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N-Trimethylsilylimidazole Hydrobromide at 133 K

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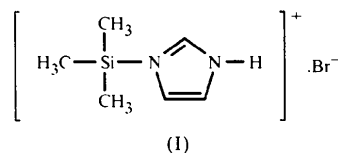
Abstract

The title compound [1-(trimethylsilyl)imidazolium bromide, C₆H₁₃N₂Si⁺·Br⁻] exhibits a 'tetracoordinated' Si centre with bond angles deviating from ideal tetrahedral geometry. The Si—N bond is the longest among those found in Me₃Si—N_{imidazole} fragments in the literature. The protonated N atom forms a hydrogen bond to the Br⁻ ion, and one further contact less than 3 Å from the Br⁻ ion to an aromatic H atom can be found.

Comment

N-Trimethylsilylimidazole (NTMSI) is well known as a powerful silylating agent for a wide range of functional

groups (Lalonde & Chan, 1985). In addition to the silylating properties, NTMSI can act as a Lewis base, and thus forms addition compounds with Lewis acids, e.g. alkylated halogenosilanes (Hensen *et al.*, 1988, 1997). Our original aim was to prepare such an addition compound between dibromodiethylsilane and NTMSI. During our efforts to prepare single crystals of this addition compound, single crystals of *N*-trimethylsilylimidazole hydrobromide, (I), were obtained. There is strong evidence for hydrolysis being the cause of the formation of (I).



Bond lengths and angles in the imidazole ring are in the usual ranges [*International Tables for Crystallography*, Vol. C; Cambridge Structural Database, Version 5.13 of April 1997 (Allen & Kennard, 1993)]. The Si atom is 'tetracoordinated', but the bond angles differ significantly from ideal tetrahedral geometry: whereas the N—Si—C angles show a mean value of 105.1(4)°, the C—Si—C angles show a mean value of 113.5(5)°. The Si—N bond length in (I) is 1.840(3) Å. This is the largest value yet found for an Me₃Si—N_{imidazole} bond. Bond lengths in comparable structures are: 1.772(9) Å in [*N,N'*-bis(trimethylsilyl)imidazole]⁺·I⁻ (Hensen *et al.*, 1988); 1.819(6) Å in [Me₃Si(*N*-methylimidazole)]⁺·Br⁻ (Burger *et al.*, 1992); 1.822(2) Å in [Me₃Si(*N*-methylimidazole)]⁺·Cl⁻ (Hensen, Zengerly, Müller & Pickel, 1983); 1.824(4) Å in [*N*-trimethylsilyl-*N'*-(dimethylpropylsilyl)imidazole]⁺·Br⁻; 1.825(2) and 1.832(2) Å for the two Si—N bonds in [*N,N'*-bis(trimethylsilyl)imidazole]⁺·Br⁻; 1.826(3) Å in [*N*-trimethylsilyl-*N'*-(dimethylethylsilyl)imidazole]⁺·Br⁻; 1.827(4) Å in [*N*-trimethylsilyl-*N'*-(dimethylisopropylsilyl)imidazole]⁺·Br⁻ (Hensen *et al.*, 1997). However, Me₃Si—N_{pyridine} bonds are markedly longer: 1.854(7) Å in [Me₃Si(4-methylpyridine)]⁺·I⁻ (Hensen *et al.*, 1992); 1.858(9) Å in [Me₃Si(pyridine)]⁺·Br⁻ and 1.858(9) Å in [Me₃Si(pyridine)]⁺·I⁻ (Hensen, Zengerly, Pickel & Klebe, 1983); 1.863(4) Å in [Me₃Si(3,4-dimethylpyridine)]⁺·Br⁻ (Hensen & Wagner, 1993); 1.87(2) Å in [Me₃Si(3-methylpyridine)]⁺·I⁻ (Hensen *et al.*, 1992). One of the Si—C bonds is nearly eclipsed with respect to the N1—C5 bond; the torsion angle C13—Si1—N1—C5 is 13.9(3)°. This is an unusual feature because in all other structures an Si—C bond is eclipsed with respect to the other N—C bond of the imidazole heterocycle, with dihedral angles ranging from 0 to 17°.

The Br⁻ ion is bound *via* a hydrogen bond to the protonated imidazole N atom: N3···Br1 3.228(3), H3···Br1 2.355 Å and N3—H3···Br1 171.36°. One fur-

ther contact less than 3 Å, from the Br⁻ ion to an aromatic H atom, can be found: Br1···C2ⁱ 3.639 (4), Br1···H2ⁱ 2.721 Å and Br1···H2ⁱ—C2ⁱ 162.69° [symmetry code: (i) 1 - x, 1 - y, z].

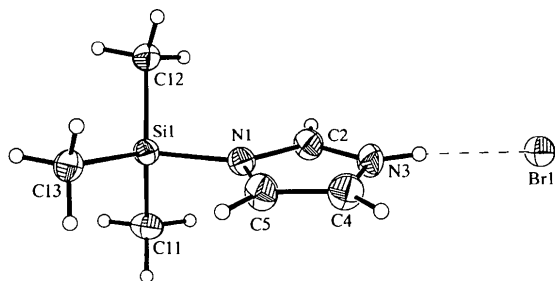


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

Experimental

Dibromodiethylsilane (5.32 mmol) was dissolved in hexane (25 ml) under an atmosphere of dry argon. During continuous stirring, *N*-trimethylsilylimidazole (15.6 mmol) was added dropwise at room temperature. Immediately, a white powder began to precipitate. The solvent was removed and the powder was dried *in vacuo* for 6 h. The primary product was Et₂SiBr₂(NTMSI)₂. Elemental analysis: C₁₆H₃₄Br₂N₄Si₃ requires (%): C 36.5, H 6.5, N 10.6, Br 30.4; found (%): C 36.7, H 6.6, N 11.9, Br 29.1. ¹H NMR (270 MHz, CDCl₃): δ = 0.67 (*m*, 9H), 1.1 (*t*, 6H), 1.44 (*q*, 4H), 7.24 (*s*, 2H, aromatic H), 8.72 p.p.m. (*s*, 1H, aromatic H). Crystals of the title compound (by-product) were obtained by sublimation *in vacuo* at 303 K.

Crystal data

C₆H₁₃N₂Si⁺.Br⁻
M_r = 221.18
 Monoclinic
*P*2₁/*c*
a = 10.8948 (10) Å
b = 7.7476 (10) Å
c = 13.2634 (10) Å
 β = 114.283 (10)°
V = 1020.493 (18) Å³
Z = 4
D_x = 1.440 Mg m⁻³
D_m not measured

Data collection

Siemens CCD three-circle diffractometer
 ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
T_{min} = 0.035, *T_{max}* = 0.442
 13 145 measured reflections
 2021 independent reflections

Mo Kα radiation
 λ = 0.71073 Å
 Cell parameters from 8192 reflections
 θ = 1–25°
 μ = 4.087 mm⁻¹
T = 133 K
 Plate
 0.90 × 0.50 × 0.20 mm
 Colourless

1637 reflections with *I* > 2σ(*I*)
R_{int} = 0.076
 θ_{max} = 26.42°
h = -13 → 12
k = -9 → 9
l = -15 → 16
 183 standard reflections
 frequency: 660 min
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.038
wR (*F*²) = 0.096
S = 1.057
 2021 reflections
 91 parameters
 H atoms: see below
w = 1/[σ²(*F_o*²) + (0.0509*P*)² + 0.4312*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.743 e Å⁻³
 Δρ_{min} = -0.815 e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

N1—C2	1.345 (4)	C2—N3	1.329 (5)
N1—C5	1.386 (5)	N3—C4	1.370 (5)
N1—Si1	1.840 (3)	C4—C5	1.353 (6)
N1—Si1—C12	105.43 (15)	N1—Si1—C11	105.21 (16)
N1—Si1—C13	104.62 (17)	C12—Si1—C11	113.29 (18)
C12—Si1—C13	113.07 (17)	C13—Si1—C11	114.07 (17)

Because of the high sensitivity of the title compound to air and moisture, a crystal of optimum size could not be mounted. The longest crystal dimension of 0.9 mm may lead to systematic errors in *U* values. The data collection nominally covered over a sphere of reciprocal space, by a combination of nine sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 6.0 cm. Coverage of the unique set is over 97% complete to at least 25° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. All H atoms could be located by difference Fourier synthesis and were refined with fixed individual displacement parameters [*U*(H) = 1.5*U_{eq}*(C_{methyl}) and *U*(H) = 1.2*U_{eq}*(C,N)] using a riding model with C—H(methyl) = 0.98, C—H(aromatic) = 0.95 or N—H = 0.88 Å.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1282). Services for accessing these data are described at the back of the journal.

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(2) is assumed to proceed *via* addition of the active methylene group of cyanothioacetamide, (2), to the double bond of (1) to give the intermediate (3). This Michael adduct then cyclizes *via* water elimination to form a 1,4-dihydrothiopyran, (5), which undergoes ring cleavage by ammonia followed by elimination of hydrogen sulfide and oxidation to give (7). The latter shows high fluorescence efficiency (Φ values as high as 0.99 were obtained), suggesting that this derivative and related analogues may be potential candidates for laser dyes, solar harvesting dyes or fluorogenic dyes.

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2-Amino-4-(4-chlorophenyl)-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile, a Strongly Fluorescent Phenanthridine Analogue

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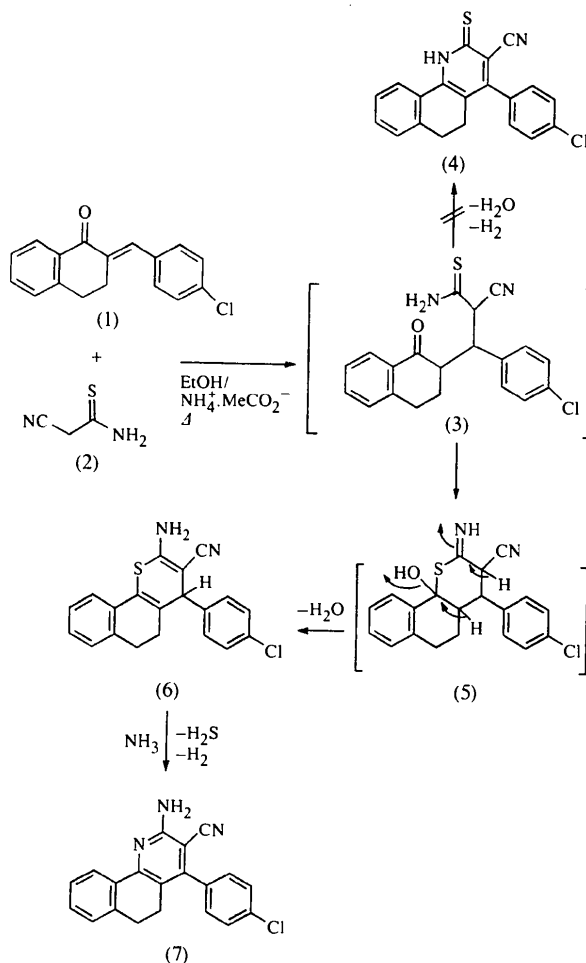
(Received 2 February 1998; accepted 6 March 1998)

Abstract

The title compound, C₂₀H₁₄ClN₃, crystallizes with two independent molecules, differing mainly in the orientation of the chlorophenyl group. The outermost rings of the tricyclic ring system subtend an interplanar angle of 18.10(9)° in one molecule and 22.51(6)° in the other. Hydrogen bonding of the form N—H...N leads to ribbons of one molecule and dimers of the other; these occupy distinct regions of the cell.

Comment

In the course of our studies aimed at the development of efficient and simple procedures for the synthesis of laser dyes (Elgemeie & Fathy, 1995; Elgemeie *et al.*, 1992, 1996), we have carried out the reaction of 2-(4-chlorophenyl)methylidene-1-tetralone, (1), with cyanothioacetamide, (2), in boiling ethanol containing a catalytic amount of ammonium acetate, leading to the phenanthridine analogue (7) rather than the expected phenanthridine (4) (see Scheme below). The mechanism for the formation of (7) from the reaction of (1) and



The X-ray structure analysis determines the product unambiguously to be (7). The compound crystallizes with two independent molecules (Fig. 1). Bond lengths and angles are as expected; in particular, the tricyclic ring systems are closely similar (r.m.s. deviation for 14 ring atoms is 0.047 Å). Minor differences are seen in, for example, the C2—N3 bond length [1.346(3) and 1.361(3) Å], which may be associated with the different hydrogen-bonding patterns (see below). The main difference between the two molecules is the orientation of the chlorophenyl group, with C4a—C4—C11—C12 torsion angles of 55.2(3) and -88.9(3)°.