Stereochemistry of 1,2,4,5-tetraazanorbornanes and diaziridines: exciting history and news†

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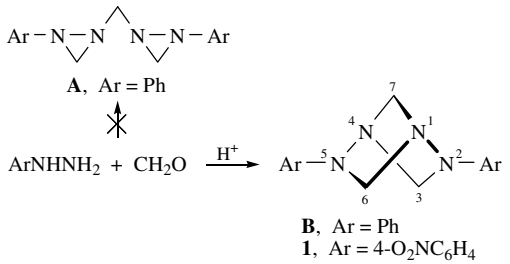
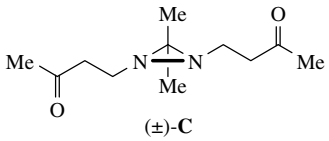
The enantiomers of asymmetric nitrogen compound 1 have been resolved; a chiral formal *meso*-form of diaziridine 2 has been obtained; a population of 1,2-*cis*-form 6a in solution has been found; and the crystal structures of 3–6 have been studied.

In 1885, Wellington and Tollens[2] were the first to obtain the product $(PhN_2)_2(CH_2)_3$ (mp 183–184 °C) of the condensation of $PhNHNH_2$ with CH_2O. Walker[3] postulated its structure as bis(diaziridine) **A** (Scheme 1). Schmitz[4] [who has discovered diaziridines (see review[5])] proposed its true isomeric structure **B**, which was confirmed later by ^{1}H NMR spectra[6] and XRD analysis[7] (the crystal structure of 3,6,7-trimethyl-**B** was also studied[8]). A similar long story of Tröger's base is depicted (see ref. 9). It was resolved by chiral chromatography, and its two analogues were shown to undergo spontaneous resolution.[9(b),(c)] Hitherto Tröger's base is considered as the first known compound with asymmetric nitrogen; however, the above data demonstrate that it should be compound **B**.



Scheme 1

In this work, for the first time, compound **1** (**B** and Tröger's base analogue) was resolved into enantiomers using enantioselective chromatography‡ (Figure 1).

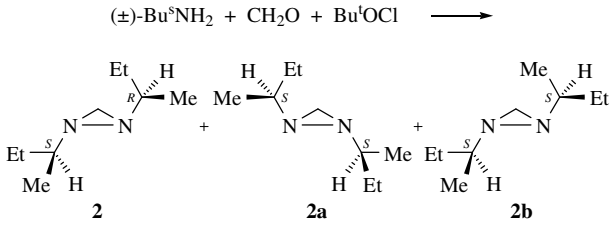


(±)-**C**

Previously, various diaziridines have been obtained in optically active forms,[10] in particular, symmetrically substituted **C**;[10(c)] the population of 1,2-*cis*-form of diaziridine[10(d)] has been detected, and the synthesis of 1-alkyldiaziridine-3,3-dicarboxylic acids derivatives[10(e)] has been worked out for the subsequent complete resolution of their diastereomers[10(f)] and enantiomers.[10(g)] They are physiologically active as brain monoaminoxidase inhibitors.[10(h)]

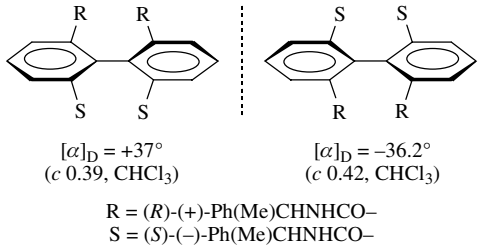
In this work, for the first time, a chiral *meso*-form of diaziridine **2** and two diastereomers of *d*,*l*-form of **2a**,**b** (Scheme 2, Figure 2) have been obtained by a usual method;[10(i)] the latter were separated by routine chromatography.‡ The resolution of enantiomers **2**, **2a**, **2b** by enantioselective chromatography, as well as the determination of the activation parameters of their enantiomerization, will be reported elsewhere.[11] Note that C_2-

† Asymmetric Nitrogen. Part 92; Geminal Systems. Part 53; previous communication see ref. 1.



Scheme 2 Only one enantiomer is shown both for **2a** and **2b**.

symmetric atropenantiomers of such a formal *meso*-form have been first obtained by Prelog *et al.*[12] (Scheme 3). Enantiomeric *meso*-forms of 3,4-disubstituted 1,3,4-oxadiazolidines have been resolved by chiral chromatography.[13] The chiral *meso*-form of a



Scheme 3 Data by V. Prelog *et al.*[12]

molecular 'hamburger' containing a central tetrakis-methylene-benzene spacer in the fixed chiral conformation of C_2 symmetry is described.[14] Thus, the chirality of such *meso*-forms is a common phenomenon in stereochemistry. For example, the enantiomers of *meso*-forms can be prepared from diaziridine **3** (Scheme 4). Amidation of **3** under the action of (*S*)-α-phenylethylamine was found to occur at the *trans*-CO_2Me group (in reference to MeN), and the monoamide diastereomers are easily resolved by crystallization.[10(f)] Subsequent amidation with (*R*)-amine gives the desirable enantiomers.

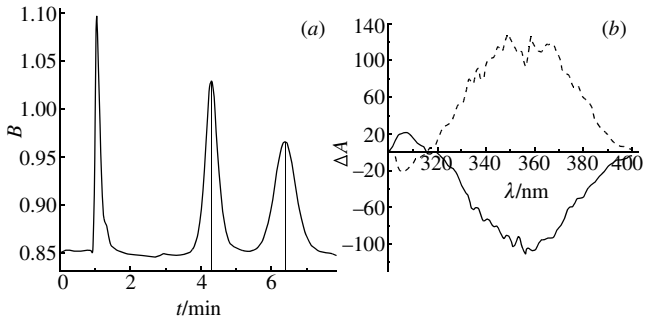
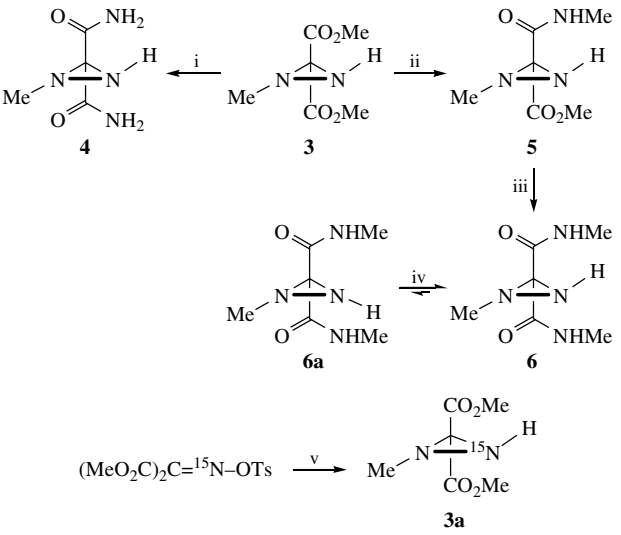


Figure 1 (*a*) Chromatographic separation of racemic compound **1** and (*b*) CD spectra of enantiomers in 1,2-dimethoxyethane.

Diaziridines **3**–**6**[10(e)] have been studied in detail in this work (Scheme 4).

A curious peculiarity of asymmetric nitrogen compounds is their optical enrichment during both crystallization from an optically active solvent and heating in it followed by evaporation.[1,15(a)] This is a test for conglomerate formation.[1] Indeed, 1-methoxy-2,2-dicarbamoylaziridine forms a conglomerate (space group $P2_12_12_1$) and, therefore, undergoes efficient spontaneous resolution.[15(b)] Upon heating in *l*-methyl lactate, diaziridine **6** is enriched with the (1*S*,2*S*)-(–)-enantiomer.[15(a)] However, the examination of the crystal structures of **3**–**6** demonstrated that all of them are true racemates.§ That is why the optical enrichment of **6** in *l*-methyl lactate is explained by inversion with the equilibrium shifting toward a more solvated enantiomer¶ (*cf.* ref. 1). Population of 1,2-*cis*-form revealed in **6** is a rare case for diaziridines.[10(d),15(c)] Formation of **6a** was detected by ^{1}H and ^{13}C NMR spectroscopy upon heating a sample of **6** in [$^2H_6$]DMSO.‡ 1,2-*cis*-Structure of **6a** was confirmed by a significantly higher value of the spin coupling constant $^3J_{^{13}CH}$ of the fragment MeNNH‡ (Figure 3) as against those for **6** and in comparison with the constant values found for 1,2-*cis*- and 1,2-*trans*-1,2-dimethyl-3-*tert*-butyldiaziridines ($^3J^{trans}_{^{13}CH}$ 3.3 Hz, $^3J^{cis}_{^{13}CH}$ 5.7 Hz in 1,2-*trans*-form, and $^3J^{cis}_{^{13}CH}$ 6.1 Hz in 1,2-*cis*-form).[15(c)]



Scheme 4 *Reagents and conditions*: i, excess of NH_3 in MeOH, 12 h at 20 °C; ii, $MeNH_2$ in MeOH, 1 h at –20 °C and 12 h at 20 °C; iii, $MeNH_2$ in MeOH, 12 h at 20 °C; iv, in [$^2H_6$]DMSO (5% H_2O), 0.5 h at 90 °C; v, excess of $MeNH_2$ in CH_2Cl_2, 3 h at –30 °C.

‡ **1**, yield 43%, mp 270–271.5 °C (1,2-dimethoxyethane) [lit.,[6] mp 269 °C (toluene)]. ^{1}H NMR ($CDCl_3$) δ: 3.55 (s, 2H, 7-CH_2), 4.12 (d, 2H, *exo*-3,6-CH, ^2J 7.4 Hz), 4.50 (d, 2H, *endo*-3,6-CH, ^2J –7.4 Hz), 7.00 (d, 4H, 2′,6′-HC=, ^3J 9.2 Hz), 8.20 (d, 4H, 3′,5′-HC=, ^3J 9.2 Hz).

Chromatographic separation of **1** was performed using a Laboratory pristroje Praha chromatograph with an injector with a 20-μl sample loop. Conditions: Chiralpak AD stationary phase (250×4.6 mm i.d.) available from Diacel Chemical Industries (Japan); mobile phase, propan-2-ol (neat); flow rate of 2 ml min^{-1}; temperature, ambient; detection UV 365 nm. A solution of **1** (5 mg in 100 μl of dimethylformamide) was injected into the chromatograph in eight portions. Retention times of enantiomers are t_1 = = 4.29 min, t_2 = 6.38 min; the void time is t_0 = 1.56 min, as determined by the injection of tri-*tert*-butylbenzene, and the separation factor α = = $(t_2 - t_0)/(t_1 - t_0)$ = 1.76.

2, **2a**, **2b**, yield 21%, bp 74 °C (40 Torr). ^{1}H NMR ($CDCl_3$) δ: 0.90–0.92 (3t, 3H, *Me*CH_2, ^3J 7.5–8.1 Hz), 1.00–1.17 (4d, *Me*CH, ^3J 6.0–6.1 Hz), 1.35–1.55 (3m, CH_2Me), 1.74–1.85 (3m, HCN), 2.21 (s, 2H, NCH_2N, **2a**), 2.25 (m, 2H, NCH_2N, AB spectrum, $\Delta\nu$ 19.0 Hz, ^2J –9.0 Hz, **2**), 2.32 (s, 2H, NCH_2N, **2b**), the ratio **2**:**2b**:**2a** = 2.1:1.2:1.0 (Figure 2). ^{13}C NMR ($CDCl_3$) δ: 9.10, 9.17, 9.99, 10.02, (4q, *Me*CH_2, ^1J 125.0 Hz), 15.34, 15.36, 18.73, 18.80, (4q, *Me*CH, ^1J 125.0 Hz), 26.95, 27.54, 27.68 (3t, CH_2Me, ^1J 126.0 Hz), 54.30 (**2a**), 55.30 (**2**), 56.30 (**2b**) (3t, NCH_2N, ^1J 174.4 Hz, ^3J 3.6 Hz), 65.77, 65.89, 65.93, 66.03 (4dm, CH, ^1J 135.0 Hz).

By chromatography on silica (eluent, Et_2O/*n*-hexane, 1:1) the mixture of **2** and **2b** (1:1) was isolated. From the studies on kinetics of epimerization **2b** → **2a** by ^{1}H NMR in [$^2H_8$]toluene at 102 °C there were found $k = 3.1\times10^{-6}$ s^{-1}, $\Delta G^{\#} = 31.3$ kcal mol^{-1}. It is in agreement with the data in ref. 11.

3a, yield 48%, mp 68–69 °C (Pr^{i}OH/*n*-pentane, 1:5). ^{1}H NMR (C_6D_6) δ: 2.53 (dd, 3H, MeN, $^3J_{HCN^{15}N}$ 2.9 Hz, $^4J_{HCNNH}$ 0.7 Hz), 3.38 (dq, 1H, HN, $^1J_{H^{15}N}$ 59.4 Hz, ^4J 0.7 Hz), 3.29 (s, 3H, *b*-MeO), 3.44 (s, 3H, *a*-MeO). ^{13}C NMR (C_6D_6) δ: 44.2 (qdd, MeN, ^1J 137.3 Hz, $^2J_{CN^{15}N}$ 3.6 Hz, $^3J_{CNNH}$ 5.8 Hz), 52.2 (q, *a*-MeO, ^1J 148.2 Hz), 53.1 (q, *b*-MeO, ^1J 148.2 Hz), 61.1 (dd, NCN, $^1J_{C^{15}N}$ 5.6 Hz, $^2J_{CNH}$ 4.4 Hz), 164.7 (dq, *a*-CO, $^2J_{CC^{15}N}$ 4.5 Hz, $^3J_{CH}$ 4.0 Hz), 167.6 (dq, *b*-CO, $^3J_{CCNH}$ 4.3 Hz, $^3J_{CH}$ 4.0 Hz, $^2J_{CC^{15}N} < 0.5$ Hz), *cf.* the spectra of aziridines ^{15}N, refs. 10(*i*)–(*k*). ^{15}N NMR ($CDCl_3$) δ: –289.06.

4, yield 56%, mp 162–164 °C (MeOH/Et_2O). ^{1}H NMR ($CDCl_3$) δ: 2.60 (s, 3H, MeN), 3.70 (s, 1H, HN), 5.80 (br. d, 2H, 2HNCO), 6.75 and 8.04 (2br. s, 2H, 2HNCO).

5, yield 94%, mp 105–106 °C (C_6H_6). ^{1}H NMR ($CDCl_3$) δ: 2.34 (s, 3H, MeN), 2.69 (d, 3H, MeNH, ^3J 5.1 Hz), 3.15 (s, 1H, HNN), 3.73 (s, 3H, MeO), 8.00 (br. s, 1H, HNMe).

6, yield 60%, after sublimation (120 °C at 1 Torr), mp 160–161 °C. ^{1}H NMR (D_2O) δ: 2.38 (s, 3H, MeNN), 2.70 (s, 3H, MeNCO), 2.78 (s, 3H, MeNCO). ^{1}H NMR ($CDCl_3$) δ: 2.49 (s, 3H, MeNN), 2.87 (d, 3H, MeNH, ^3J 5.0 Hz), 2.89 (d, 3H, MeNH, ^3J 5.0 Hz), 3.68 (s, 1H, HNN), 7.26 (br. s, HNCO), 8.23 (br. s, 1H, HNCO). ^{13}C NMR ($CDCl_3$) δ: 25.71 (q, MeNH, ^1J 129.0 Hz), 26.77 (q, MeNH, ^1J 128.5 Hz), 41.33 (qd, MeNN, ^1J 128.1 Hz, ^3J 5.0 Hz), 59.95 (dq, NCN, $^2J = {}^3J$ = 4.0 Hz), 165.70 (m, CO), 166.33 (m, CO). ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.26 (s, 3H, MeNN), 2.58 (d, 3H, MeNH, ^3J 4.7 Hz), 2.61 (d, 3H, MeNH, ^3J 4.7 Hz), 4.00 (s, 1H, HNN), 7.86 (br. q, 1H, HNCO, ^3J 4.7 Hz), 8.08 (1H, HNCO). After heating **6** (1 h at 100 °C) for **6a** ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.28 (s, 3H, MeNN), 2.62 (d, 3H, MeNH, ^3J 4.8 Hz), 2.67 (d, 3H, MeNH, ^3J 4.8 Hz), 4.05 (s, 1H, HNN), 7.80 (br. q, 1H, HNCO), 8.35 (br. q, 1H, HNCO).

§ *XRD data for* **3**–**6** *at 120 K*.

Crystals of **3** ($C_6H_{10}N_2O_4$) are triclinic, space group $P\bar{1}$, a = 6.7669(5), b = 7.7414(6) and c = 8.2660(6) Å, α = 77.957(2)°, β = 72.428(2)°, γ = = 82.368(2)°, V = 402.59(5) Å^3, Z = 2 (Z' = 1), M = 174.16, d_{calc} = = 1.437 g cm^{-3}, μ(MoKα) = 1.21 cm^{-1}, F(000) = 184.

Crystals of **4** ($C_4H_8N_4O_2$) are triclinic, space group $P\bar{1}$, a = 7.0775(6), b = 9.4230(8) and c = 9.7375(8) Å, α = 82.725(2)°, β = 80.681(2)°, γ = = 85.462(2)°, V = 634.54(9) Å^3, Z = 4 (Z' = 2), M = 144.14, d_{calc} = = 1.509 g cm^{-3}, μ(MoKα) = 1.23 cm^{-1}, F(000) = 304.

Crystals of **5** ($C_6H_{11}N_3O_3$) are monoclinic, space group $P2_1/c$, a = 6.607(1), b = 17.403(4) and c = 7.927(2) Å, β = 111.085(4)°, V = = 850.4(3) Å^3, Z = 2 (Z' = 1), M = 173.18, d_{calc} = 1.353 g cm^{-3}, μ(MoKα) = = 1.09 cm^{-1}, F(000) = 368.

Crystals of **6** ($C_6H_{12}N_4O_2$) are orthorhombic, space group *Pbcn*, a = 17.386(2), b = 7.9419(9) and c = 12.116(1) Å, V = 1673.0(3) Å^3, Z = 8 (Z' = 1), M = 172.20, d_{calc} = 1.367 g cm^{-3}, μ(MoKα) = 1.05 cm^{-1}, F(000) = 736.

Intensities of 2890 (**3**), 7592 (**4**), 9292 (**5**) or 11748 (**6**) reflections were measured with a Smart 1000 CCD diffractometer at 120 K [λ(MoKα) = 0.71072 Å, $2\theta < 58$] and 2084 (**3**), 3368 (**4**), 2250 (**5**) or 2179 (**6**) independent reflections [R_{int} = 0.0193 (**3**), 0.0181 (**4**), 0.0210 (**5**), 0.0432 (**6**)] were used in the further refinement. The structures were solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The hydrogen atoms were located from the Fourier density synthesis. The refinement converged to: wR_2 = 0.1042 and GOF = 1.055 [R_1 = 0.0465 for 1677 observed reflections with $I > 2\sigma(I)$] for **3**; wR_2 = 0.1118 and GOF = 0.984 [R_1 = 0.0457 for 2873 observed reflections with $I > 2\sigma(I)$] for **4**; wR_2 = 0.0921 and GOF = 0.985 [R_1 = 0.0361 for 2030 observed reflections with $I > 2\sigma(I)$] for **5**; wR_2 = 0.1151 and GOF = 0.995 [R_1 = = 0.0511 for 1438 observed reflections with $I > 2\sigma(I)$] for **6**. All calculations were performed using SHELXTL PLUS 5.0.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 257663–257666. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2004.

¶ In 1893, Van't Hoff wrote: 'it should be possible to find a difference in the solubility of enantiomers in an optically active solvent', and later '...Le Bel might already have carried out experiments in this direction, and previously Pasteur also considered possibility'.[16]

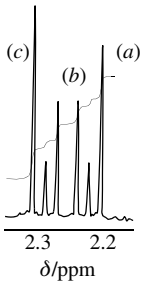


Figure 2 ^{1}H NMR spectrum of NCH_2N protons in a mixture of **2**, **2a** and **2b**: (*a*) minor diastereomer **2a**; (*b*) AB-spectrum of *meso*-**2**; (*c*) predominant diastereomer **2b**.

Starting from (*S*,*S*)-(–)-**3**,[10(g)] (*S*,*S*)-(–)-**6**, $[\alpha]^{20}_{546}$ –76.0° (*c* 0.8, MeOH), was obtained. The kinetics of racemization was studied for (–)-**3** in C_6H_6 at 70 °C ($k = 1.7\times10^{-5}$ s^{-1}, $\Delta G^{\neq} = 27.7$ kcal mol^{-1}) and for (–)-**6** in MeOH at 70 °C ($k = 1.2\times10^{-5}$ s^{-1}, $\Delta G^{\#}_{inv} = 27.9$ kcal mol^{-1}). The data are very close to those for **5**.[10(f)] Noticeably faster isomerization of **6** into **6a** can be explained by proton exchange in HN under the action of H_2O in the solvent (Scheme 4).

By XRD study§ of **3**–**6**, the regiospecificity of the low-temperature amidation **3** → **5** and the structures of all of the products have been unambiguously proved (Figure 4). The basic geometrical parameters of **3**–**6** are practically constant: limits of bond lengths changing are 1.501(2)–1.507(2) for N(1)–N(2), 1.442(2)–1.453(2) for C–N (ring), and 1.471(2)–1.474(2) Å for N(1)–C(1N).

To elucidate the cause of unusual population of *cis*-form in **6a**, a theoretical investigation of **6** and **6a** in correlation with the experimental structure of **6** in a crystal (Figure 4) was carried out. The geometry of **6** as individual species (Figure 4) simulates perfectly the experimental one; in particular, the N(1)–N(2) distance is equal to 1.501 Å (1.507 Å in a crystal), the torsion angle H(2N)N(2)N(1)C(1N) is 149.6° (149.5° in a crystal). Like in a crystal, the intramolecular bond N(5)H(5N)···N(1) is revealed in individual **6**. The shortening of the distance N(5)···N(1) to 2.706 Å as against crystal (2.773 Å) indicates a strengthening of this bond in the individual state (Figure 3). The bond length N(1)–N(2) in **6a** is slightly reduced to 1.493 Å, the torsion angle H(2N)N(2)N(1)C(1N) is 12.3°. As distinct from **6**, in addition to the bond N(5)H(5N)···N(1) [N(5)···N(1) 2.682 Å], there is the intramolecular bond N(8)–H(8N)···O(1) [N(8)···O(1) 2.733 Å] in **6a**, which leads to the formation of a six-membered H-bonded ring.

As an individual species, **6a** is more stable than **6** by 1.07 kcal mol^{-1} (Figure 4). The isomerization **6** → **6a** can proceed by means of the nitrogen inversion of either N–Me (TS1) or NH (TS2) (Figure 4). Seeking TS showed that the energy of TS2 with taking into account ZPE is lower by only 0.54 kcal mol^{-1} than those of TS1, and inversion barriers **6** → **6a** *via* TS1 and TS2 are 33.74 and 34.28 kcal mol^{-1}, respectively.

Presumably, due to the presence of an additional NH···O bond, as well as to shortening H(5N)···N(1) distance in **6a**, the intramolecular H-bonds provide its stability in individual state.

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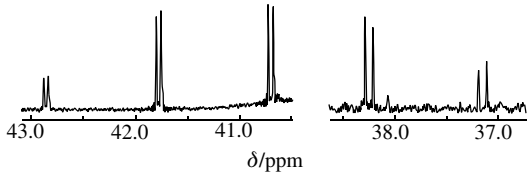

Figure 3 ^{13}C NMR ([$^2H_6$]DMSO) spectrum of carbons MeNNH of **6a** (in a high field) and **6** (in a low field), signals of the partly deuterated solvent are ommited for clarity.

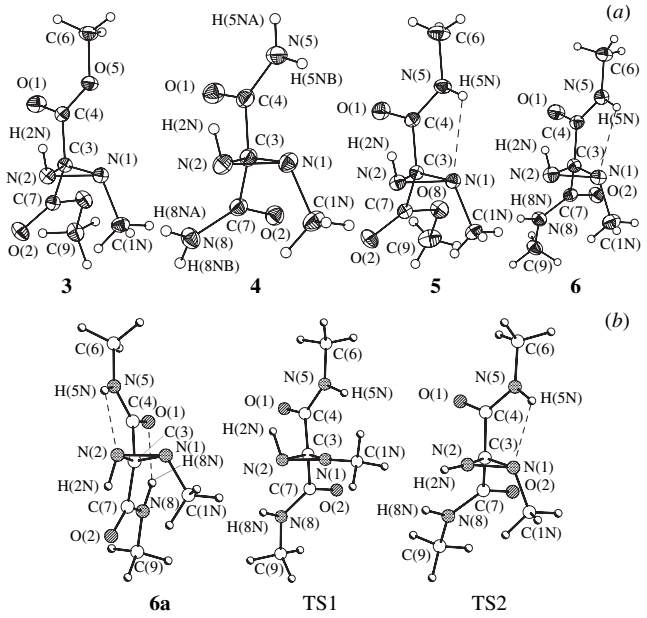

Figure 4 (*a*) Molecular structures of **3**–**6**; (*b*) calculated structures of **6** and **6a**.

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