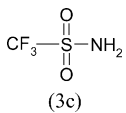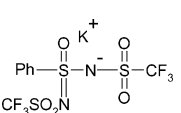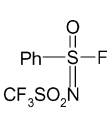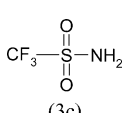
R—S(=O)(CF₃SO₂N)—F + R'—S(=X)(=O)—NH₂ →[a] R—S(=O)(CF₃SO₂N)—N⁻—S(=X)(=O)—R' PyH⁺ →[b or c] R—S(=O)(CF₃SO₂N)—N⁻—S(=X)(=O)—R' K⁺

R, R' = CF₃, Ph; X = O, NSO₂CF₃

Scheme 2 (a) Py, CH₂Cl₂; (b) Dowex 50WX8-200 (K⁺ form), MeOH; (c) K₂CO₃, CH₂Cl₂.

Table 1 Potassium salts of imides **4a–e**

Potassium sats of imides **4a–e**	Starting sulfoximidoyl fluorides **1–2**	Starting sulfoximidoyl amides **3a–c**	Mp/°C	Yield (%)
(4a)	(1)	(3a)	205–208	70
(4b)	(2)	(3a)	110–113	50
(4c)	(2)	(3b)	121–124	40
(4d)	(2)	(3c)	98–101	80
(4e)	(1)	(3c)	123–126	25
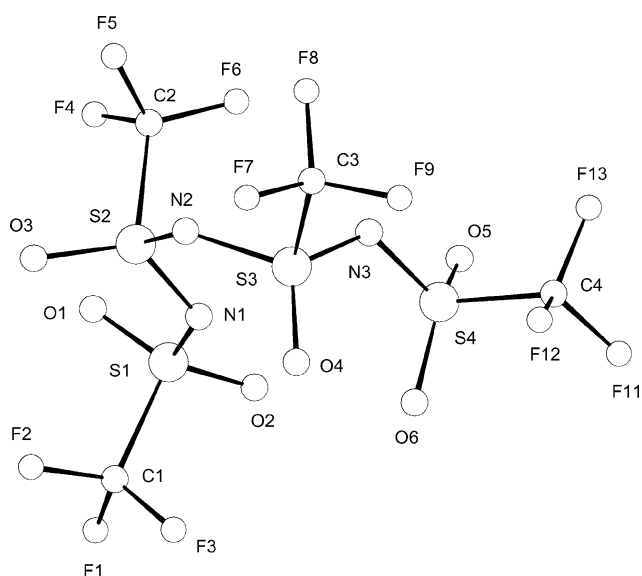
Fig. 1 A perspective view and labelling scheme for the anion **4c**. Selected bond lengths (Å) and angles (°): S(1)–O(1) 1.425(5), S(1)–O(2) 1.408(4), S(1)–N(1) 1.598(5), S(1)–C(1) 1.816(7), S(2)–O(3) 1.419(4), S(2)–N(1) 1.550(5), S(2)–N(2) 1.544(2), S(2)–C(2) 1.854(8), S(3)–O(4) 1.415(4), S(3)–N(2) 1.578(5), S(3)–N(3) 1.546(5), S(3)–C(3) 1.862(7), S(4)–O(5) 1.421(4), S(4)–O(6) 1.416(4), S(4)–N(3) 1.590(4), S(4)–C(4) 1.828(6), S(1)N(1)S(2) 124.8(3), S(2)N(2)S(3) 125.7(3), S(3)N(3)S(4) 125.5(3).
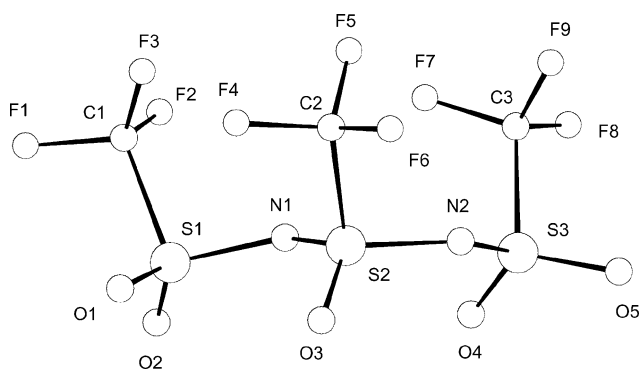
**Fig. 2** A perspective view and labelling scheme for the anion **4d**. Selected bond lengths (Å) and angles (°): S(1)–O(1) 1.430(9), S(1)–O(2) 1.410(10), S(1)–N(1) 1.588(7), S(1)–C(1) 1.850(10), S(2)–O(3) 1.426(8), S(2)–N(1) 1.531(7), S(2)–N(2) 1.564(8), S(2)–C(2) 1.852(13), S(3)–O(4) 1.419(8), S(3)–O(5) 1.419(6), S(3)–N(2) 1.576(9), S(3)–C(3) 1.844(12), S(1)N(1)S(2) 126.7(5), S(2)N(2)S(3) 128.8(5).
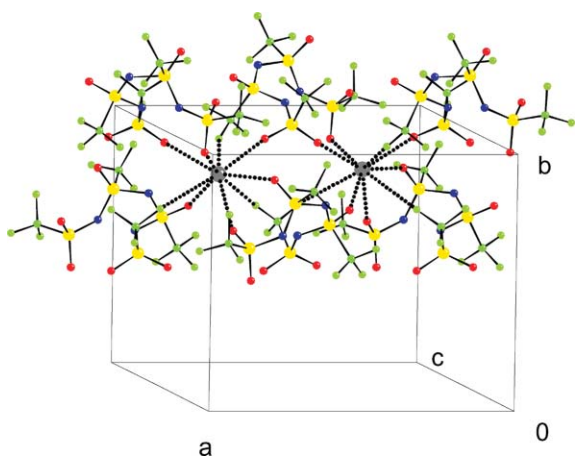

Fig. 3 Crystal packing for the structure **4c**.

N - (Trifluoromethylsulfonylimino) trifluoromethanesulfonyl amide **3b**,[7] prepared recently by the action of ammonia on fluoride **2**, has one chiral center and the presence of two isomers
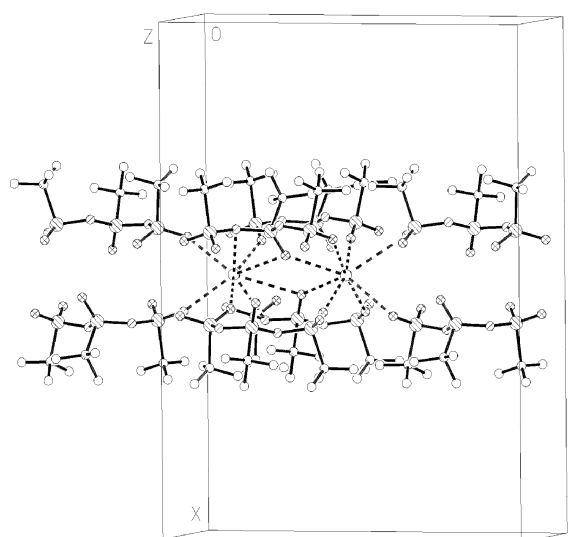

Fig. 4 Crystal packing for the structure **4d**.

in the ratio 1 : 1 was observed in non-polar solvents (CDCl$_3$) from ^{19}F and ^{1}H NMR spectra. Passing through the potassium form of an ion-exchange resin produced its potassium salt **4j** (Scheme 3).
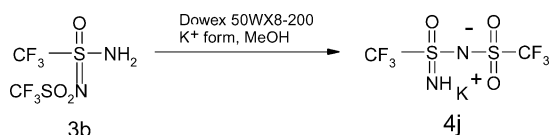
Scheme 3

The action of an excess of concentrated sulfuric acid on potassium salt **4d** results in near quantitative yield of bis[*N*-(trifluoromethylsulfonylimino)]trifluoromethanesulfonic acid **5** that can be represented as an analog of trifluoromethansulfonic acid, in which both oxygen atoms are substituted by =NTf fragment (Scheme 4)
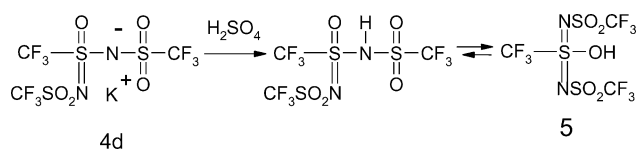
Scheme 4 Synthesis of new organic super acids: *N*-(trifluoromethylsulfonyl)imino derivatives of trifluoromethanesulfonic acid and bis(trifluoromethylsulfonyl) imide.

Acid **5** is soluble in water, quite stable to hydrolysis and does not undergo decomposition for any period of time at rt. It can also be distilled under a high vacuum but it is extremely hygroscopic. Presumably, at first it was isolated essentially as hydrate. In ^{1}H NMR spectra recorded without solvent and with an external standard we have detected only a slight signal of a NH-proton (14.3m, d) and the major peak of H$_3$O$^+$(6.1m, d). Unfortunately, there is no way of determining the degree of hydration, since it increases during the process of elemental analyses. The NMR method is also not applicable for acid **5**, which is not soluble in non-polar solvents (CDCl$_3$, CD$_2$Cl$_2$, CCl$_4$) and protic polar solvents (CH$_3$CN, (CD$_3$)$_2$CO) and reacts violently with dimethylsylfoxide. Physico–chemical, chemical, electrochemical and catalytic properties of the acid **5**, amide **3b** and imides **4a–j** are now under investigation.

In summary, two new methods of the synthesis of potassium salts of symmetrical and unsymmetrical imides **4a–j** containing one or two chiral centers were developed. Such stable anions with super-delocalized charge may gain widespread acceptance in organic synthesis as optically active catalysts and as electrolytes.

Experimental

Materials

All reactions were carried out under a dry Ar atmosphere. THF and glyme were dried over Na-benzophenone ketyl; CH_2Cl_2 was dried over CaH_2; pyridine was dried over KOH (platelets) and distilled at atmospheric pressure. All solvents were distilled immediately before use. All glassware was flame dried before use. ^1H and ^{19}F spectra were recorded with a Varian VX-300 spectrometer at 299.8 and 282.2 MHz, respectively, with HMDS and CCl_3F as standards.

Procedure for the reaction of *N*-(trifluoromethylsulfonyl)-phenylsulfonimidoyl fluoride (1) with Li₃N to obtain the bis[*N*-(trifluoromethylsulfonyl)phenylsulfonimidoyl] imide (4a) as potassium salt. A solution of *N*-(trifluoromethylsulfonyl)phenyl-sulfonimidoyl fluoride (**1**) (22 mmol) in THF (10 ml) and a catalytic amount of DMAP (0.5 mmol) were added slowly to a stirred suspension of 10 mmol Li₃N in dry THF (10 ml) at 20 °C. The reaction mixture was warmed up to 65 °C under magnetic stirring for 12 h. A precipitate of LiF was filtered off; THF and excess fluoride (**1a**) were removed *in vacuo* and a cold saturated aq. solution of KCl was added. The potassium salt of bis[*N*-(trifluoromethylsulfonyl) phenylsulfonimidoyl] imide (**4a**) was obtained as colourless crystals and could be recrystallised from H_2O. Two diastereomers in ratio 2 : 1: ^{19}F NMR (CD_3CN): δ −78. 31(s, CF_3, first diastereomer), −78.37 (s, CF_3, second diastereomer); ^1H NMR (CD_3CN): δ 7.94 (d, 2H), 7.57 (m, 3H) (first diastereomer); 7.87 (d, 2H), 7.65 (m, 3H) (second diastereomer); analytical data: $C_{14}H_{10}F_6KN_3O_6S_4$ [597], calc.: C 28.14, N 7.03, H 1.67%; found: C 28.11, N 6.88, H 1.64%.

General procedure for the reaction of fluoride (1) with amides (3a–c) in pyridine to obtain potassium salts of imides (4b–d). A mixture of the fluoride (**1**) (11 mmol) and amide (**3a–c**) (10 mmol) was dissolved in pyridine (20 ml) and warmed at 70 °C for 12h. An excess of fluoride and pyridine were removed *in vacuo* (0.04 mmHg) and the residue was washed with water. The resulting pyridine salts (light-brown oils) were transformed into potassium salts by two routes: 1) they were dissolved in a minimal quantity of methanol and were passed through an ion-exchange resin (Dowex 50 WX8-200) in potassium form. Methanol and water were partialy removed *in vacuo* and the rest was recrystallised from water; or 2) the solution of pyridinium salt in CH_2Cl_2 was stirred with dry K_2CO_3 (5 mmol) at rt for 3–4 h, the precipitate was removed, washed by methylene chloride and extracted with Et_2O. The extract was evaporated under a reduced pressure and the white residue was recrystallized from water. **4e**: ^{19}F NMR (DMSO-d_6): δ −77.82 (s, CF_3), ^1H NMR (DMSO-d_6): δ 7.8 (m); analytical data: $C_8H_5F_6KN_2O_5S_3$ [458] calc.: C 20.96, N 6.11, H 1.09%; found: C 21.01, N 6.09, H 1.13%.

General procedure for the reaction of fluoride (2) with amides (3a–c) in presence of pyridine to obtain potassium salts of imides (4b–d). Pyridine (20 mmol) was added to the solution of the amide (**3a–c**) (10 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred and a solution of the fluoride (**2**) (11 mmol) in 10 ml of CH_2Cl_2 was added at 0 °C and the mixture was stirred for 3–5 h at rt. The solvent was completely evaporated under a reduced pressure. The resulted pyridinic salts (yellows oils) were transformed into potassium salts by the procedures described below. **4b**: two diastereomers in ratio 2 : 1: ^{19}F NMR ((CD_3)$_2$CO): δ −78.49 (s, CF_3), −78.67 (s, CF_3), −78.97 (s, CF_3) (first diastereomer); −78.378 (s, CF_3), −78.77 (s, CF_3), −79.02 (s, CF_3), (second diastereoisomer); ^1H NMR ((CD_3)$_2$CO): δ 7.98 (d, 2H), 7.66 (m, 3H) (first diastereomer); 7.92 (d, 2H), 7.74 (m, 3H) (second diastereomer); analytical data: $C_9H_5F_9KN_3O_6S_4$ [589], calc.: C 18.34, N 7.13, H 0.85%; found: C 18.31, N 7.07, H 0.92%; **4c**: two diastereomers in ratio 3 : 2: ^{19}F NMR ((CD_3)$_2$CO): δ −78.4 (s, 6F, CF_3), −78.77 (s, 6F, CF_3), (first

diastereomer); −78.42 (s,6H, CF_3), −78.81 (s, 6H, CF_3), (second diastereoisomer); analytical data: $C_4F_{12}KN_3O_6S_4$ [581], calc.: C 8.26, N 7.23, F 39.24%; found: C 8.20, N 7.17, F 39.31%; **4d**: ^{19}F NMR (DMSO-d_6): δ −78.5 (s, 6F, CF_3), −78.92 (s, 3F, CF_3); analytical data: $C_3F_9KN_2O_5S_3$ [450], calc.: C 8.00, N 6.22, F 38.00%; found: C 7.97, N 6.17, F 37.89%.

N-(Trifluoromethylsulfonylimino)trifluoromethanesulfonyl amide 3b. ^{19}F NMR ($CDCl_3$): δ −79.02 (s, 3F, CF_3), −80.34 (s, 3F, CF_3) (first isomer); −79.46 (s, 3F, CF_3), −80.34 (s, 3F, CF_3) (second isomer); ^1H NMR ($CDCl_3$): δ 6.735 (br s, NH) (first isomer); 6.49 (br s, NH) (second isomer).

Potassium salt of N-(trifluoromethylsulfonylimino)trifluoro-methanesulfonyl amide 4j. The amide **3b** was dissolved in a minimal quantity of water and was passed through an ion-exchange resin (Dowex 50 WX8-200) in potassium form. Aqueous solution was concentrated. Mp 125–130 °C; yield 70%; ^{19}F NMR ((CD_3)$_2$CO): δ −79.2 (s, 3F, CF_3), −81.2 3 (s, 3F, CF_3); ^1H NMR (CD_3)$_2$CO): δ 4.18 (br s, NH) analytical data: $C_2HF_6KN_2O_3S_2$ calc.: C 7.55, N 8.8, H 0.31%; found: C 7.6, N 8.73, H 0.28%.

Bis[N-(trifluoromethylsulfonylimino)]trifluoromethanesulfonic acid 5. The salt **4d** (2 g, 4.4 mmol) was dissolved in 5 ml of concentrated H_2SO_4 and acid **5** was distilled in 0.004 mm at 50 °C. Yield 1.76 g (95%); mp 30 °C; ^{19}F NMR (without solvent): δ −79.20 (s, 6F, CF_3), −79.59 (s, 3F, CF_3); ^{13}C NMR (without solution): δ 129.99; 121.725; 117.452; 113.213 (SO_2CF_3, J_{CF} = 319.4); 125.785; 121.555; 117.32; 113.073 (CF_3SOH, J_{CF} = 322.3); ^1H NMR (without solvent): δ 14.26.

X-Ray crystal structure determination of compounds 4c and 4d. Crystal data, data collection and processing parameters are given in Table 2. All crystallographic measurements were performed at 18 °C on a CAD-4-Enraf-Nonius diffractometer

Table 2 Crystal data and structure refinement parameters for compounds **4c** and **4d**

	4c	4d
Empirical formula	$C_4F_{12}K_1N_3O_6S_4$	$C_3F_9K_1N_2O_5S_3$
Cell parameters		
a/Å	13.479(7)	22.385(6)
b/Å	11.203(4)	16.653(4)
c/Å	24.545(8)	7.093(4)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å³	3706.3(2.5)	2643.4(1.6)
Z	8	8
D_{calc}/g·cm^{-3}	2.084	2.26
Crystal system	Orthorhombic	Orthorhombic
Space group	P*bca*	P*bcn*
μ/cm^{-1}	8.596	9.865
$F(000)$	2272.0	1760.0
Crystal size/mm	0.12 × 0.34 × 0.46	0.14 × 0.25 × 0.37
Index ranges	0 ≥ h ≥ 17	0 ≥ h ≥ 26
	0 ≥ k ≥ 14	0 ≥ k ≥ 19
	−1 ≥ l ≥ 31	0 ≥ l ≥ 8
θ_{max}/°	27	25
Number of reflections:		
Collected	4237	2701
Independent	3584	2332
In refinement	1645	1087
Cutoff	$I \geq 3\sigma(I)$	$I \geq 2.5\sigma(I)$
Number of refined parameters	271	209
Final R indices:		
$R_1(F)$	4.01	6.74
$R_w(F)$	4.42	6.49
GOF	1.150	1.166
Weighting coefficients:	0.81; 0.38; 0.56	0.91; −0.16; 0.66; −0.20; 0.17
Largest peak/hole/e·cm^{-3}	−0.73/0.70	−0.37/0.44

(Mo–K$_a$ radiation, ω-2θ scan mode, the ratio of the scanning rates ω/2θ = 1.2). All data were corrected for Lorentz and polarization effects and an empirical absorption correction based on azimuthal scan data[13] was applied. The structures were solved by direct methods. All atoms were refined on F$_{obs}$ ($I \geq 3\sigma(I)$ and $I \geq 2.5\sigma(I)$ correspondingly) by full-matrix least-squares technique in the anisotropic approximation. Chebushev weighting scheme[14] was used. All structural calculations were carried out using CRYSTALS program package.[15]

Crystallographic data† (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center and can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge UK CB2 1EZ (fax: (internat.) +44 (0)1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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