Crystal structure of 1,3-bis(trimethylsilyl)imidazolium trifluoromethanesulfonate, $(C_9H_{21}N_2Si_2)(CF_3SO_3)$

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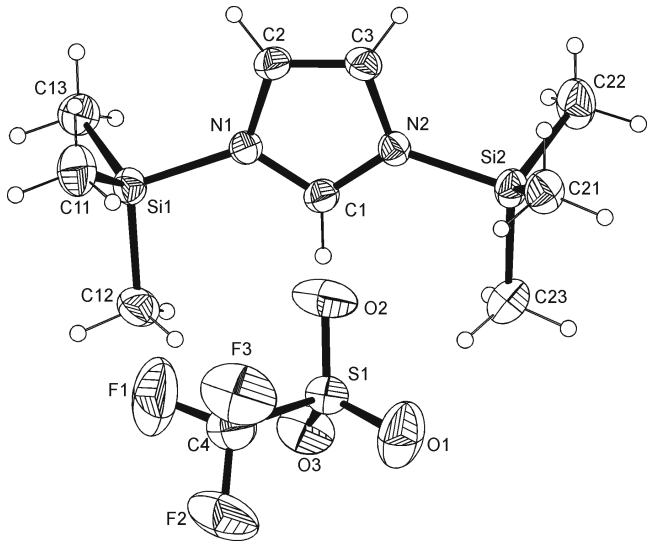

Abstract

$C_{10}H_{21}F_3N_2O_3SSi_2$, orthorhombic, *Pbca* (no. 61), a = 14.6136(4) Å, b = 12.5955(5) Å, c = 19.9486(7) Å, V = 3671.9 Å^3, Z = 8, $R_{gt}(F)$ = 0.050, $wR_{ref}(F^2)$ = 0.110, T = 233 K.

Source of material

The imidazolium salt was prepared by mixing equimolar amounts of 1-trimethylsilylimidazole and trimethylsilyl triflate without solvent under inert gas. Single crystals were obtained by diffusion of hexane into a solution of the product in dichloromethane at room temperature. Needless to say that this compound is very sensitive to moisture.

Discussion

The title compound has been investigated for its role in silylation mixtures [1,2]. In solution, 1,3-bis(trimethylsilyl)imidazolium salts are known to exist in an equilibrium with 1-trimethylsilylimidazole and the respective silylating agent by a dissociation-reassociation mechanism, depending on the leaving group ability and nucleophilicity of the anion involved and, of course, the temperature [2,3]. In the present case, the equilibrium lies on the side of the imidazolium salt [2,3]. In addition, some anions such as tetrafluoroborate or hexafluorophosphate [4], are simply not compatible with a silylating agent because they form fluorotrimethylsilane [5,6]. Crystal structures of related quaternary *N*-trimethylsilyl-substituted heterocycles have been reported [7-10]. As described previously [7-10], the coordination of the Si atom deviates markedly from ideal tetrahedral. Thus, the angles ∠N–Si–C range from 104.1° to 107.0°, whereas ∠C–Si–C are between 112.7° and 113.5°. The Si—N bond lengths are d(Si1–N1) = 1.811(2) Å and d(Si2–N2) = 1.809(2) Å and ∠N1–C1–N2 = 111.5°. The triflate ions adopt a staggered conformation and are arranged in layers parallel to the (100) plane. Each triflate anion is surrounded by four imidazolium cations. Weak interionic contacts are observed (d(H···acceptor) and d(donor···acceptor), ∠donor–H···acceptor): O1···H–C1^{i} (2.65 Å and 3.213 Å, 119°), O2···H–C13^{ii} (2.55 Å and 3.380 Å, 143°), O3···H–C3^{iii} (2.31 Å and 3.198 Å, 158°), and O3···H–C12 (2.63 Å and 3.575 Å, 164°). Symmetry codes: (i) $1–x,½+y,½–z$; (ii) $¾–x,½+y,z$; (iii) $–½+x,y,½–z$.

Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.04 × 0.3 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.42 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17567, 3207
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2513
$N(param)_{refined}$:	190
Programs:	SHELXS-97, SHELXL-97 [11]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	8*c*	0.5852	0.0999	0.2379	0.056
H(2)	8*c*	0.8328	0.0437	0.1658	0.061
H(3)	8*c*	0.8497	0.1472	0.2684	0.059
H(11A)	8*c*	0.7524	0.0548	0.0350	0.119
H(11B)	8*c*	0.6732	0.1395	0.0440	0.119
H(11C)	8*c*	0.6582	0.0398	–0.0032	0.119
H(12A)	8*c*	0.4966	–0.0373	0.1583	0.101
H(12B)	8*c*	0.4860	–0.0209	0.0800	0.101
H(12C)	8*c*	0.5024	0.0782	0.1273	0.101
H(13A)	8*c*	0.7445	–0.1541	0.1053	0.106
H(13B)	8*c*	0.6495	–0.1886	0.0738	0.106
H(13C)	8*c*	0.6613	–0.1833	0.1527	0.106
H(21A)	8*c*	0.7818	0.3614	0.3234	0.098
H(21B)	8*c*	0.6977	0.4063	0.3646	0.098
H(21C)	8*c*	0.6872	0.3825	0.2870	0.098
H(22A)	8*c*	0.8100	0.1716	0.4090	0.119
H(22B)	8*c*	0.7308	0.0876	0.4199	0.119
H(22C)	8*c*	0.7287	0.1970	0.4590	0.119
H(23A)	8*c*	0.5400	0.1358	0.3677	0.104
H(23B)	8*c*	0.5242	0.2311	0.3172	0.104
H(23C)	8*c*	0.5345	0.2537	0.3950	0.104

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	8*c*	0.51306(5)	0.34411(6)	0.16591(4)	0.0543(4)	0.0539(5)	0.0610(5)	–0.0031(3)	0.0018(3)	0.0134(4)
O(1)	8*c*	0.4952(2)	0.4425(2)	0.1966(2)	0.192(3)	0.073(2)	0.102(2)	0.022(2)	0.002(2)	–0.018(2)
O(2)	8*c*	0.6064(2)	0.3125(2)	0.1685(1)	0.056(1)	0.132(2)	0.121(2)	0.008(1)	–0.006(1)	0.051(2)
O(3)	8*c*	0.4515(2)	0.2607(2)	0.1797(1)	0.073(1)	0.088(2)	0.104(2)	–0.029(1)	0.007(1)	0.033(2)
F(1)	8*c*	0.5084(3)	0.2867(3)	0.0419(1)	0.261(4)	0.180(3)	0.072(2)	0.034(3)	0.002(2)	–0.025(2)
F(2)	8*c*	0.4129(2)	0.4064(3)	0.0659(1)	0.098(2)	0.188(3)	0.126(2)	0.012(2)	–0.036(2)	0.069(2)
F(3)	8*c*	0.5534(2)	0.4448(3)	0.0569(1)	0.125(2)	0.178(3)	0.128(2)	–0.026(2)	0.013(2)	0.098(2)
Si(1)	8*c*	0.64140(5)	–0.01142(6)	0.10972(4)	0.0527(4)	0.0444(5)	0.0494(4)	–0.0009(3)	–0.0058(3)	–0.0071(4)
Si(2)	8*c*	0.67949(6)	0.22327(6)	0.34768(4)	0.0658(5)	0.0401(4)	0.0438(4)	0.0084(4)	–0.0029(4)	–0.0029(3)
N(1)	8*c*	0.6924(1)	0.0520(2)	0.1822(1)	0.041(1)	0.039(1)	0.045(1)	–0.0021(9)	0.0001(9)	–0.002(1)
N(2)	8*c*	0.7073(1)	0.1446(2)	0.2746(1)	0.047(1)	0.035(1)	0.043(1)	0.001(1)	–0.004(1)	–0.002(1)
C(1)	8*c*	0.6491(2)	0.0990(2)	0.2327(1)	0.041(1)	0.048(2)	0.051(2)	0.001(1)	0.003(1)	–0.005(1)
C(2)	8*c*	0.7849(2)	0.0682(2)	0.1931(1)	0.040(1)	0.055(2)	0.057(2)	0.002(1)	0.004(1)	–0.005(1)
C(3)	8*c*	0.7942(2)	0.1247(2)	0.2493(1)	0.039(1)	0.052(2)	0.057(2)	–0.003(1)	–0.005(1)	–0.004(1)
C(4)	8*c*	0.4958(3)	0.3716(3)	0.0787(2)	0.084(3)	0.095(3)	0.072(2)	0.007(2)	0.004(2)	0.021(2)
C(11)	8*c*	0.6867(3)	0.0647(3)	0.0378(2)	0.098(3)	0.089(3)	0.052(2)	–0.007(2)	0.003(2)	–0.002(2)
C(12)	8*c*	0.5168(2)	0.0040(3)	0.1200(2)	0.056(2)	0.063(2)	0.083(2)	–0.003(2)	–0.015(2)	–0.010(2)
C(13)	8*c*	0.6786(2)	–0.1508(2)	0.1105(2)	0.070(2)	0.051(2)	0.092(2)	0.004(2)	–0.011(2)	–0.019(2)
C(21)	8*c*	0.7158(2)	0.3594(2)	0.3284(2)	0.080(2)	0.042(2)	0.073(2)	0.002(2)	–0.008(2)	–0.007(2)
C(22)	8*c*	0.7450(3)	0.1627(3)	0.4172(2)	0.117(3)	0.071(2)	0.051(2)	0.022(2)	–0.015(2)	0.003(2)
C(23)	8*c*	0.5548(2)	0.2093(3)	0.3581(2)	0.078(2)	0.060(2)	0.070(2)	0.006(2)	0.017(2)	–0.004(2)

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