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3,4-Di-*tert*-butyl-1,3,4-oxadiazolidine: synthesis and structure

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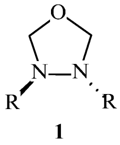
3,4-Di-*tert*-butyl-1,3,4-oxadiazolidine **1d** has been synthesized and for the first time fully characterized; an envelope conformation has been established by X-ray diffraction analysis of **1d** in the crystal, and a semi-chair conformation with a *trans*-diaxial orientation of Bu^t groups determined by NMR spectroscopy in solution and, additionally, by MNDO and *ab initio* calculations in the gas phase; the lower limit of the barrier to sterically-hindered nitrogen inversion was evaluated as $\Delta G^{\neq} > 22.8$ kcal mol^{-1} at 130 °C.

Unlike mononitrogen heterocycles, the inversion barrier of nitrogen atoms in cyclic hydrazines rises with increasing size of the N-substituents.[1,2] Judging by the data for 1,3,4-oxadiazolidines[3,4] **1** and 1,2-diazetidines[5] **2** (Table 1) one could expect that in the appropriate conformational situation involving a bulky R group, steric hindrance (or even full prohibition) of nitrogen inversion would be sufficient to resolve such molecules into antipodes under normal conditions.

In this respect 3,4-di-*tert*-butyl-1,3,4-oxadiazolidine **1d** and the recently synthesized 1,2-di-*tert*-butyldiaziridine[6] seemed to be the most interesting. However, in the preliminary communication on **1d**[3] no data on it were provided, except for those given in Table 1, and no mention at all in the detailed



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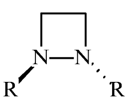

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	R
a	Me
b	Et
c	Pr^i
d	Bu^t

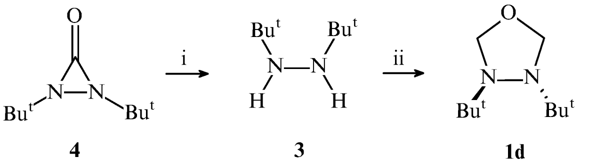
publication.[4] Photoelectron spectra of **1d** were studied later[7] but no features were reported except for the first three vertical ionization potentials.

Therefore, the synthesis and investigation of oxadiazolidine **1d** were carried out. The source 1,2-di-*tert*-butylhydrazine **3** was obtained *via* 1,2-di-*tert*-butyldiaziridinone **4**[8] (Scheme 1).

An analytically pure sample of **1d** was obtained from the picrate of non-stoichiometric composition under the action of aqueous KOH in benzene.[†] The structure of **1d** was unambiguously confirmed by X-ray diffraction analysis,[‡] and its unsymmetrical, envelope conformation established (Figure 1, Table 2).

Table 1 Inversion barriers, $\Delta G^{\neq}$/kcal mol^{-1} (T_c /°C).

Compound	Ref.	**a**	**b**	**c**	**d**
1	3,4	10.6 (−61°)	12.0 (−31°)	19.4 (111°)	>21.0 (166°)
2	5	16.4 (67°)	16.5 (66°)	16.8 (66°)	21.8 (155°)



Scheme 1 *Reagents and conditions*: i, HCl, then KOH; ii, CH_2O in C_6H_6 with MeOH (traces).

However, it follows from NMR investigations[§] that **1d** has a symmetrical conformation in solution. The high-field doublet in the ^{1}H NMR spectrum (Figure 2) is attributed to the axial proton H$_a$ because of the greater spin coupling constant $^1J_{\mathrm{CH_a}}$ (measured by the ^{13}C and ^{1}H NMR satellite in the ^{13}C spectra) and greater spin coupling constant $^3J_{\mathrm{CNCH_a}}$ as compared to $^3J_{\mathrm{CNCH_e}}$. In addition, in contrast to $^3J_{\mathrm{COCH_e}}$ a spin coupling constant $^3J_{\mathrm{COCH_a}}$ was not observed, *i.e.* the dihedral angle H$_a$COC is close to 90°. When CF_3CO_2H was added to [$^2H_8$]toluene only signal broadening of H$_a$ was observed (the assignment was confirmed by the ^{1}H NMR satellite in the ^{13}C spectra of this sample: depending on the quantity of acid, the additional signals from H$_a$ and H$_e$

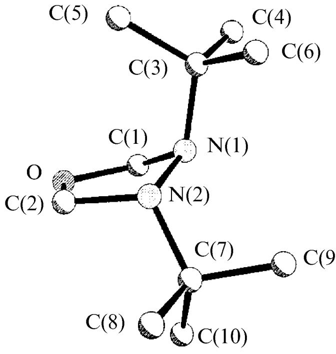


Figure 1 Molecular structure of **1d**.

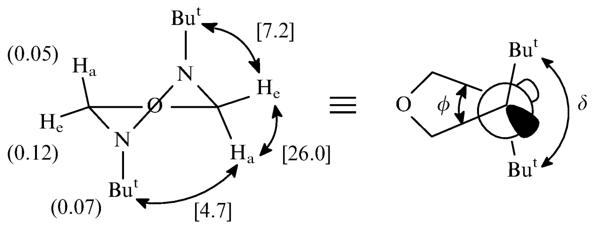
Table 2 Geometry of **1d** established by X-ray analysis and optimized by calculations (Å and °).

Parameter	Experiment[a]	MNDO	6-31 G*	6-31 + G*
N–N	1.439 (3)	1.3958	1.4178	1.4181
C–N (ring)	1.452 (3) 1.505 (3)	1.5041	1.4512	1.4516
C–O	1.402 (3) 1.404 (3)	1.4042	1.4017	1.4034
C–H$_a$	1.068 (25) 0.990 (28)	1.1782	1.0816	1.0816
C–H$_e$	1.062 (24) 0.983 (24)	1.1239	1.0777	1.0776
N–C (Bu^t)	1.505 (3) 1.516 (4)	1.5206	1.4873	1.4887
C–C (Bu^t)	1.506 (4)-1.552 (5)	1.5604-1.5652	1.5306-1.5397	1.5308-1.5399
H$_a$....H (Bu^t)	2.13	3.8	2.2173	2.2259
H$_e$....H (Bu^t)	2.00	2.2	2.0885	2.0891
NNC (ring)	104.2 (2) 104.9 (2)	113.3	104.8	104.9
NCO	108.3 (2) 108.5 (2)	108.1	106.7	106.7
COC	107.0 (2)	107.0	104.8	104.9
NNC (Bu^t)	112.1 (2) 113.2 (2)	115.3	114.7	114.8
CNC (Bu^t)	115.2 (2) 114.0 (2)	112.1	115.9	116.0
H$_a$CH$_e$	101.0 (2) 110.0 (2)	110.9	108.6	108.8
NNCO	15.7 (5) 26.5 (5)	13.3	24.2	24.1
H$_a$COC	103.0 (3) 121.0 (3)	110.5	110.6	110.6
H$_e$COC	120.0 (3) 138.0 (3)	132.6	130.8	130.8
H$_a$CNC (Bu^t)	131.0 (3) 144.0 (3)	132.3	138.1	138.0
H$_e$CNC (Bu^t)	12.0 (3) 24.0 (3)	7.8	16.5	16.0
NCOC	16.9 (2) 0.6 (2)	4.99 4.69	9.2 9.1	9.1 9.1
α	49.0 38.2	31.9	39.5	39.8
δ	135.0	123.0	132.8	132.2
ϕ	25.0	23.6	29.3	29.2
Sum of valent angles at N	331.5 (2) 332.1 (2)	338.7	335.4	335.7

[a] Plane N(2)C(2)OC(1) is kept to an accuracy of 0.003 Å with a deviation of the N(1) atom from the plane by 0.388 Å; the angle of the envelope bending is 25.9 (2)°. Nitrogen atoms have a pyramidal configuration. Their deviations from the planes of neighbouring atoms are equal to 0.46 Å.

[†] Compound **1d** was obtained from 0.75 g (5.2 mmol) 1,2-di-*tert*-butylhydrazine and 0.37 g (12 mmol) α-polyhydroxymethylene in a mixture of benzene (10 ml) and MeOH (1 ml) in the presence of a catalytic quantity of KOH. After being kept for 1.5 h in argon subsequent evaporation and distillation yielded **1d**, 0.45 g (46.3%). The product was purified by precipitation from ether as the picrate (no sharp mp, 120–137 °C). The latter was dissolved in benzene and washed with aqueous KOH. After evaporation of benzene pure **1d** was isolated as a colourless liquid (bp 60 °C/5 torr) in 97% yield. Found: C 64.30, H 11.75, N 15.30. Calc. for $C_{10}H_{22}N_2O$: C 64.47, H 11.90, N 15.04%.

[‡] *Crystallographic data for* **1d**: Crystals of **1d** are monoclinic, space group $P2_1/n$, at −56 °C: a = 6.192 (6) Å, b = 17.18 (1) Å, c = 10.903 (8) Å, β = 94.0 (1)°, V = 1157 (1) Å^3, z = 4, F(000) = 416, μ(MoKα) = 0.69 cm^{-1}, d_{calc} = 1.173 g cm^{-3}. The intensities of 2457 reflections were measured on a Syntex P21 diffractometer at –56 °C (MoKα radiation, $\theta/2\theta$ scan, $2\theta < 50°$), and 1610 independed observed ones with $I > 2\sigma(I)$ were used in the calculations and refinement. Compound **1d** is a liquid at room temperature, and a single crystal suitable for the X-ray diffraction study was grown in a thin-walled capillary (diameter *ca.* 0.4 mm) by very slow cooling of its melt near the melting point (*ca.* −16 °C). The single crystal so obtained was slowly cooled further to –56 °C. The structure was solved by direct methods and refined by least-squares in an anisotropic–isotropic (H-atoms) approximation. The refinement converged at R = 6.1%, wR = 6.4%, GOF = 1.45. All calculations were performed using the program SHELXTL PLUS.[9] Full lists of bond lengths, bond angles, atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Notice to Authors, *Mendeleev Commun.*, 1996, issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1135/2.



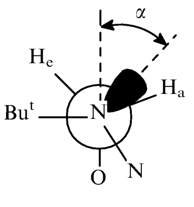
Scheme 2

approach each other and exchange positions). This is in agreement with the fact that the dihedral angle HNCH$_e$ is close to 90° in the case of the protonated nitrogen atoms. Thus, the conformation of **1d** was concluded to be consistent with a semi-chair and diaxial *trans*-orientation of the N-substituents of C_2 symmetry (Scheme 2, Table 2).

This is also confirmed by the ASIS-effect ($\nu_{CDCl_3} - \nu_{[^2H_8]toluene}$, ppm) and NOE [%, outgassed sample].

A similar conformation of **1d** in the gas phase is predicted by geometry optimization of this molecule using MNDO and *ab initio* methods (Table 2). This agrees with the photoelectron spectra data, however, the latter gives values of angles that are too large, $\delta = 176°$ and $\phi = 56°$ [7] (*cf.* Table 2).

Obviously, a compromise of all three effects results in a feasible conformation for **1d** . These effects are: Bu^t groups and nitrogen lone-pair repulsions; 1,2- and 1,3-interaction of ring protons with Bu^t groups; and stabilizing $n_N \rightarrow \sigma^*_{CO}$ interactions. Achievement of the latter depends on the value of α (Scheme 3).



Scheme 3

The differences in the conformations of **1d** (*cf.* ref. 10) dependent upon phase are probably caused by the particular nature of its crystal structure but they have not yet been studied by us.

Attempts to determine the barrier to nitrogen inversion in **1d** by ^{1}H dynamic NMR method have failed because of the too great value of $\Delta\nu$ for ring protons. Heating the sample from 30 to 100 °C in [$^2H_8$]toluene only increases the value of $\Delta\nu$ by 6.7 Hz and no changes in the AB system of the ring proton spectrum were observed.

In contrast to the large value of $\Delta\nu$ for the ring protons, the values of Δ^1J_{CH} for the endocyclic carbons and Δ^3J_{CNCH} of exocyclic carbons *C*Me$_3$ are rather small (14.5 and 3.0 Hz in [$^2H_8$]toluene at 30 °C, respectively). Therefore, an attempt was made to determine the inversion barrier by coalescence of the spectral lines related to the different spin coupling constants, $^1J_{CH_a}$ and $^1J_{CH_b}$, as well as $^3J_{CNCH_a}$ and $^3J_{CNCH_e}$, in the ^{13}C NMR spectrum (Figure 2). These constants should be equal under conditions of fast inversion on the NMR time scale. However, only a slight change is observed even at 130 °C, Δ^1J_{CH} = 13.7 Hz and Δ^3J_{CH} = 2.7 Hz. Therefore, the values of $\Delta G_{inv}^{\ddagger}$ at 130 °C are expected to be > 22.7 and > 23.8 kcal mol^{-1}, respectively. Thus, for compounds of the type **1d** it should be possible to obtain them in an optically active form under normal conditions. Work in this direction is in progress.

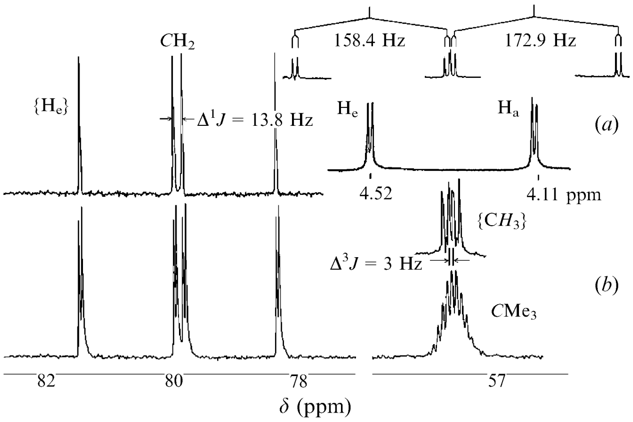


Figure 2 NMR spectra of **1d**: (*a*) ^{1}H NMR spectrum ([$^2H_8$]toluene, 30 °C) of ring protons and satellite of ^{13}C (above); (*b*) ^{13}C NMR spectrum ([$^2H_6$]benzene, 30 °C) of carbon *C*Me$_3$: normal and decoupled from methyl protons (above); carbon CH$_2$: normal and low-power decoupled from H$_e$ proton (above).

Table 3 Atom coordinates in the molecule **1d**.

Atom	x	y	z
O	2729 (1)	5828 (1)	−81 (1)
N (1)	2028 (1)	6192 (1)	1896 (1)
N (2)	4160 (1)	6469 (1)	1678 (1)
C (1)	1061 (1)	6008 (1)	678 (1)
C (2)	4660 (1)	6111 (1)	509 (2)
C (3)	2095 (1)	5530 (1)	2802 (1)
C (4)	−225 (2)	5294 (1)	2986 (2)
C (5)	3376 (1)	4813 (2)	2381 (1)
C (6)	3149 (2)	5812 (2)	4008 (1)
C (7)	4331 (2)	7349 (1)	1691 (2)
C (8)	6709 (1)	7536 (2)	1629 (2)
C (9)	3573 (2)	7637 (1)	2908 (2)
C (10)	2987 (1)	7758 (1)	645 (2)

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§ *Spectroscopic data*: NMR (δ/ppm, J/Hz).

1d: ^{1}H ([$^2H_8$]toluene, 30 °C): 1.0 (s, 18H, Me$_3$C); 4.31 (dd, 4H, NCH$_2$O, AB system, $\Delta\nu$ = 164.5; $^2J_{AB}$ −4.9). ^{13}C (C_6D_6, 30 °C): 28.19 (qhept, *Me*$_3$C, $^1J_{CH}$ 125.7; $^3J_{CH}$ 4.4); 57.34 (dddec, *C*Me$_3$, $^3J_{CNCH_a}$ 7.0; $^3J_{CNCH_b}$ 4.0; $^2J_{CCH}$ 3.6); 79.87 (ddd, CH$_2$, $^1J_{CH_a}$ 164.2; $^1J_{CH_b}$ 150.4; $^3J_{COCH_e}$ 4.4).

3: ^{1}H (CDCl$_3$): 1.01 (s, *cf.* ref. 8).

4: ^{1}H (CDCl$_3$): 1.27 (s, *cf.* ref. 8). ^{13}C (CDCl$_3$): 26.7 (Me, $^1J_{CH}$ 126.4; $^3J_{CH}$ 4.4); 58.98 (CN, $^2J_{CH}$ 4.4); 158.95 (CO).