

1,2-Di-*tert*-butyldiaziridine

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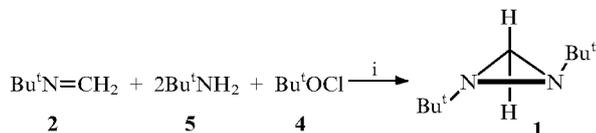
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1,2-Di-*tert*-butyldiaziridine **1** has been synthesized for the first time and its ¹H and ¹³C NMR spectra studied in comparison with model diaziridines **8**–**10**. Its photoelectron and mass spectra have been measured and its structure optimized by semiempirical and *ab initio* calculations; considerable steric deformation of the CH₂ ring fragment and mutual approach of *tert*-butyl groups is shown.

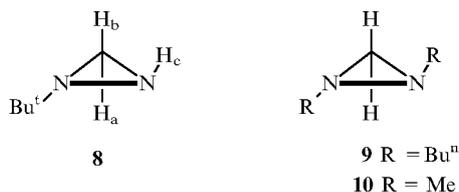
The preparation of 1,2-di-*tert*-butyldiaziridine was earlier reported to be unsuccessful due to steric hindrance.¹ So, although 1,2-di-*tert*-alkyldiaziridines are very attractive objects for studying sterically-hindered nitrogen inversion, any attempt to synthesise them faced a psychological barrier. However, we succeeded in our efforts to synthesise diaziridine **1** in >6% yield by the Schmitz method² using a reaction of *N*-methylene-*tert*-butylamine **2** with *N*-chloro-*tert*-butylamine **3**, generated under the action of *tert*-butylhypochlorite **4** on *tert*-butylamine **5**, Scheme 1. The latter was used as a base to trap HCl.[†]



Scheme 1 Conditions: i, in Et₂O, 5 days at 20 °C.

According to NMR and chromato-mass spectrometry (GC, phase SE-30) a crude product was contaminated with compounds **3**–**5**, Bu^tNCl₂ **6** and Bu^tOH **7**. After distillation upon molten Na and chromatography on silica gel (eluent *n*-hexane) an analytically pure sample of **1** was isolated and characterized by spectroscopic data.[‡]

Model diaziridines **8**³ and **9**, **10**¹ were synthesized for comparative investigations.



Besides compound **8**, *tert*-butylaminoacetonitrile **11**, erroneously described earlier as 2-*tert*-butyl-2,4-diazabicyclo[1.1.0]butane,³ was isolated by the same method³ and identified in accordance with the reported data on an analogous compound.⁴

The high-field shift of the ¹³C signal of the ring carbon observed for **1** and **8** was considerably stronger compared to

[†] Compound **1** was obtained from 15.3 g (0.18 mol) of **2**, 6.3 g (0.36 mol) of **5** and 19.5 g (0.18 mol) of **4** in 60 ml absolute Et₂O. The mixture was kept for 5 days at 20 °C and the resulting precipitate was filtered off. The filtrate was kept for 1 day at 20 °C and the precipitate was again filtered off. The resulting solution was heated for 2 h under granulated KOH and distilled under CaH₂. The crude **1** (3 g, 10.7%) bp 45 °C (25 torr) was obtained. After purification by distillation under molten Na and by chromatography on silica (eluent *n*-hexane) analytically pure **1** was isolated, yield 1.76 g (6.2%), bp 42 °C (18 torr).

all known data on *trans*-diaziridines^{5–10} (Table 1). This can be explained by the contraction of the HCH (α) angle due to the steric effect of the bulk *N*-substituents, as in the case of transition from three- to four-membered 1,3-bridges in bicyclic **12**, **13**⁷ and tricyclic **14**, **15** *trans*-diaziridines^{11,12} (Table 1).

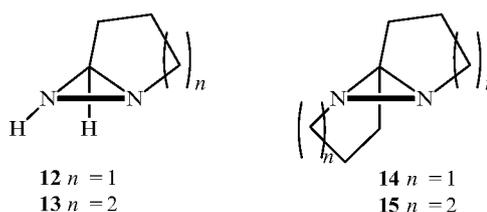


Table 1 ¹³C NMR chemical shifts of the diaziridine ring carbon.

Compound	1	8	9	10	12	13	14	15
δ ¹³ C/ppm	41.9	41.6	55.8	57.7	65.7	55.9	78.7	58.6

The above interpretation is also confirmed by the fact that the contraction of α is accompanied by a dihedral angle change that results in a decrease of ³*J*, the virtual spin

[‡] Characteristics of the compounds: yield, %; bp, °C (Torr); spectroscopic data: ¹H NMR [400 MHz, CDCl₃/CCl₄ (1 : 1)]; ¹³C (100.61 MHz, CDCl₃), δ /ppm, *J* and $\Delta\nu$ /Hz, standard TMS; mass spectrometry (electron impact, 70 eV), *m/z* (relative intensity, %).

For **1**: 6.2; 42 (18); ¹H: 0.96 (s, Me₃C), 2.29 (s, NCH₂N); ¹³C: 26.04 (q hept, Me, ¹*J* 125.7, ³*J* 4.4), 41.9 (t, NCH₂N, ¹*J* 172.2), 54.40 (dec t, CMe₃, ²*J* = ³*J* = 3.6); 156 M⁺ (6.4), 141 (0.8), 100 (13.8), 85 (11.7), 70 (10.0), 57 (100), 45 (10.0), 44 (9.0), 41 (10.0), 29 (10.0).

For **2**: 65; 63–65 (760); ¹H: 1.19 (s, Me₃C), 7.32 (q, CH₂, AB, $\Delta\nu_{AB}$ 27.50, ²*J*_{AB} –15.9).

For **3**: ¹H: 1.21 (s, Me₃C); 107 M⁺ (8.6), 92 (97), 57 (100), 56 (25.8), 42 (35.5), 41 (47.3), 39 (11), 29 (36.6).

For **4**: ¹H: 1.33 (s, Me₃C).

For **5**: ¹H: 1.09 (s, Me₃C).

For **6**: ¹H: 1.22 (s, Me₃C); 141 M⁺ (3.2), 126 (4.3), 106 (1), 92 (6.5), 71 (4.3), 57 (100), 41 (34.4), 29 (30).

For **7**: ¹H: 1.23 (s, Me₃C).

For **8**: 15; 30 (18); ¹H: 1.00 (s, Me₃C), 1.64 (br m., H_cN), 2.51 (dd, H_a, ²*J*_{AB} 4.9, ³*J*_{ac} 7.0), 2.79 (dd, H_b, ³*J*_{bc} 7.6); ¹³C: 25.08 (q hept, Me, ¹*J* 125.7, ³*J* 4.4), 41.6 (ddd, NCH₂N, ¹*J*_{CHa} 173.7, ¹*J*_{CHb} 175.8, ²*J*_{CHc} 3.6), 54.83 (m, CMe₃, ²*J*_{CH} = ³*J*_{CHa} = ³*J*_{CHb} = ³*J*_{CHc} = 3.6).

For **9**: 70; 37 (0.1); ¹H: 0.92 (t, Me, ³*J* 7.0), 1.38 (qt, CH₂Me, ³*J* 7.0 and 7.3), 1.57 (tdd, CH₂Et, ³*J* 7.3, 7.0 and 7.9), 2.35 (m, ABX₂, $\Delta\nu_{AB}$, 103.2, ²*J* –11.9, ³*J*_{AX} 7.0, ³*J*_{BX} 7.9), 2.43 (s, NCH₂N); ¹³C: 13.16 (qt, Me, ¹*J* 124.9, ²*J* 3.6), 19.69 (tqt, CH₂Me, ¹*J* 125.0, ²*J* 2.9), 30.04 (ttt, CH₂Et, ¹*J* 127.9, ²*J* 5.8 and 2.9), 55.77 (t quint, NCH₂N, ¹*J* 172.9, ³*J* ≈ 2.9), 60.17 (tt, CH₂N, ¹*J* 135.2, ²*J* 4.4).

For **10**: 52; 50 (760); ¹H: 2.36 (s, CH₂), 2.41 (s, Me); ¹³C: 46.46 (qt, Me, ¹*J* 135.2, ³*J* 5.1), 57.7 (t hept, CH₂, ¹*J* 174.4, ³*J* 5.1).

For **11**: 22.3; 80 (15); ¹H: 1.14 (s, Me₃C), 3.5 (s, CH₂); ¹³C: 27.57 (q hept, Me₃C, ¹*J* 125.7, ³*J* 4.4), 29.94 (t, CH₂, ¹*J* 141.7), 50.1 (dec, CMe₃, ²*J* 3.6), 119.3 (t, CN, ²*J*_{CH} 7.3).

Table 2 Geometry of molecule **1** optimized by PM3 and 3-21G methods.

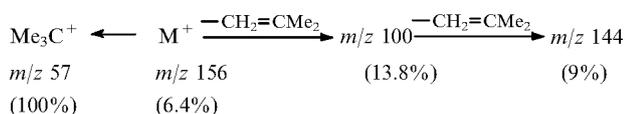
	PM3	3-21G
Bond lengths (Å)		
N–N	1.500	1.503
N–C (ring)	1.476	1.466
C–H (ring)	1.103	1.069
N–C (Bu ^t)	1.500	1.494
C–C (Bu ^t)	1.532–1.538	1.538
C–H (Bu ^t)	1.098–1.099	1.081–1.085
Valence angles (°)		
N–N–C	59.5	59.1
N–C–N	61.1	61.7
H–C–H (α)	110.9	115.8
Angle between HCH and ring planes	84.6	84.6
Sum of valence angles at N atom	302.1	293.1
Out-of-plane angle of N–C(Bu ^t) bond	53.1	58.2
Dihedral angles (°)		
C–N–N–C (δ)	132.8 ^a	124.2
C–N–C–H (<i>cis</i>)	1.9	17.3
C–N–C–H (<i>trans</i>)	139.6	162.8
Contact (Å):		
(ring) C–H \cdots H (Bu ^t)	2.24	2.18

^a From AM1¹³ calculations 136°.

coupling constant of the ¹³CMe₃ carbon with ring protons, observed for **1** in comparison with **10**, ³J_{obs} = 3.6 and 5.1, respectively. In the case of **8** the contraction of α is displayed by a convergence of the values of spin coupling constants ³J_{ac} and ³J_{bc} and in the equality of the three ³J_{CH} constants of carbon CMe₃ with the ring protons.

From semi-empirical data and *ab initio* calculations on **1** (Table 2) the angle α is 115.8° while estimation by the correlation of α and δ ¹³C^{11,12} gives a value of \approx 105°. In comparison, for **10** from electron diffraction (ED) data¹⁴ the value of this angle is considerably higher, α = 121(6)°.

The calculations predict an asymmetric deformation of the CH₂ ring fragment (the angle between HCH and ring planes < 90°) due to the short contacts H \cdots H between CH₂ and Bu^t groups (Table 2). The high strain in molecule **1** caused by this is manifested in the fact that its main fragmentation route under electron impact[†] include cleavage of N–Bu^t bonds:

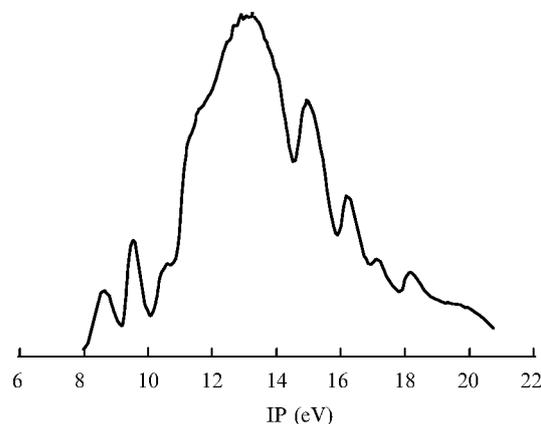


It follows from the calculations (Table 2) that the above-mentioned nonbonded interaction in molecule **1** is partly compensated by the approach of Bu^t groups to each other, as shown in the decrease in out-of-plane angles of N–C(Bu^t) bonds and dihedral angle CNNC (δ) (Table 2). For **10** from the ED data¹⁴ these angles are equal to 64.1 and 151.9°.

Table 3 Vertical ionization potentials IP (eV) and calculated MO energies ϵ (eV) of 1,2-di-*tert*-butyldiaziridine **1**.

IP (exp.)	IP (calc.) ^a	– ϵ (AM1)	Orbital
8.65	8.75	9.65	n ⁺ _{NN}
9.57	9.90	10.64	n [–] _{NN}
10.60	10.76	11.38	σ
	11.09	11.66	σ
	11.15	11.72	σ

^a Outer valence Green's function (AM1).¹³

**Figure 1** Photoelectron spectrum of diaziridine **1** (measured as described in ref. 18).

respectively. The angle (δ) is connected with the dihedral angle φ between the nitrogen electron lone pairs. Angle φ is determined from photoelectron spectroscopy (PES) data, from these data for **10** φ = 102°.^{15,16} Based on our PES investigations of **1** (Table 3, Figure 1) the dihedral angle $\varphi \approx$ 110° can be estimated from the two n_N ionizations. This angle is close to AM1 calculated for **1** φ = 115°.

The remarkable point is that **1** has a lower first vertical IP, compared to all previously studied diaziridines,^{15–18} with the exception of **15** (the first two IPs: 8.51, 9.10 eV).¹⁷

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