New kinds of organic superacids. Bis(perfluoroalkylsulfonylimino)-trifluoromethanesulfonic acids and their trimethylsilyl esters†

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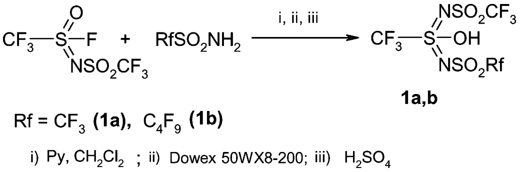
A synthesis of new unsymmetric trifluoromethylsulfonylimino(nonafluoro-n-butyl-sulfonylimino)-trifluoromethanesulfonic acid (**1b**) is reported. During the silylation reactions studies of bis(perfluoroalkylsulfonylimino)trifluoromethanesulfonic acids (**1a,b**) it was shown that reaction proceeds exclusively on the central oxygen atom to give trimethylsilyl esters. The obtained esters along with several trimethylsilylesters of sulfonic acids have been studied by ^{29}Si-NMR spectroscopy and an attempt to estimate the strength of bis(perfluoroalkylsulfonylimino)trifluoromethanesulfonic acids by the ^{29}Si-NMR chemical shifts of their trimethylsilylesters was made, resulting in the conclusion that these compounds may be cited as the strongest organic Brønsted acids.

Introduction

The synthesis of symmetric[1] and unsymmetric bis(perfluoroalkylsulfonylimino)trifluoromethanesulfonic acids **1** through the condensation of *N*-(trifluoromethylsulfonyl)trifluoromethanesulfoximidoyl fluoride with perfluoroalkylsulfonamides has been developed (Scheme 1).



Scheme 1 The synthesis of symmetric[1] and unsymmetric bis(perfluoroalkylsulfonylimino)trifluoromethanesulfonic acids.

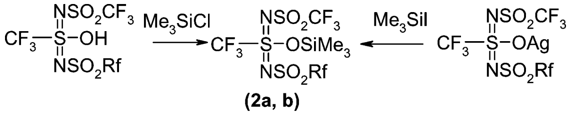
These acids may be envisioned as analogues of trifluoromethanesulfonic acid in which both oxygen atoms are substituted by fragments: =NTf or =NNf. It was shown by us earlier that such a replacement in different substituents with an E=O (E = C, S, P, I) fragment causes the growth of electron-withdrawing properties of the group[2] *via* considerable extension of the anionic charge delocalization. This suggests that the strength of new bis(perfluoroalkylsulfonylimino)trifluoromethanesulfonic acids **1** must be considerably above the TfOH and $HN(Tf)_2$, which are the strongest organic acids with the exception of the carborane acids.[3] Thus the straight acidity measurement of the strength of acids **1** in the standard manner is probably impracticable.

The relationship between the chemical shift of trimethylsilyl group bonded to a moiety R in ^{29}Si-NMR spectra and electron-withdrawing properties of substituent R has been long in use.[4] The linear correlation dependencies between the shifts in the ^{29}Si-NMR spectra of trimethylaroxysilanes,[5] trimethylsilylesters of carbonic acids[6] and acidity (pK_a) of phenols and carbonic acids, respectively, were found. The structure and spectroscopic properties of silyl cations have been studied broadly for the last two decades.[7] To the best of our knowledge correlations for sulfonic acids are not described.

In this paper we report the synthesis of trimethylsilyl esters of bis(perfluoroalkylsulfonylimino)trifluoromethanesulfonic acids **1a** and **1b** and the results of their ^{29}Si-NMR spectroscopy study. We also present an attempt to create pK_a-vs-δ_{29Si}, $-H_o$-vs-δ_{29Si}, and $\Delta G°$-vs-δ_{29Si} dependencies in order to estimate the strength of new acids **1a,b** using the acidity data presented in literature and received by varied methods.

Results and discussion

Trimethylsilyl esters of bis(perfluoroalkylsulfonylimino)trifluoromethanesulfonic acids **1a** and **1b** have been prepared by two routes—upon boiling acids **1** with chlorotrimethylsilylane or by reaction of silver salts of acids **1** with iodotrimethylsilane in CH_2Cl_2 at room temperature (Scheme 2).



Scheme 2 The synthesis of trimethylsilyl esters of bis(perfluoroalkylsulfonylimino)trifluoromethanesulfonic acids.

The resulting esters **2a,b** are sufficiently stable liquids in an inert atmosphere at room temperature. The fact that the silyl group is attached to the central oxygen atom is confirmed by the presence of only two signals of CF_3 groups with intensity 1 : 2 in the ^{19}F NMR spectra of the compound **2a**. The Me_3Si group rearrangement to the nitrogen atom is of limited extent (less than 5% in two months).

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† Electronic supplementary information (ESI) available: Tables of ^{29}Si NMR chemical shifts of phenols, carbonic and sulfonic acid trimethylsilyl esters, and their acidity data in combination with diagrams; references for literature data used in the tables. See DOI: 10.1039/b815155e

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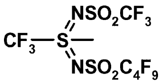
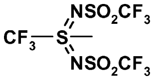
Table 1 ^{29}Si-NMR chemical shifts of trimethylsilyl esters of sulfonic acids $ROSiMe_3$

		δ_{29Si} (ppm)		
N	R	Neat	CH_2Cl_2 (50%)	$-H_o$
1	4-$CH_3C_6H_4SO_2$	31.62	32.10	About 6.5–7.5[10b]
2	CH_3SO_2	32.03	32.27	About 6.5–7.5[10b]
3	$C_6H_5SO_2$	32.19	32.57	About 6.5–7.5[10b]
4	4-$ClC_6H_4SO_2$	33.03	33.40	About 6.5–7.5[10b]
5	$ClSO_2$	44.36	44.12	About 13–15[10c]
6	$C_4F_9SO_2$	43.95	44.40	About 13–15[10c]
7	CF_3SO_2	44.10	44.26 (42.00 in CCl_4)	About 13–15[10c]
1b		62.00	61.50	About 24–25
1a		63.51	62.85 (62.00 in CCl_4)	About 24–25

For ^{29}Si-NMR chemical shifts measurements of sulfonic acids trimethylsilyl esters in equal terms, we prepared trimethylsilyl esters of methyl-, aryl-, chloro- and perfluoroalkanesulfonic acids by literature procedures.[8] The ^{29}Si-NMR spectra have been recorded for trimethylsilyl esters of above mentioned sulfonic acids without solvent and in methylene chloride (50% solution). The data are presented in Table 1.

It is well known that quantitative determination of acidity, notably for very strong acids, is a relative value and it is greatly dependent on the investigative techniques, solvents, concentration, indicators, temperature.[9,13] Thus we resolved that the correlation of ^{29}Si-NMR chemical shifts data with acidity data derived from different literature sources would give the most impartial assessment and it may allow us to evaluate the strength of acids **1a,b** compared to other sulfonic acids. We operated on the premise that the dependence between the shift of the ^{29}Si-NMR spectroscopy signal of trimethylsilyl esters of sulfonic acids and acidity function is linear by analogy with carbonic acids.

All dependencies discussed below were obtained by preparation of diagrams in which the rectilinear trend was made and the corresponding equations were calculated.

The acidity function H_o values presented in the Table 1 has been determined by UV absorption spectrometry at 22 °C.[10] The corresponding rectilinear trend equation $-H_o = -11.92 + 0.59\delta_{29Si}$ **(A)** shows that the values of H_o for acids **1a,b** are about 24–25. The cross-point of the curve with the δ^{29}Si datum line has a value of about 20 ppm that fits with PhOH.[5] This makes it possible to consider this data as related to PhOH. In the same conditions the value for a 11% solution of SbF_5 in $C_4F_9SO_3H$ ("magic acid") is 18.32.[10c]

As noted above, the linear correlation dependence pK_a-vs-δ_{29Si} for phenols[5] and carbonic acids was found.[6] If the assumption is made that the correlation for carbonic acids applies to sulfonic acids, we arrive at pK_a values of about –28.5 to –17 for acids **1a,b**. For trimethylsilyl esters of phenols and carbonic acids $ROSiMe_3$, the δ_{29Si}-vs-pK_a values were taken from literature data[5,6] and the rectilinear trend equations were as follows: $pK_a = 19.052 - 0.5011\delta_{29Si}$ **(B)** (phenols data relative to picric acid) and $pK_a = 14.426 - 0.4291\delta_{29Si}$ **(C)** (carbonic acids data relative to trifluoroacetic acid).

An interconnection between the ^{29}Si-NMR chemical shifts of the trimethylsilyl esters and the acid strength of an assorted number of organic and inorganic initial acids was described previously[4d] by Marsmann and Horn. An extrapolation of our data on the acidity diagram obtained by these authors is represented as the rectilinear trend equation: $pK_a = 14.426 - 0.43\delta_{29Si}$ **(D)** and pK_a values for acids **1a,b** are about –14.25 to –14.9 relative to polyphosphonic acid.

The pK_a value of hydriodic acid in 1, 2-dichloroethane (DCE) was determined by Bos and Dahmen[11] from conductivity measurements. A glass electrode was calibrated for dichloroethane in the potentiometric titration of hydriodic acid with tetramethylguanidine. According to this acidity scale the pK_a value of acids **1a,b** is about 0; the rectilinear trend equation is $pK_a = 25.473 - 0.41\delta_{29Si}$ **(E)**.

Dissociation of trifluoromethanesulfonic acid in non-aqueous solvents has been investigated mainly by conductometry and compared with that of *p*-toluenesulfonic, methanesulfonic, fluorosulfuric and perchloric acids.[12] Trifluoromethanesulfonic acid is completely dissociated in rather basic solvents such as dimethyl sulfoxide, dimethylacetamide and dimethylformamide, while it is associated to some extent in the other solvents, especially in methyl isobutyl ketone and acetic acid. The strength of trifluoromethanesulfonic acid is almost the same as that of perchloric acid in all the solvents. We correlated our measurements with the pK_a value of *p*-toluenesulfonic, methanesulfonic, and trifluoromethanesulfonic acids in glacial acetic acid, the rectilinear trend equation is $pK_a = 17.838 - 0.29\delta_{29Si}$ **(F)**; the pK_a values for acids **1a**, **b** are about zero.

Guthrie[13] has estimated pK_a values for a set of strong acids from a linear correlation between free energies of hydrolysis of their methyl esters and acidity. The pK_a values resulting from this work[13] have been matched with our ^{29}Si-NMR spectroscopy study and the relationship is calculated according to the rectilinear trend equation $pK_a = 7.0566 - 0.3\delta_{29Si}$ **(G)**. The pK_a values for acids **1a,b** are about –11.07 to –11.5 [relative to $C_6H_5CH_2C(O)OH$] (Table 2).

Using the PM3 method quantum chemical calculations of potentially superacidic neutral Brønsted acids were carried out and it was shown that this method can be used to predict the gas phase acidities only if empirical corrections were made.[14] The

Table 2 ^{29}Si-NMR chemical shifts of trimethylsilyl esters of sulfonic acids and pK_a values from a linear correlation between free energies of hydrolysis of their methyl esters and acidity[13]

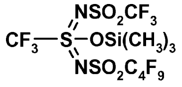
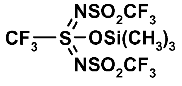
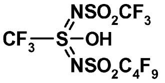
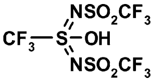
N	Trimethylsilyl esters	δ_{29Si}	pK_a
1	$(CH_3)_3SiO–SO_2CH_3$	32.27	–1.92
2	$(CH_3)_3SiO–SO_2C_6H_5$	32.57	–2.8
3	$(CH_3)_3SiO–SO_2C_6H_4$-*p*-Br	33.4	–3.1
4	$(CH_3)_3SiO–SO_2CF_3$	44.26	–5.9
5	$(CH_3)_3SiO–SO_2Cl$	44.12	–6.0
1b		61.5	about –11.07
1a		62.85	about –11.5

Table 3 ^{29}Si-NMR chemical shifts of trimethylsilyl esters of sulfonic acids and $\Delta G°$ values[15]

N	Acid	δ_{29Si}	$\Delta G°$/kcal mol^{-1}
1	CH_3SO_2OH	32.27	312.7
2	$CF_3\ SO_2OH$	44.26	292.5
3	$Cl\ SO_2OH$	44.12	287.2
4	FSO_3SbF_5H	—	250.5
1b	 $CF_3{-}S(=NSO_2CF_3)(=NSO_2C_4F_9){-}OH$	61.5	about 255.8
1a	 $CF_3{-}S(=NSO_2CF_3)(=NSO_2CF_3){-}OH$	62.85	about 252.6

intrinsic gas phase equilibrium acidity value $\Delta G°$ scale used may be referred to pK_a scale upon the fact that $\Delta G°$ 10 kcal mol^{-1} is about 7 pK_a units. In accordance with calculations of deprotonation enthalpies (DPE= 266 kcal mol^{-1}) the acidity of acid **1a** is in excess of TfOH by 30 kcal mol^{-1} (*i.e.* more than 21 pK_a units).[14] It was instructive to consider the relationships between quantum chemical calculations of the gas phase acidities and ^{29}Si-NMR chemical shifts of trimethylsilyl esters of relevant acids taking into consideration the difference in the phase state. The ^{29}Si-NMR spectroscopy study data were correlated with $\Delta G°$ estimated data[15] and cited in Table 3. The rectilinear trend equation $\Delta G° = 374.39 - 1.9\delta_{29Si}$ **(H)** obtained shows that gas phase acidity of acids **1a,b** is in excess of TfOH about by 26 pK_a units. This value of $\Delta G°$ = 252.6–255.8 kcal mol^{-1} is approximately equal to $\Delta G°$ for solution SbF_5 in HF ("magic acid").

It can be proposed gingerly from equation **(H)**, that a value of δ_{29Si} for the free $[Me_3Si]^+$ cation must be 195.7 (when $\Delta G° = 0$ kcal mol^{-1}), though it does not fit with earlier calculations (400 ppm).[16]

On the base of the ^{29}Si-NMR chemical shifts of several trimethylsilyl esters of sulfonic acids and the rectilinear trend equations **A–H** the indeterminate pK_a, $\Delta G°$ and $-H_o$ values were calculated and these data are cited in Table 4. Hereby, the intra subgroup acidity (alkane-, arenesufonic acids ⇒ chloro-, fluoro-, perfluoroalkylsulfonic acids ⇒ acids **1a,b**) are very close. It is interesting to note that on the base of the ^{29}Si-NMR data the following order of acid strengths was observed: $C_4F_9SO_2OH > CF_3SO_2OH > ClSO_2OH$ in methylene chloride, and $ClSO_2OH > CF_3SO_2OH > C_4F_9SO_2OH$ without solvent (Table 1). Such renumbering has been reported previously on the basis of conductometric studies: $CF_3SO_2OH > HClO_4 > FSO_2OH > H_2SO_4$ in acetic acid.[17] and $FSO_2OH > ClSO_2OH \sim CF_3SO_2OH >> HClO_4$ in sulfuric acid.[18]

Conclusions

In summary, it must be emphasized that in all instances the acidity of the acids **1a,b** is in excess of TfOH by 5.5–9.3 pK_a units (and by 3–3.5 pK_a units in excess of $HNTf_2$) in the test conditions. According to the gas phase acidity data, they are in excess of TfOH by ~26 pK_a units (and ~10 pK_a units relative to $HNTf_2$). As for the gas phase acidities calculations and the acidity function H_o determined by UV absorption spectrometry, the strength of the acids **1a,b** is equal or in excess of the "magic acids", the solutions of Lewis acids in strong Brønsted acids, so they deserve to be assigned as new organic superacids.

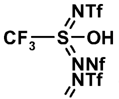
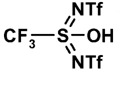
Experimental

All reactions were carried out under a dry Ar atmosphere. CH_2Cl_2 was dried over CaH_2. All solvents were distilled immediately before use. All glassware was flame dried before use. ^{1}H and ^{19}F spectra were recorded with a Varian VX-300 spectrometer at 299.8 and 188.14 MHz respectively with Me_4Si and CCl_3F as external standards. ^{13}C and ^{29}Si spectra were recorded with Bruker Avance DRX 500 at 125.76 and 79.45 MHz with Me_4Si as external standard.

Trifluoromethylsulfonylimino(nonafluoro-n-butylsulfonylimino)-trifluoromethanesulfonic acid (1b)

Pyridine (20 mmol) was added to the solution of the nonafluoro-n-butylsulfonamide (10 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred and a solution of the *N*-(trifluoromethylsulfonyl)-trifluoromethanesulfonimidoyl fluoride (11 mmol) in 10 ml of CH_2Cl_2 was added at 0 °C and the mixture was stirred for 3–5 h

Table 4 The acidity of sulfonic acids calculated from the rectilinear trend equations pK_a-vs-δ_{29Si}, $-H_o$-vs-δ_{29Si}, $\Delta G°$-vs-δ_{29Si} dependencies

N	Sulfonic acids	δ_{29Si} (ppm)	$-H_o$ from **A**	pK_a from **B**	pK_a from **C**	pK_a from **D**	pK_a from **E**	pK_a from **F**	pK_a from **G**	$\Delta G°$/kcal mol^{-1} from **H**
1	$4\text{-}CH_3C_6H_4SO_3H$	32.10	6.95	2.97	0.66	−0.55	12.29	8.63	−2.4	312.99
2	CH_3SO_3H	32.27	7.05	2.88	0.58	−0.63	12.22	8.58	−2.45	312.66
3	$C_6H_5SO_3H$	32.57	7.22	2.73	0.45	−0.77	12.1	8.55	−2.54	312.09
4	$4\text{-}ClC_6H_4SO_3H$	33.40	7.71	1.83	0.2	−1.15	11.76	8.26	−2.28	310.5
5	$ClSO_3H$	44.12	14.01	−3.06	−4.5	−6.15	7.36	5.18	−5.95	290.0
6	$C_4F_9SO_3H$	44.40	14.18	−3.2	−4.62	−6.28	7.24	5.1	−6.03	289.46
7	CF_3SO_3H	44.26	14.09	−3.13	−4.56	−6.22	7.3	5.14	−5.99	289.73
8	 $CF_3{-}S(=NTf)(=NNf){-}OH$ (**1b**)	61.50	24.22	−11.77	−11.96	−14.25	−0.22	0.19	−11.07	255.8
9	 $CF_3{-}S(=NTf)(=NTf){-}OH$ (**1a**)	62.85	25.02	−12.44	−12.54	−14.88	−0.33	−0.19	−11.47	252.6
	Imides[19,20]									
10	$(FSO_2)_2NH$	44.9[19]	14.47	−3.45	−4.87	−6.55	7.04	4.96	−6.18	288.51
11	$(CF_3SO_2)_2NH$	55.9[20]	20.93	−8.96	−9.56	−11.64	2.52	1.8	−9.42	267.4

at room temperature. The solvent was completely evaporated under reduced pressure. The resulted pyridinic salt (yellow oil) was dissolved in minimal quantity of methanol and was passed through an ion-exchange resin (Dowex 50 WX8-200) in acid form. The resulting aquatic solution was extracted by Et_2O. The extract was evaporated under reduced pressure. The residue was distilled over a fivefold amount of concentrated sulfonic acid.

1b. Colorless liquid; bp 115 °C/0.07 mmHg (89% isolated yield); ^{19}F NMR (200 MHz, CH_2Cl_2): δ −74.8 (s, 3F, CF_3), −76.09 (s, 3F, CF_3), −80 (t, 3F, CF_3), −109.42 (t, 2F, CF_2), −120.08 (br.s, 2F, CF_2) −125.2 (t, 2F, CF_2); ^{13}C NMR (125.76 MHz, $CDCl_3$)): δ 116.25 (q, J_{CF} 322 Hz, CF_3S), 115.95 (q, J_{CF} 320.8 Hz, CF_3S), 117.45 (t, J_{CF} 66 Hz, CF_2), 117.45 (t, J_{CF} 66 Hz, CF_2), 115.68 (t, J_{CF} 33 Hz, CF_2), 115.16 (t, J_{CF} 33 Hz, CF_2), 113.26 (t, J_{CF} 37 Hz, CF_2), 111.63 (t, J_{CF} 31.4 Hz, CF_2), 110.86 (t, J_{CF} 32.7 Hz, CF_2), 109.48 (m), 107.5 (m), 105.4 (m), 95.05.

Trimethylsilyl bis(trifluoromethylsulfonylimino)trifluoromethanesulfonate (2a), Trimethylsilyl trifluoromethylsulfonylimino(nonafluoro-n-butylsulfonylimino)trifluoromethanesulfonate (2b)

Method A. Chlorotrimethylsilane (1.5 mmol) is gradually added to acid **1** (1 mmol with stirring and protection from moisture. The mixture is refluxed until hydrogen chlorine evolution ceased (about 12 h for **2a**; 18 h for **2b**) and the product is isolated by distillation.

Method B. Iodotrimethylsilane (4 mmol) is gradually added to solution of silver salt of acid **1** (4 mmol) in 20 ml CH_2Cl_2 with effective stirring and protection from moisture and light. The mixture is stirred for 2–4 h at room temperature and AgI was filtered off. The solvent is removed *in vacuo* and residue was distilled.

2a. Colorless liquid; bp 75 °C/0.07 mmHg (86% isolated yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.64 (s); ^{19}F NMR (200 MHz, $CDCl_3$): δ −76.06 (s, 3F, CF_3), −76.7 (s, 6F, CF_3); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 118.72 (q, J_{CF} 322 Hz, CF_3SO_2), 118.98 (q, J_{CF} 320.8 Hz, $CF_3S(NTf)_2$), 0.004 (s, $SiMe_3$); ^{13}C NMR (125.76 MHz, neat): δ 118.46 (q, J_{CF} 320.8 Hz, $CF_3S(NTf)_2$), 118.27 (q, J_{CF} 322 Hz, CF_3SO_2), −1.77 (s, $SiMe_3$).

2b. Colorless liquid; bp 95 °C/0.05 mmHg (78% isolated yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.61 (s); ^{19}F NMR (200 MHz, $CDCl_3$): δ −77.63 (s, 3F, CF_3), −78.3 (s, 3F, CF_3), −81.66 (t, 3F, CF_3), −111.65 (br.s., 2F, CF_2), −121.69 (br.s., 2F, CF_2) −126.75 (br.s, 2F, CF_2); ^{13}C NMR (125.76 MHz, $CDCl_3$)): δ 116.25 (q, J_{CF} 322 Hz, CF_3SO_2), 115.95 (q, J_{CF} 320.8 Hz, $CF_3S(NTf)_2$), 117.45 (m), 117.45 (m), 115.68 (m), 115.16 (m), 113.26 (m), 111.63 (m), 110.86 (m), 109.48 (m), 107.5 (m), 105.4 (m), 95.05, −1.75 (s, $SiMe_3$).

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