1,2-Di-*tert*-butyldiaziridine

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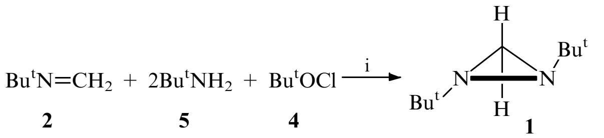
1,2-Di-*tert*-butyldiaziridine 1 has been synthesized for the first time and its ^{1}H and ^{13}C NMR spectra studied in comparison with model diaziridines 8–10. Its photoelectron and mass spectra have been measured and its structure optimized by semiempirical and *ab initio* calculations; considerable steric deformation of the CH_2 ring fragment and mutual approach of *tert*-butyl groups is shown.

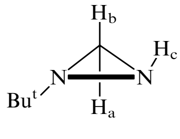
The preparation of 1,2-di-*tert*-butyldiaziridine was earlier reported to be unsuccessful due to steric hindrance.[1] So, although 1,2-di-*tert*-alkyldiaziridines are very attractive objects for studying sterically-hindered nitrogen inversion, any attempt to synthesise them faced a psychological barrier. However, we succeeded in our efforts to synthesise diaziridine **1** in >6% yield by the Schmitz method [2] 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 Et_2O, 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^{t}NCl$_2$ **6** and Bu^{t}OH **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.



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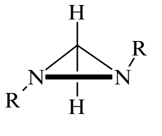
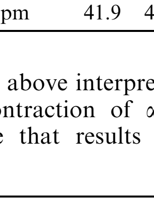


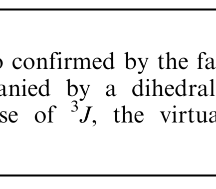
9 R = Bu^n
10 R = Me

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 method [3] and identified in accordance with the reported data on an analogous compound.[4]

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



12 *n* = 1
13 *n* = 2



14 *n* = 1
15 *n* = 2

Table 1 ^{13}C 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 ^3J, the virtual spin

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[†] 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 Et_2O. 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 CaH_2. 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).

[‡] Characteristics of the compounds: yield, %; bp, °C (Torr); spectroscopic data: ^{1}H NMR [400 MHz, $CDCl_3/CCl_4$ (1:1)]; ^{13}C (100.61 MHz, $CDCl_3$), 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); ^{1}H: 0.96 (s, Me_3C), 2.29 (s, NCH_2N); ^{13}C: 26.04 (q hept, Me, ^1J 125.7, ^3J 4.4), 41.9 (t, NCH_2N, ^1J 172.2), 54.40 (dec t, *C*Me$_3$, $^2J = {}^3J = 3.6$); 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); ^{1}H: 1.19 (s, Me_3C), 7.32 (q, CH_2, AB, $\Delta\nu_{AB}$ 27.50, $^2J_{AB}$ −15.9).

For **3**: ^{1}H: 1.21 (s, Me_3C); 107 M$^+$ (8.6), 92 (97), 57 (100), 56 (25.8), 42 (35.5), 41 (47.3), 39 (11), 29 (36.6).

For **4**: ^{1}H: 1.33 (s, Me_3C).

For **5**: ^{1}H: 1.09 (s, Me_3C).

For **6**: ^{1}H: 1.22 (s, Me_3C); 141 M$^+$ (3.2), 126 (4.3), 106 (1), 92 (6.5), 71 (4.3), 57 (100), 41 (34.4), 29 (30).

For **7**: ^{1}H: 1.23 (s, Me_3C).

For **8**: 15; 30 (18); ^{1}H: 1.00 (s, Me_3C), 1.64 (br m., H$_c$N), 2.51 (dd, H$_a$, $^2J_{ab}$ 4.9, $^3J_{ac}$ 7.0), 2.79 (dd, H$_b$, $^3J_{bc}$ 7.6); ^{13}C: 25.08 (q hept, Me, ^1J 125.7, ^3J 4.4), 41.6 (ddd, NCH_2N, $^1J_{CHa}$ 173.7, $^1J_{CHb}$ 175.8, $^2J_{CHc}$ 3.6), 54.83 (m, CMe$_3$, $^2J_{CH} = {}^3J_{CHa} = {}^3J_{CHb} = {}^3J_{CHc} = 3.6$).

For **9**: 70; 37 (0.1); ^{1}H: 0.92 (t, Me, ^3J 7.0), 1.38 (qt, C*H*$_2$Me, ^3J 7.0 and 7.3), 1.57 (tdd, C*H*$_2$Et, ^3J 7.3, 7.0 and 7.9), 2.35 (m, ABX$_2$, $\Delta\nu_{AB}$, 103.2, ^2J −11.9, $^3J_{AX}$ 7.0, $^3J_{BX}$ 7.9), 2.43 (s, NCH_2N); ^{13}C: 13.16 (qt, Me, ^1J 124.9, ^2J 3.6), 19.69 (tqt, *C*H$_2$Me, ^1J 125.0, ^2J 2.9), 30.04 (ttt, *C*H$_2$Et, ^1J 127.9, ^2J 5.8 and 2.9), 55.77 (t quint, NCH_2N, ^1J 172.9, $^3J \approx 2.9$), 60.17 (tt, CH_2N, ^1J 135.2, ^2J 4.4).

For **10**: 52; 50 (760); ^{1}H: 2.36 (s, CH_2), 2.41 (s, Me); ^{13}C: 46.46 (qt, Me, ^1J 135.2, ^3J 5.1), 57.7 (t hept, CH_2, ^1J 174.4, ^3J 5.1).

For **11**: 22.3; 80 (15); ^{1}H: 1.14 (s, Me_3C), 3.5 (s, CH_2); ^{13}C: 27.57 (q hept, Me_3C, ^1J 125.7, ^3J 4.4), 29.94 (t, CH_2, ^1J 141.7), 50.1 (dec, *C*Me$_3$, ^2J 3.6), 119.3 (t, CN, $^2J_{CH}$ 7.3).

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

	PM3	3-21G
Bond lengths (A)		
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 (*cis*)	1.9	17.3
C–N–C–H (*trans*)	139.6	162.8
Contact (A):		
(ring) C–H···H (Bu^t)	2.24	2.18

[a] From AM1[13] calculations 136°.

coupling constant of the ^{13}CMe$_3$ 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 *C*Me$_3$ 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 ^{13}C[11,12] gives a value of ≈ 105°. In comparison, for **10** from electron diffraction (ED) data[14] the value of this angle is considerably higher, α = 121(6)°.

The calculations predict an asymmetric deformation of the CH$_2$ ring fragment (the angle between HCH and ring planes < 90°) due to the short contacts H···H between CH$_2$ 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:

$$\underset{\substack{m/z\ 57\\(100\%)}}{\mathrm{Me_3C^+}} \longleftarrow \underset{\substack{m/z\ 156\\(6.4\%)}}{\mathrm{M^+}} \xrightarrow{-\mathrm{CH_2{=}CMe_2}} \underset{(13.8\%)}{m/z\ 100} \xrightarrow{-\mathrm{CH_2{=}CMe_2}} \underset{(9\%)}{m/z\ 144}$$

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 data[14] these angles are equal to 64.1 and 151.9°, 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 φ ≈ 110° can be estimated from the two n_N ionizations. This angle is close to AM1 calculated for **1** φ = 115°.

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]

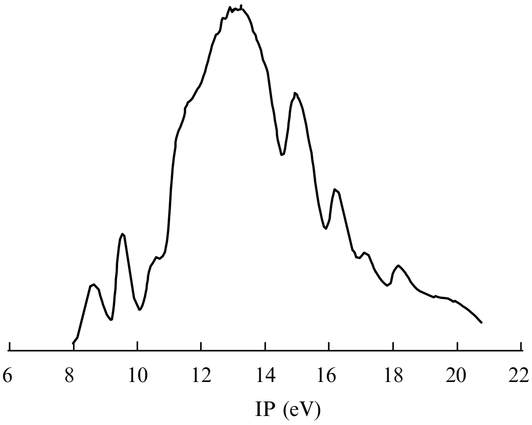

Figure 1 Photoelectron spectrum of diaziridine **1** (measured as described in ref. 18).

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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