Nitrogen chirality *via* the sterical veto of N inversion†

Sergey V. Usachev,[a] Grygorii A. Nikiforov,[b] Yurii A. Strelenko,[c] Ivan I. Chervin,[a] Konstantin A. Lyssenko[d] and Remir G. Kostyanovsky*[a]

[a] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 938 2156; e-mail: kost@chph.ras.ru*
[b] *N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 137 4101; e-mail: komissarova@polymer.chph.ras.ru*
[c] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 135 5328; e-mail: strel@ioc.ac.ru*
[d] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 135 5085; e-mail: kostya@xrlab.ineos.ac.ru*

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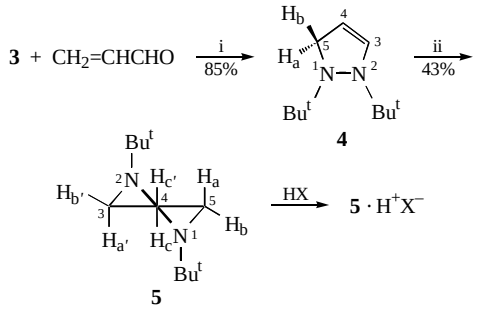
Novel cyclic hydrazines 4–8 with sterically hindered (4, 6, 7) or arrested (5, 8) nitrogen inversion were synthesised; pyrazolydine 5 was separated into enantiomers by chiral chromatography; the crystal structures of salts 5a and 5b were studied by X-ray diffraction analysis.

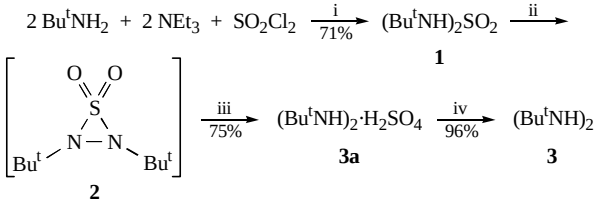
The synthesis of 1,2-dialkyl-substituted five-membered cyclic hydrazines was reported in our previous publication.[1] Unlike 3,4-dialkyl-1,3,4-oxadiazolines,[2] these hydrazines are highly chemically stable; they form stable salts with acids and iodine methylates. In a case of 3,4-di-*tert*-butyl-1,3,4-oxadiazolidine, nitrogen inversion occurs by a dissociative mechanism with O–CH_2 bond cleavage,[3] whereas the activation parameters of 1,2-diisopropylpyrazolidine inversion ($\Delta G^{\neq}$ = 67.7 kJ mol^{-1}, $\Delta H^{\neq}$ = 61.1 kJ mol^{-1}, $\Delta S^{\neq}$ = –22.2 J K^{-1} mol^{-1}) testify to a pyramidal character of the process. On the basis of a comparative analysis of inversion barriers, we suggested[1] a more than two-fold increase in the inversion barrier when transferring from 1,2-diisopropylpyrazolidine to a 1,2-di-*tert*-butyl analogue, that would provide an opportunity for obtaining the compound in an optically active form under normal conditions.



Scheme 2 *Reagents and conditions*: i, 2 h at 20 °C; ii, HCO_2H in 1,4-dioxane at 90–95 °C; X = HSO_4^- (**5a**) and TsO^- (**5b**).

This work is aimed at the experimental evidence of the above assumption.

Initial di-*tert*-butylhydrazine **3** was prepared without isolation of rather labile intermediate 1,2-di-*tert*-butylthiadiaziridine oxide[4] **2** (Scheme 1); this resulted in an increase in the yield of **3** up to 75% (*cf.* 56%[4]).



Scheme 1 *Reagents and conditions*: i, 3 h at –5 °C; ii, NaH in hexane at 60 °C, then Bu^tOCl at –30 °C; iii, boiling in THF/H_2O 2 h at 65 °C; iv, KOH/H_2O.

† Asymmetric nitrogen. Part 87, previous communication see ref. 1.

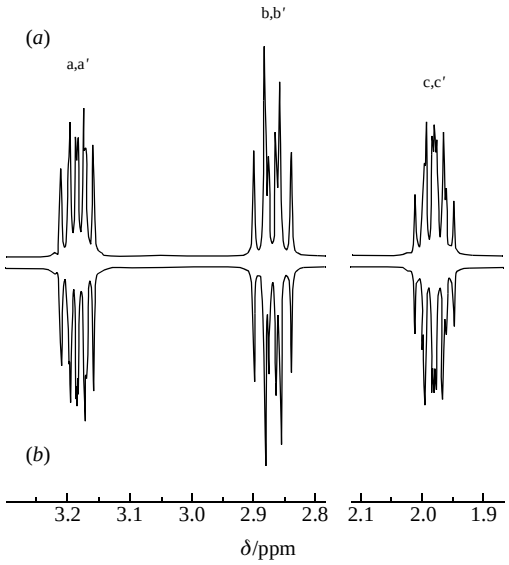


Figure 1 ^{1}H NMR spectra of **5**: (*a*) experimental (500 MHz, in $CDCl_3$ at 20 °C) and (*b*) calculated using CALM.

Reaction of 1,2-di-*tert*-butylhydrazine **3** with acrolein gives pyrazoline **4**; its reduction with 98% HCO_2H‡ results in 1,2-di-*tert*-butylpyrazolidine **5** (Scheme 2).

The structures of compounds **4** and **5** were confirmed by NMR data.§ In the case of pyrazoline **4**, a flat screen for N(1) inversion is created due to the flattening of the enamine N(2) atom. Thus, its inversion is hindered in the NMR time scale at 20 °C (^{1}H NMR, δ: 5-CH_2, $\Delta\nu$ 23 Hz. ^{13}C NMR, δ: 5-CH_2, Δ^1J 3.8 Hz), and the signal of 5-C dd at 55.68 ppm in [$^2H_8$]toluene is not transformed (dd → t) under heating up to 100 °C.

The NMR spectra of 1,2-di-*tert*-butylpyrazolidine **5** (Figure 1) are indicative of the C_2 molecular symmetry and strongly hindered nitrogen inversion. The non-equivalence of geminal H_a and H_b protons is observed, the signal of 3,5-C at 42 ppm dd with Δ^1J 10 Hz is not transformed into a triplet in [$^2H_8$] toluene at 100 °C.

‡ This method was used in reduction of enamines.[5]

§ ^{1}H and ^{13}C NMR spectra were measured on Bruker DRX-500, WM-400 and AM-300 spectrometers.

1 prepared in accordance with Scheme 1, 71% yield, mp 140–142 °C (lit.,[4] mp 141–142 °C). ^{1}H NMR ($CDCl_3$ at 20 °C) δ: 1.33 (s, 18H, 2Bu^t), 4.41 (s, 2H, NH).

3a prepared in accordance with Scheme 1, 75% yield, mp 174–175 °C. ^{1}H NMR ([$^2H_6$]DMSO at 20 °C) δ: 1.82 (s, 18H, 2Bu^t), 3.48 (s, 4H, –NH–NH– H_2SO_4). Base **3**, 96% yield, bp 134–137 °C (lit.,[9] bp 137–138 °C). ^{1}H NMR ($CDCl_3$ at 20 °C) δ: 1.01 (s, 18H, 2Bu^t), 2.81 (s, 2H, 2NH).

Attempts to separate enantiomers **5** by means of diastereomeric salts with (1*S*)-(+)-10-camphorsulfonic acid have failed. Therefore, HPLC was used for resolution on microcrystalline triacetyl cellulose;¶ however, it was not efficient. Complete separation of **5** was detected by GLC[7] on a Chirasil-β-Dex chiral stationary phase, and narrow non-overlapped peaks of enantiomers, which are configurationally stable even at 110 °C, were observed (Figure 2).

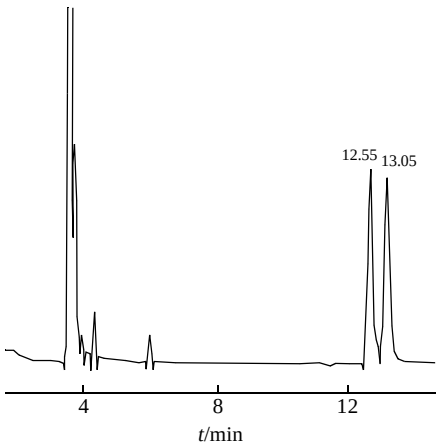


Figure 2 Separation of the enantiomers of **5** by GLC on Chirasil-β-Dex (column 25 m, i.d. 0.25 mm, H_2, 0.1 atm) at 110 °C.

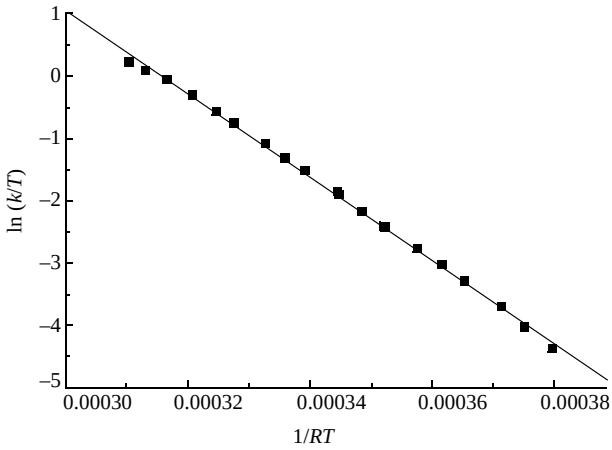
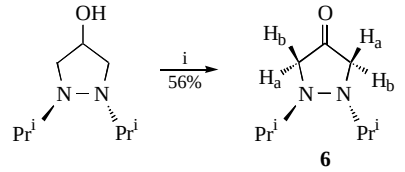


Figure 3 Kinetics of N atom inversion in **6** (*R*-factor: 0.99924; standard deviation: 0.0542).

The further increase of the configurational stability of pyrazolidines is possible due to the elimination of 1,3-non-bonded interactions, which destabilise the ground state. That is why 1,2-diisopropylpyrazolidin-4-one **6** was synthesised[1] (Scheme 3) using oxidation of 1,2-diisopropylpyrazolidin-4-ol[1] under the action of DMSO activated with $(COCl)_2$[††] with higher yield (*cf.* 12%[1]).



6

Scheme 3 *Reagents and conditions*: i, CH_2Cl_2, DMSO/$(COCl)_2$, Et_3N, 15 min at –60 °C.

From the full line shape analysis in the ^{1}H DNMR spectra, the following activation parameters of the nitrogen inversion in pyrazolidine **6** were obtained: $\Delta G^{\neq}$ = 73.3±0.6 kJ mol^{-1} at 25 °C, $\Delta H^{\neq}$ = 66.4±0.6 kJ mol^{-1}, $\Delta S^{\neq}$ = –23.3±1.7 J K^{-1} mol^{-1} (Figure 3). The real inversion barrier is about 5.6 kJ mol^{-1} higher than that for 1,2-di-*tert*-butylpyrazolidine.[1]

To arrest completely nitrogen inversion, previously unknown 1,2-diisopropyl-3,5-dimethylpyrazolidine **8** (Scheme 4) was synthesised veto of N atoms inversion.[1] Methyl propenyl ketone

4 prepared in accordance with Scheme 2 and separated by chromatography (SiO_2 40/60 μ. Eluent: $CHCl_3$) 85% yield. n_D^{20} 1.5257. ^{1}H NMR ([$^2H_8$]toluene at 20 °C) δ: 1.05 (s, 9H, Bu^t-1), 1.12 (s, 9H, Bu^t-2), 3.42 (ddd, 1H, H_a, ^2J –15.2 Hz, ^3J 2.81 Hz, ^4J 1.58 Hz), 3.55 (ddd, 1H, H_b, ^2J –15.2 Hz, ^3J 2.77 Hz, ^4J 1.47 Hz), 4.94 (ddd, 1H, 4-CH, ^3J 5.34 Hz, ^3J 2.77 Hz, ^3J 2.81 Hz), 5.95 (ddd, 1H, 3-CH, ^3J 5.34 Hz, ^4J 1.47 Hz, ^4J 1.58 Hz). ^{13}C NMR ([$^2H_8$]toluene at 20 °C) δ: 27.63 (q, *Me*$_3$C, ^1J 125.5 Hz), 28.23 (q, *Me*$_3$C, ^1J 125.5 Hz), 54.68 (dddd, CH_2, ^1J 135.97 and 139.63 Hz, $^2J \sim {}^3J$ 7.6 Hz), 110.48 (dm, 4-C, ^1J 169.9 Hz), 137.99 (dm, 3-C, 177.6 Hz), 58.18 (s, *C*Me$_3$), 60.14 (s, *C*Me$_3$).

5 prepared in accordance with Scheme 2 and separated by chromatography (SiO_2 40/60 μ. Eluent: $CHCl_3$) 43% yield. ^{1}H NMR (500 MHz, $CDCl_3$ at 20 °C) δ: 1.12 (s, 18H, 2Bu^t), 1.98 (m, 2H, $H_cH_{c'}$), 2.87 (m, 2H, $H_bH_{b'}$), 3.18 (m, 2H, $H_aH_{a'}$), $^2J_{ab}$ = $^2J_{a'b'}$ = –12.37 Hz, $^2J_{cc'}$ –11.93 Hz, $^3J_{ac}$ = $^3J_{a'c'}$ = 3.84 Hz, $^3J_{bc}$ = $^3J_{b'c'}$ = 7.62 Hz, $^3J_{a'c}$ = $^3J_{ac'}$ = 10.09 Hz, $^3J_{b'c}$ = = $^3J_{bc'}$ = 10.21 Hz, $^4J_{bb'}$ = 0.45 Hz, $^4J_{aa'}$ = 0.75 Hz. ^{13}C NMR (125 MHz, $CDCl_3$ at 20 °C) δ: 28.32 (*Me*$_3$C), 29.49 (4-CH_2), 47.44 (3,5-CH_2), 57.67 (*C*Me$_3$). ^{13}C NMR (100 MHz, [$^2H_8$]toluene at 20 °C) δ: 29.40 (q, *Me*$_3$C, ^1J 124.7 Hz), 30.57 (t, 4-CH_2, ^1J 129.2 Hz), 48.57 (dd, 3,5-CH_2, ^1J 131.7 Hz, ^1J 140.8 Hz), 58.73 (s, *C*Me$_3$). Found (%): C, 71.37; H, 13.43; N, 15.50. Calc. for $C_{11}H_{24}N_2$ (%): C, 71.68; H, 13.12; N, 15.20.

Hydrogen sulfate **5a**: mp 131–132 °C (acetone). ^{1}H NMR ([$^2H_6$]DMSO at 20 °C) δ: 1.19 (br. s, 9H, Me$_3$CN-2), 1.32 (br. s, 9H, Me$_3$CN$^+$-1), 2.21 (br. s, 2H, $H_bH_{a'}$), 3.11 (br. s, 1H, $H_{c'}$), 3.51 (br. s, 1H, H_c), 3.61 (br. s, 1H, H_a), 3.82 (br. s, 1H, $H_{b'}$), 9.30 (br. s, 1H, HN$^+$).

p-Toluenesulfonate **5b**: mp 145–146 °C (acetone). ^{1}H NMR ($CDCl_3$ at 20 °C) δ: 1.27 (s, 9H, Me$_3$CN-1), 1.42 (s, 9H, Me$_3$CN$^+$-2), 2.28 (m, 2H, CH_2-4, $\Delta\nu$ 45.6 Hz), 2.31 (s, 3H, *Me*C_6H_4), 3.33 (m, 2H, CH_2-N-1, AB spectrum, $\Delta\nu$ 142.6 Hz, ^2J –12.7 Hz, $^3J_{ax}$ = $^3J_{ay}$ = 9.1 Hz, $^3J_{bx}$ 9.8 Hz, $^3J_{by}$ 3.5 Hz), 3.88 (m, 2H, CH_2-N$^+$-2, AB spectrum, $\Delta\nu$ 220.0 Hz, ^2J –12.8 Hz), 7.12 and 7.74 (2d, 2×2H, C_6H_4, ^3J 8.0 Hz), 10.17 (br. s, 1H, HN$^+$).

6 prepared in accordance with Scheme 4 and separated by chromatography (SiO_2 40/60 μ. Eluent: $CHCl_3$) 56% yield. ^{1}H NMR (400 MHz, [$^2H_8$]toluene at 20 °C) δ: 0.74 (d, 6H, 2Me-A, ^3J 6.4 Hz), 0.85 (d, 6H, 2Me-B, ^3J 6.4 Hz), 2.50 (hept, 2H, 2HCN), 2.82 (m, 4H, 2,5-CH_2, AB spectrum, $\Delta\nu$ 100.0 Hz, ^2J –19.0 Hz). ^{13}C NMR {^{1}H} ([$^2H_8$]toluene at 20 °C) δ: 19.72 (Me), 23.28 (CHN), 55.52 (CH_2N), 217.24 (CO). Found (%): C, 63.18; H, 10.78; N, 16.11. Calc. for $C_9H_{18}N_2O$ (%): C, 63.49; H, 10.66; N, 16.45.

7 prepared in accordance with Scheme 4, 43% yield, bp 83–85 °C (25 torr). ^{1}H NMR ($CDCl_3$ at 20 °C) δ: 0.89 (d, 3H, Me-A, ^3J 6.2 Hz), 0.94 (d, 3H, Me-B, ^3J 6.2 Hz), 0.97 (d, 3H, Me-A′, ^3J 6.2 Hz), 1.00 (d, 3H, Me-B′, ^3J 6.2 Hz), 1.15 (d, 3H, 5-Me, ^3J 6.7 Hz), 1.65 (s, 3H, 3-Me), 2.89 (hept, 1H, HCN-1, ^3J 6.2 Hz), 3.22 (hept, 1H, HCN-2, ^3J 6.2 Hz), 3.64 (br. m, 1H, 5-H, ^3J 6.7 Hz), 4.48 (br. s, 1H, 4-H).

8 prepared in accordance with Scheme 4, 80% yield, bp 88–90 °C (23 torr), n_D^{20} 1.4446. ^{1}H NMR ($CDCl_3$ at 20 °C) δ: 0.99 (d, 6H, 2Me-A, ^3J 6.35 Hz), 1.04 (d, 6H, 2Me-B, ^3J 6.6 Hz), 1.10 (d, 6H, 3,5-Me, ^3J 6.5 Hz), 1.76 (t, 2H, $H_bH_{b'}$, ^3J 6.5 Hz), 2.78 (hept, 2H, HCMe$_2$, ^3J 6.6 Hz), 3.13 (qt, 2H, $H_aH_{a'}$, ^3J 6.5 Hz). ^{13}C NMR ([$^2H_6$]benzene at 20 °C) δ: 21.3 (qq, Me-A, ^1J 124.8 Hz, ^3J 4.5 Hz), 22.2 (qm, Me-B, ^1J 124.8 Hz), 24.2 (qt, Me-C, ^1J 124.9 Hz, ^3J 9.0 Hz), 43.8 (t, 4-C, ^1J 129.0 Hz), 56.3 (dm, CHN, ^1J 132.2 Hz, ^2J 3.0 Hz), 57.8 (dqt, 3,5-C, ^1J 133.5 Hz, ^2J 4.0 Hz).

Hydrochloride **8**: mp 178–179 °C (acetone). ^{1}H NMR ($CDCl_3$ at 20 °C) δ: 1.18 (d, 3H, A-*Me*CHN-1, ^3J 6.5 Hz), 1.24 (d, 3H, B-*Me*CHN-1, ^3J 6.5 Hz), 1.26 (d, 3H, C-*Me*CHN-1, ^3J 6.3 Hz), 1.38 (d, 3H, A-*Me*–CHN$^+$-2, ^3J 6.3 Hz), 1.38 (d, 3H, B-*Me*CHN$^+$-2, ^3J 6.3 Hz), 1.51 (d, 3H, C-*Me*CHN$^+$-2, ^3J 6.8 Hz), 1.68 (dt, 1H, H_b, ^2J –13.3 Hz, ^3J 13.3 Hz, ^3J 11.4 Hz), 2.42 (dt, 1H, $H_{b'}$, ^2J –13.3 Hz, ^3J 13.3 Hz, ^3J 6.6 Hz), 3.60 (qdd, 1H, H_a, ^3J 6.3 Hz, ^3J 13.3 Hz, ^3J 6.6 Hz), 3.64 (hept, 1H, HCN-1, ^3J 6.5 Hz), 3.70 (hept, 1H, HCN$^+$-2, ^3J 6.3 Hz), 3.97 (qdd, 1H, $H_{a'}$, ^3J 6.6 Hz, ^3J 6.8 Hz, ^3J 11.4 Hz); 12.3 (br. s, 1H, HN$^+$-2).

Meso-form **8**: ^{1}H NMR [$CDCl_3$–C_6D_6 (7:1) at 20 °C] δ: 1.06 (d, 6H, 2Me-A, ^3J 6.5 Hz), 1.1 (d, 6H, 2CH*Me*-B, ^3J 6.5 Hz), 1.24 (d, 6H, 3,5-Me, ^3J 6.5 Hz), 1.48 (dt, 1H, H_b, ^2J –11.7 Hz, ^3J 11.7 Hz), 1.89 (dt, 1H, $H_{b'}$, ^2J –11.7 Hz, ^3J 6.5 Hz), 3.07 (hept, 2H, 2HCN, ^3J 6.5 Hz), 3.1–3.4 (br. s, 2H, $H_aH_{a'}$).

¶ Enantiomers of the substituted diaziridines are well separated on this phase.[6]

†† This method was used for mild oxidation of alcohols to aldehydes and ketones.[8]

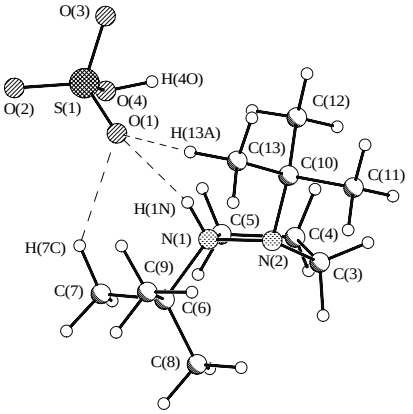
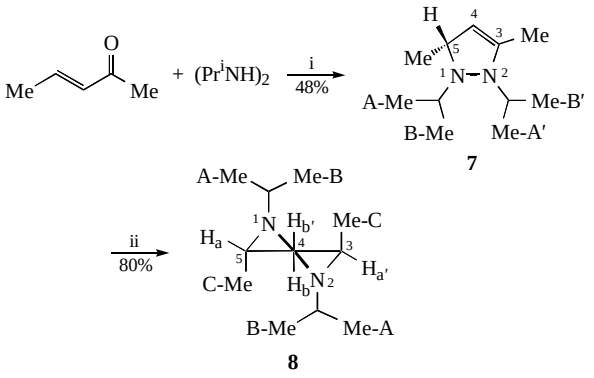


Figure 4 The general view of a close ion pair in the crystal of sulfate **5a**. Selected bond lengths (Å): N(1)–N(2) 1.479(3), N(1)–C(5) 1.538(4), N(1)–C(6) 1.561(4), N(2)–C(3) 1.482(4), N(2)–C(10) 1.520(4), C(3)–C(4) 1.531(5), C(4)–C(5) 1.507(5), S(1)–O(2) 1.429(2), S(1)–O(1) 1.446(2), S(1)–O(3) 1.486(2), S(1)–O(4) 1.534(3); bond angles (°): N(2)–N(1)–C(5) 109.2(2), N(2)–N(1)–C(6) 111.5(2), C(5)–N(1)–C(6) 112.9(2), N(1)–N(2)–C(3) 103.8(2), N(1)–N(2)–C(10) 112.6(2), C(3)–N(2)–C(10) 114.9(2), N(2)–C(3)–C(4) 107.7(2), C(5)–C(4)–C(3) 104.2(3), C(4)–C(5)–N(1) 105.7(2), O(2)–S(1)–O(1) 113.7(2), O(2)–S(1)–O(3) 110.3(2), O(1)–S(1)–O(3) 111.4(2), O(2)–S(1)–O(4) 106.6(2), O(1)–S(1)–O(4) 108.2(1), O(3)–S(1)–O(4) 106.1(1). Hydrogen bond: N(1)–H(1)···O(1) [N(1)···O(1) 2.853(1) Å, H(1)···O(1) 1.97 Å, N(1)H(1N)O(1) 155°].

was condensed with *N*,*N*′-diisopropylhydrazine to yield pyrazoline **7**, the reduction of which with 98% HCO_2H results in **8** (according to NMR, it is a mixture of d,l/meso forms in a ratio of ~5:1).§



Scheme 4 *Reagents and conditions*: i, *n*-pentane, 1 h at 4–6 °C; ii, HCO_2H in 1,4-dioxane, 1 h at 60–65 °C.

The ^{1}H MNR data are indicative of the C_2 molecular symmetry of **8**. Apparently, the inversion of N atoms in **8** is impossible due to strong steric hindrances in the epimeric form.

Thus, the nitrogen chirality *via* sterical veto of N inversion became a preparative reality.

Salts **5a** and **5b** were studied by X-ray diffraction analysis‡‡ for searching the conglomerates and defining the geometry of molecules. We found that **5a** and **5b** are racemates, and they exist in crystals in the form of close ion pairs due to the N–H···O hydrogen bonds formed by the protonated nitrogen and the oxygen of the anions and also due to the number of the C–H···O contacts (Figures 4 and 5). Note that in spite of some differences of anion nature the N(1)···O(1) distances, which characterise the N–H···O bond strength, in **5a** and **5b** are equal. Thus, probably, the N···O distance is controlled by steric (*tert*-butyl groups) rather than electronic factors. The comparison of the bond lengths and angles in **5a** and **5b** revealed that they are close to the corresponding values in 3,4-di-*tert*-butyl-1,3,4-oxadiazolidine **A**,[10] but the conformation of a five-membered ring is more sensitive to the peculiarities of crystal packing. Thus, in **5b** and **A**, the ring is characterised by the envelope conformation with the deviation of the N(2) atom by 0.385 and 0.388 Å, respectively, while in **5a**, by the envelope with deviation of the C(3) atom by 0.45 Å. The *tert*-butyl groups in all the structures are in axial positions; the nonprotonated nitrogen atom is pyramidal with a deviation from its neighbours by ~0.47 Å (0.48 Å in **A**). The main difference between the salts of **5** and **A** is reflected in some lengthening of all bonds formed by the N(1) atom. In particular, the N(1)–N(2) bond [1.485(2) and 1.479(3) Å] in the salt of **5** is elongated by ~0.05 Å in comparison with **A**.

The analysis of the crystal packing in **5a** and **5b** demonstrated that anions assemble molecules in double layers parallel to the crystallographic plane *ab* by a number of C–H···O contacts (H···O 2.33–2.55 Å, CHO 131–172°). In **5a** salt within the layers HSO_4^- anions are assembled into centrosymmetric dimers by the

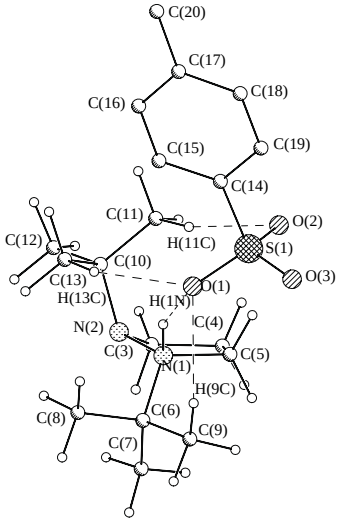


Figure 5 The general view of a close ion pair in the crystal of *p*-toluenesulfonate **5b**. The selected bond lengths (Å): N(1)–N(2) 1.485(2), N(1)–C(5) 1.535(2), N(1)–C(6) 1.556(2), N(2)–C(3) 1.490(2), N(2)–C(10) 1.515(2), C(3)–C(4) 1.535(2), C(4)–C(5) 1.514(2), S(1)–O(1) 1.471(1), S(1)–O(2) 1.458(1), S(1)–O(3) 1.455(1), S(1)–C(14) 1.783(1); bond angles (°): N(2)–N(1)–C(5) 109.0(1), N(2)–N(1)–C(6) 111.8(1), C(5)–N(1)–C(6) 114.0(1), N(1)–N(2)–C(3) 104.1(1), N(1)–N(2)–C(10) 112.6(1), C(3)–N(2)–C(10) 115.1(1), N(2)–C(3)–C(4) 108.6(1), C(5)–C(4)–C(3) 105.7(1), C(4)–C(5)–N(1) 105.7(1), O(3)–S(1)–O(2) 113.22(7), O(3)–S(1)–O(1) 113.59(7), O(2)–S(1)–O(1) 112.35(7), O(3)–S(1)–C(14) 105.82(7), O(2)–S(1)–C(14) 105.82(7), O(1)–S(1)–C(14) 105.14(7). Hydrogen bond N(1)–H(1)···O(1) [N(1)···O(1) 2.862(1) Å, H(1)···O(1) 2.00 Å, N(1)H(1N)O(1) 159°].

‡‡ *X-ray structure analysis*. Crystals of sulfate **5a** ($C_{11}H_{26}N_2O_4S$) at 170 K are monoclinic, space group $P2_1/n$: a = 10.550(4) Å, b = = 11.511(4) Å, c = 11.951(4) Å, β = 98.645(8)°, V = 1434.9(9) Å^3, Z = 4, d_{calc} = 1.307 g cm^{-3}, μ = 2.35 cm^{-1}, $F(000)$ = 616; crystals of *p*-toluenesulfonate **5b** ($C_{18}H_{32}N_2O_3S$) at 110 K are monoclinic, space group $P2_1/c$: a = 8.088(3) Å, b = 8.767(4) Å, c = 27.865(8) Å, β = 93.749(14)°, V = = 1972(1) Å^3, Z = 4, d_{calc} = 1.201 g cm^{-3}, μ = 1.82 cm^{-1}, $F(000)$ = 776.

Intensities of 8346 (**5a**) and 12879 (**5b**) reflections were measured on a SMART 1000 CCD diffractometer at 110 K [λ(MoKα) = 0.71072 Å, ω-scan technique, $2\theta < 52°$ (**5a**) and 60° (**5b**)], 2705 (**5b**) and 5361 (**5a**) independent reflections [R_{int} = 0.0250 (**5b**) and 0.0193(**5a**)] were used in the further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The refinement converged to wR_2 = = 0.1497 and GOF = 1.074 for all independent reflections [R_1 = 0.0667 was calculated against F for 2305 observed reflections with $I > 2\sigma(I)$] for **5a** and to wR_2 = 0.1061 and GOF = 1.076 for all independent reflections [R_1 = 0.0443 was calculated against F for 4301 observed reflections with $I > 2\sigma(I)$] for **5b**. 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 212043 and 212044. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.

O(4)–H(4O)···O(3A) (–*x*, –*y* – 1, –*z* + 1) [O(4)···O(3A) 2.617(2) Å, 1.79 Å, 165º] intermolecular H-bond.

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