Chiral 1-alkoxyaziridines: resolution, nitrogen inversion, stucture and diastereomeric transformations†

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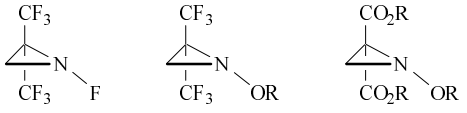
The resolution of enantiomers by chiral chromatography and the determination of nitrogen inversion activation parameters by dynamic chromatography have been carried out for aziridines 1–3; the structures of aziridines 4–7 have been studied; the complete diastereomeric transformation of (*S*,*R*)-(+)-8a into (*R*,*R*)-(–)-8b has been performed, and the conglomerate of high-melting diastereomer (±)-9 has been found.

Three new classes of aziridines **A**,[2] **B**[3] and **C**[4] containing electronegative substituents at N and C atoms of the ring (Scheme 1) have been synthesised by us as long as three decades ago in seeking a solution to the problem of asymmetric nitrogen. In contrast to all other known aziridines, these derivatives exhibit high configurational, thermal and chemical stabilities. Their nitrogen inversion barriers are 29–32 kcal mol^{-1} (121.6–134.2 kJ mol^{-1}) and most of them remain unchanged even at 200 °C. Aziridines **A** and **B** (R = = EtOCO$^-$) are stable under distillation from concentrated H_2SO_4 and a concentrated solution of KOH; stable acids **B** (R = $HO_2CCH_2^-$, $HO_2CCMe_2^-$) and their chlorides have been obtained. Upon the introduction of proper functional groups, the complete resolution of enantiomers of **B**[3(*e*)–(*g*)] and **C**[4(*d*)–(*f*)] through diastereomeric derivatives with optically active reagents have been carried out.

In this work, for the first time, the resolution of **1**,[3(*e*),(*f*)] **2**‡ and **3**‡ (Scheme 2) into enantiomers by chromatography on a chiral stationary phase has been achieved, and the nitrogen inversion activation parameters have been determined by a dynamic chromatography.§ The values of the inversion barriers ($\Delta G^{\#}$) are in a good agreement with those found previously for similar aziridines from the kinetics of *cis–trans* isomerization and racemization.[3,4] Also, the unexpected fact[6] of a noticeable rise of the inversion barrier with increasing the volume of the N-substituent in **2** in comparison with **1** has been confirmed [*cf.* refs. 3(*f*),(*g*)], and may be explained by a sterically controlled destabilisation of the planar transition state of inversion caused by



A **B** **C**

Scheme 1

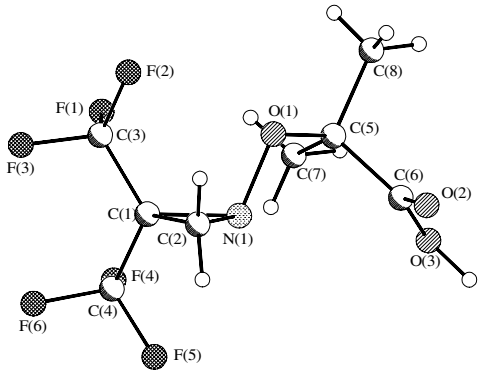


Figure 1 The general view of one of the independent molecules of **4**. The principal bond lengths for one of the independent molecules (Å): O(1)–N(1) 1.434(3), O(1)–C(5) 1.437(4), N(1)–C(2) 1.454(4), N(1)–C(1) 1.486(4), C(1)–C(2) 1.488(4), C(1)–C(4) 1.494(4), C(1)–C(3) 1.501(4); bond angles (°): N(1)–O(1)–C(5) 108.7(2), O(1)–N(1)–C(2) 111.0(2), O(1)–N(1)–C(1) 112.1(2), C(2)–N(1)–C(1) 60.8(2), N(1)–C(1)–C(2) 58.5(2), N(1)–C(1)–C(4) 110.8(3), C(2)–C(1)–C(4) 119.9(3), N(1)–C(1)–C(3) 120.9(3), C(2)–C(1)–C(3) 119.2(3), C(4)–C(1)–C(3) 115.3(3), N(1)–C(2)–C(1) 60.7(2). The pseudotorsion angle XN(1)O(1)C(5) is 163.8° [X is the centroid of the C(1)–C(2) bond].

† Asymmetric Nitrogen. Part 85. For previous communication see ref. 1.

‡ **2**: obtained by the method for synthesis of the corresponding methyl ester,[3(*e*),(*f*)] yield 90%, bp 76 °C (16 Torr). ^{1}H NMR ($CDCl_3$) δ: 1.30 (t, 3H, *Me*CH_2, ^3J 7.0 Hz), 1.38 (s, 3H, MeC), 1.53 (s, 3H, MeC), 2.50 (dq, 1H, H_a, $^2J_{H_aH_b}$ 3.5 Hz, $^4J_{H_a,CF_3\text{-}B}$ 2.5 Hz), 2.89 (d, 1H, H_b, ^2J 3.5 Hz), 4.20 (m, 2H, CH_2O, ABX_3 spectrum, $\Delta\nu \approx 28$ Hz, ^2J –10.9 Hz, $^3J_{AX} = {}^3J_{BX} =$ = 7.0 Hz).

3: synthesised by a known method,[4(*e*)] however, for the first time, it was obtained in a crystalline form, mp 41.3 °C (from acetone–hexane, 1:1). ^{1}H NMR ($CDCl_3$) δ: 2.55 (d, 1H, H_a, ^2J –2.8 Hz), 2.86 (d, 1H, H_b, ^2J –2.8 Hz), 3.62 (s, 3H, Me-A), 3.77 (s, 3H, MeON), 3.83 (s, 3H, Me-B).

5: obtained by treatment of **2** with an excess of $MeNH_2$ in abs. MeOH (in a sealed ampoule, 2 days at 20 °C), yield 78%, mp 92.5 °C (from Et_2O). ^{1}H NMR (C_6D_6) δ: 1.38 (s, 3H, MeC), 1.45 (s, 3H, MeC), 1.70 (dq, 1H, H_a, ^2J –4.0 Hz, $^4J_{H_a,CF_3\text{-}B}$ 2.6 Hz), 2.08 (d, 1H, H_b, ^2J –4.0 Hz), 2.50 (d, 3H, MeN, $^3J_{HCNH}$ 4.8 Hz), 5.68 (br. s, 1H, HN).

(*R*,*R*)-(–)-**8b**: 0.5 g of (*S*,*R*)-(+)-**8a** [mp 56 °C (CCl_4), $[\alpha]_D^{20}$ = 32° (*c* 2.0, $CHCl_3$), *cf.* ref. 3(*h*)] was dissolved in 15 ml of toluene, heated for 10 h at 100–110 °C up to complete evaporation. Upon removing solvent residues *in vacuo* (1 Torr), 0.48 g of the product was obtained, mp 112 °C, $[\alpha]_D^{20}$ = = –70° (*c* 2.0, $CHCl_3$), *cf.* ref. 3(*h*). ^{1}H NMR ([$^2H_4$]methanol) δ: 1.20 (d, 3H, MeC, ^3J 7.0 Hz), 2.72 (dq, 1H, H_a, $^2J_{H_aH_b}$ –5.1, $^4J_{H_a,CF_3\text{-}B}$ 2.8 Hz), 3.15 (dq, 1H, H_b, ^2J –5.1 Hz, $^4J_{H_a,CF_3\text{-}A}$ 1.2 Hz), 4.30 (q, 1H, H_c, ^3J 7.0 Hz).

§ The enantiomers (invertomers) of **1**–**3** were analytically separated by gas chromatography on Chirasil-β-Dex, and the nitrogen inversion barriers were determined by enantioselective dynamic gas chromatography between 65.8 and 106.9 °C for **1**, between 65 and 95 °C for **2** and at 80 °C for **3**. The elution profiles, which are characterised by a plateau formation, were evaluated by computer simulation with the ChromWin program using the 'stochastic model plus' and 'find enantiomerization barrier II' methods. Activation parameters of nitrogen inversion were obtained by temperature-dependent measurements for **1** and **2** and using linear regression of the Eyring plots (for details, see ref. 5).

For **1**: $\Delta G^{\#}$ = 116.2±0.6 kJ mol^{-1} (at 25 °C), $\Delta H^{\#}$ = 102.8±1.2 kJ mol^{-1}, $\Delta S^{\#}$ = –45±4 J K^{-1} mol^{-1}. 36 experiments/12 data points were considered for the linear regression (reliability factor r^2 = 0.998).

For **2**: $\Delta G^{\#}$ = 120.4±0.8 kJ mol^{-1} (at 25 °C), $\Delta H^{\#}$ = 114.7±1.4 kJ mol^{-1}, $\Delta S^{\#}$ = –19±6 J K^{-1} mol^{-1}. 21 experiments/7 data points were considered for the linear regression (reliability factor r^2 = 0.993).

For **3**: $\Delta G^{\#}$ = 120.6±1.2 kJ mol^{-1} (at 80 °C).

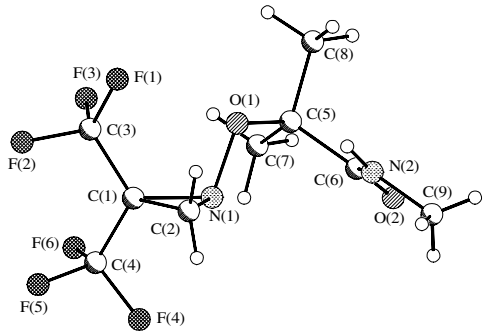
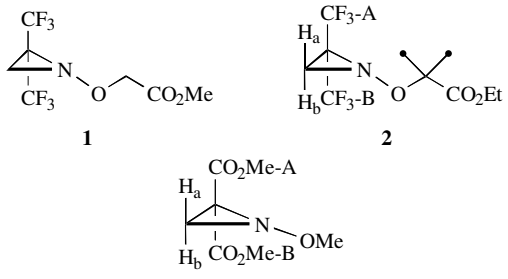


Figure 2 The general view of one of the independent molecules of **5**. The principal bond lengths for one of the independent molecules (Å): O(1)–N(1) 1.440(2), O(1)–C(5) 1.446(3), N(1)–C(2) 1.461(3), N(1)–C(1) 1.479(3), C(1)–C(2) 1.478(4), C(1)–C(3) 1.494(4), C(1)–C(4) 1.516(4); bond angles (°): N(1)–O(1)–C(5) 108.1(1), O(1)–N(1)–C(2) 110.2(2), O(1)–N(1)–C(1) 110.2(2), C(2)–N(1)–C(1) 60.4(2), C(2)–C(1)–N(1) 59.2(2), C(2)–C(1)–C(3) 119.2(3), N(1)–C(1)–C(3) 120.8(2), C(2)–C(1)–C(4) 119.7(3), N(1)–C(1)–C(4) 110.9(2), C(3)–C(1)–C(4) 115.1(2), N(1)–C(2)–C(1) 60.4(2). The pseudotorsion angle XN(1)O(1)C(5) is 175.0° [X is the centroid of the C(1)–C(2) bond].

the overlapping the lone pairs of N and O atoms. The true pyramidal mechanism of inversion in **1** and **2** is confirmed by typical[6] small values of the activation enthropy ($\Delta S^{\#} = -45$ and -19 J K^{-1} mol^{-1}, respectively),§ whereas these values are much more negative in case of dissociative inversion (from –104 to –231 J K^{-1} mol^{-1}).[5]



Scheme 2

Next, the possibilities for spontaneous resolution of aziridines **B** and **C** and their racemic diastereomeric derivatives, as well as complete transformation into one enantiomer by crystallization under conditions of either fast inversional enantiomerization or epimerization in a solution or melt (the absolute asymmetric synthesis), are considered. The necessary condition for spontaneous crystallization resolution is the formation of homochiral left and right crystals (conglomerate), which show a non-centrosymmetric (chiral) space group, ability for enantiomeric enrichment under crystallization from an optically active solvent, and, frequently, a higher melting point in comparison with a heterochiral racemic crystal.[7]

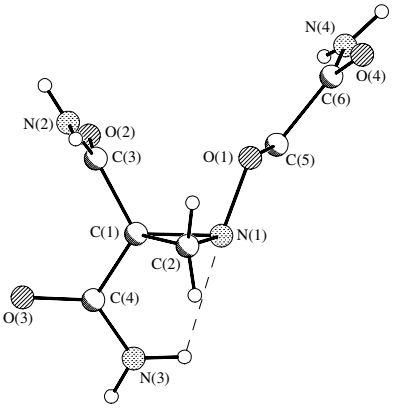
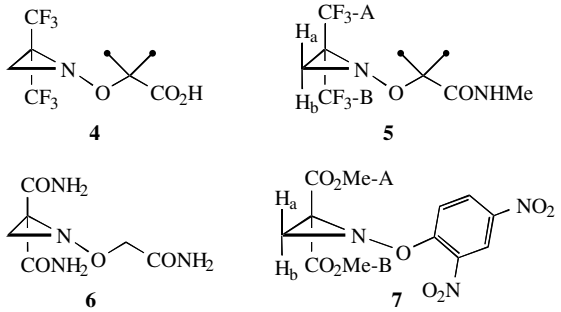


Figure 3 The general view of **6**. The principal bond lengths (Å): O(1)–C(5) 1.419(2), O(1)–N(1) 1.450(2), N(1)–C(2) 1.468(3), N(1)–C(1) 1.497(2), C(1)–C(2) 1.491(2), C(1)–C(4) 1.501(2), C(1)–C(3) 1.508(2); bond angles (°): C(5)–O(1)–N(1) 107.5(1), O(1)–N(1)–C(2) 106.8(1), O(1)–N(1)–C(1) 109.2(1), C(2)–N(1)–C(1) 60.4(1), C(2)–C(1)–N(1) 58.8(1), C(2)–C(1)–C(4) 120.2(1), N(1)–C(1)–C(4) 115.8(1), C(2)–C(1)–C(3) 122.0(1), N(1)–C(1)–C(3) 117.9(1), C(4)–C(1)–C(3) 111.9(1), N(1)–C(2)–C(1) 60.8(1). The pseudotorsion angle XN(1)O(1)C(5) is –142.6° [X is the centroid of the C(1)-C(2) bond].

The only conglomerate found earlier in the series of aziridines is a bicyclic derivative of aziridine-2-carboxylic acid (space group $P2_1$), which was found to undergo spontaneous resolution.[8]

In this work, in searching for conglomerates, the well-formed crystalline aziridines of types **A** (**4**[3(e),(f)] and **5**†) and **B** (**6**[4(j)] and **7**[4(h)]) (Scheme 3) have been studied by X-ray diffraction analysis.¶



Scheme 3

The aziridinoxyl fragment was found to show similar structural parameters in **4**, **5** (Figures 1, 2) and **6**, **7** (Figures 3, 4), as well as in the optically active diastereomers of types **B**[3(d),(h)] and **C**,[4(g),(j)] respectively. However, **4**–**7** are crystallised in achiral

¶ *Crystallographic data for* **4**–**7**: at 110 K crystals of $C_8H_9F_6NO_3$ **4** are orthorhombic, space group $Pna2_1$, $a = 13.657(9)$, $b = 17.621(17)$, $c = 9.269(8)$ Å, $V = 2231(3)$ Å^3, $Z = 8$, $M = 294.21$, $d_{calc} = 1.674$ g cm^{-3}, μ(MoKα) = 1.88 cm^{-1}, $F(000) = 1136$;

at 298 K crystals of $C_9H_{12}F_6N_2O_2$ **5** are triclinic, space group $P\bar{1}$, $a = 8.320(2)$, $b = 9.690(2)$, $c = 16.367(2)$ Å, $\alpha = 88.27(3)°$, $b = 85.13(2)°$, $\gamma = 88.00(3)°$, $V = 1313.5(5)$ Å^3, $Z = 4$, $M = 294.21$, $d_{calc} = 1.488$ g cm^{-3}, μ(MoKα) = 1.60 cm^{-1}, $F(000) = 600$;

at 150 K crystals of $C_6H_8N_4O_4 \cdot H_2O$ **6** are triclinic, space group $P\bar{1}$, $a = 7.224(2)$, $b = 8.298(2)$, $c = 9.670(2)$ Å, $\alpha = 114.08(2)°$, $\beta = 98.61(2)°$, $\gamma = 105.98(2)°$, $V = 485.6(2)$ Å^3, $Z = 2$, $M = 218.18$, $d_{calc} = 1.492$ g cm^{-3}, μ(MoKα) = 1.30 cm^{-1}, $F(000) = 228$;

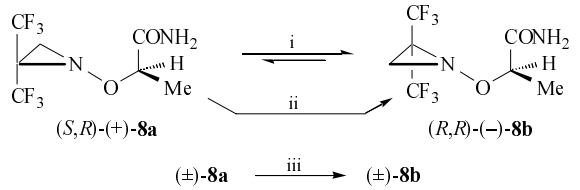
at 150 K crystals of $C_{12}H_{11}N_3O_9$ **7** are triclinic, space group $P\bar{1}$, $a = 8.180(2)$, $b = 8.546(2)$, c = 10.562(2) Å, $\alpha = 90.89(3)°$, $\beta = 105.00(3)°$, $\gamma = 94.94(3)°$, $V = 709.9(2)$ Å^3, $Z = 2$, $M = 341.24$, $d_{calc} = 1.596$ g cm^{-3}, μ(MoKα) = 1.40 cm^{-1}, $F(000) = 352$.

Intensities of 16131 (**4**), 4962 (**5**), 2375 (**6**) and 3012 (**7**) reflections were measured with a Smart 1000 CCD diffractometer at 110 K (**4**), Nonius CAD4 at 298 K (**5**) and Siemens P3/PC at 150 K (**6** and **7**) [λ(MoKα) = 0.71072 Å, ω-scans for **4**; $\theta/2\theta$-scans for **5**–**7**, $2\theta < 58°$ (**4**), 50° (**5**), 52° (**6**) and 55° (**7**)] and 5804 (**4**), 4611 (**5**), 2201(**6**), 2804 (**7**) independent reflections were used in 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. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to $wR_2 = 0.0681$ and GOF = 0.803 for all independent reflections [$R_1 = 0.0483$ was calculated against F for 2650 observed reflections with $I > 2\sigma(I)$] for **4**; $wR_2 =$ = 0.1618 and GOF = 1.020 ($R_1 = 0.0494$ for 3277 observed reflections) for **5**; $wR_2 = 0.1351$ and GOF = 1.015 ($R_1 = 0.0489$ for 1749 observed reflections) for **6**; $wR_2 =$ = 0.1469 and GOF = 0.988 ($R_1 = 0.0519$ for 2342 observed reflections) for **7**. All calculations were performed using SHELXTL PLUS 5.0 on IBM PC AT.

Analysis of the crystal packing showed that the H-bonds O–H···O and N–H···O in **4** and **5**, respectively, combine molecules into homochiral (in **4**) and heterochiral (in **5**) chains. As for the structure of **6**, due to the presence of three amido groups and a solvation molecule of water, the intermolecular H-bonds N–H···O and O–H···O combine molecules into a three-dimensional H-bonded frame.

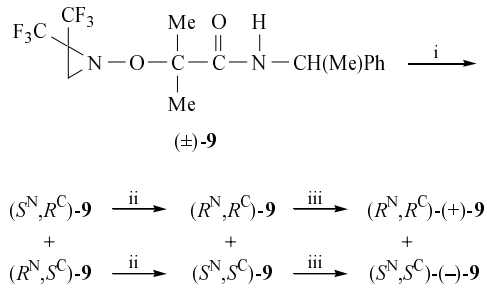
Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2002. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/111.

space groups.¶ Nevertheless, in case of **7**, the second instance was detected when a compound not forming a conglomerate (space group $P\bar{1}$) undergoes resolution by crystallization from an optically active solvent.[4(h)] The first instance of such an unusual phenomenon (*cf.* ref. 7) was observed for the tetraamide of 2-methoxy-1,2-oxazolidine-3,3,5,5-tetracarboxylic acid.[9(a)] The latter is enriched with (+)-enantiomer when being crystallised from pure methyl (*S*)-(–)-lactate and with (–)-enantiomer from an aqueous solution of the same ester, whereas according to X-ray data this tetraamide does not form a conglomerate.[9(b)] The above facts can be explained as follows: the optical enrichment of racemates occurs at the heating (used for preparing a supersaturated solution) due to an asymmetric reaction of inversion caused by different energies of diastereomeric solvates. Indeed, upon prolonged heating, similar configurationally stable asymmetric nitrogen compounds in *l*-methyl lactate followed by its removing *in vacuo* the optical enrichment takes place up to ee 7%.[4(e)] For 2,2-dimethylaziridine containing asymmetric N-substituents, the equilibrium of diastereomers in the ratio 1.1–1.8 is observed as a result of fast inversional epimerization in solution at a lower temperature.[10] Upon crystallization, similar diastereomeric 2,2-bis(trifluoromethyl)diaziridines (in [$^2H_6$]acetone the equilibrium ratio of diastereomers is 1.8; $\Delta G^{\#}_{inv}$ = = 91–93 kJ mol^{-1} at 20 °C) are transformed into one, more stable diastereomer.[11] In case of configurationally stable aziridine **8**, the inversional equilibrium is reached on heating (**8b/8a** = 2.1, $\Delta G^{\#}_{inv}$ = 120–122 kJ mol^{-1}).[4(h),(i)] Thus, we performed the complete diastereomeric transformation of **8** into one, thermodynamically more stable, epimer by withdrawing it from equilibrium under heating and slow evaporation of the solvent (Scheme 4).‡



Scheme 4 *Conditions*: i, in [$^2H_4$]methanol sealed in an ampoule, 20 h at 90 °C;[4(h),(i)] ii, in toluene, 10 h at 100–110 °C until complete evaporation; iii, in benzene, 20 h at 70 °C until complete evaporation.

A similar diastereomeric transformation followed by spontaneous resolution could be expected for aziridine **9**[3(g)] (Scheme 5).



Scheme 5 *Conditions*: i, crystallization at 0–20 °C; ii, crystallization at 100 °C with complete evaporation of the solvent; iii, spontaneous resolution by crystallization at 0–20 °C.

All four possible individual diastereomers of **9** have been synthesised earlier, and it was shown that the melting points of (*R*,*R*)-(+)-**9** and (*S*,*S*)-(–)-**9** are by 75.5 °C higher than those of two others.[3(g)] Crystallization of the racemate of high-melting diastereomer (±)-**9** (mp 94–95 °C) from a hexane-benzene mixture (3:1) was found to give a mixture of crystals, and an individual crystal is not different in melting point (122–123 °C) from high-melting diastereomers (*R*,*R*)-(+)- and (*S*,*S*)-(–)-**9** crystallised from the same solvent. Therefore, this racemate is crystallised as a conglomerate. The accurate documented example of conglomerate formation for diastereomeric salt of (±)-2-phenylpropionic acid and (±)-α-phenylethylamine as well as their resolution by entrainment was described earlier.[12]

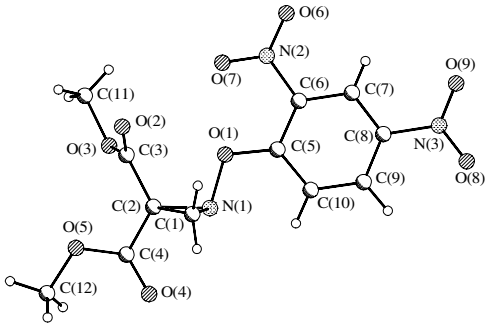


Figure 4 The general view of **7**. The principal bond lengths (Å): O(1)–C(5) 1.353(2), O(1)–N(1) 1.460(2), N(1)–C(1) 1.478(2), N(1)–C(2) 1.495(2), C(1)–C(2) 1.478(2), C(2)–C(4) 1.504(2), C(2)–C(3) 1.510(2); bond angles (°): C(5)–O(1)–N(1) 111.1(1), O(1)–N(1)–C(1) 109.0(1), O(1)–N(1)–C(2) 105.9(1), C(1)–N(1)–C(2) 59.6(1), N(1)–C(1)–C(2) 60.8(1), C(1)–C(2)–N(1) 59.6(1), C(1)–C(2)–C(4) 116.9(1), N(1)–C(2)–C(4) 110.9(1), C(1)–C(2)–C(3) 116.9(1), N(1)–C(2)–C(3) 117.4(1), C(4)–C(2)–C(3) 120.3(1). The pseudotorsion angle XN(1)O(1)C(5) is –134.4° [X is the centroid of the C(1)–C(2) bond].

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References

1 R. G. Kostyanovsky, V. R. Kostyanovsky, G. K. Kadorkina and K. A. Lyssenko, *Mendeleev Commun*., 2001, 1.

2 (a) R. G. Kostyanovsky, I. I. Chervin, A. A. Fomichov, Z. E. Samoilova, C. N. Makarov, Yu. V. Zeifman and B. L. Dyatkin, *Tetrahedron Lett*., 1969, 4021; (*b*) R. G. Kostyanovsky, G. K. Kadorkina, I. I. Chervin, and I. K. A. Romero-Maldonado, *Khim. Geterotsikl. Soedin*., 1988, 757 [*Chem. Heterocycl. Compd*. (*Engl. Transl*.), 1988, **24**, 616].

3 (a) R. G. Kostyanovsky, G. K. Kadorkina and A. A. Fomichov, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1972, 1672 (*Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1972, **21**, 1623); (*b*) R. G. Kostyanovsky and G. K. Kadorkina, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1972, 1676 (*Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1972, **21**, 1629); (*c*) R. G. Kostyanovsky, G. K. Kadorkina and K. S. Zakharov, *Dokl. Akad. Nauk SSSR*, 1975, **221**, 126 [*Dokl. Phys. Chem.* (*Engl. Transl.*), 1975, **221**, 205]; (*d*) R. G. Kostyanovsky, G. K. Kadorkina, G. V. Shustov and K. S. Zakharov, *Dokl. Akad. Nauk SSSR*, 1975, **221**, 370 [*Dokl. Phys. Chem.* (*Engl. Transl.*), 1975, **221**, 242]; (*e*) R. G. Kostyanovsky, G. K. Kadorkina, I. I. Chervin, Sh. S. Nasibov and S. V. Varlamov, *Khim. Geterotsikl. Soedin*., 1980, 1495 [*Chem. Heterocycl. Compd*. (*Engl. Transl*.), 1980, **16**, 1133]; (*f*) R. G. Kostyanovsky, G. K. Kadorkina, G. V. Shustov, I. I. Chervin, Sh. S. Nasibov and S. V. Varlamov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 145 (*Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1982, **31**, 136); (*g*) R. G. Kostyanovsky, G. K. Kadorkina, A. B. Zolotoi, O. A. D'yachenko, L. O. Atovmyan, I. I. Chervin and Sh. S. Nasibov, *Dokl. Akad. Nauk SSSR*, 1983, **269**, 1103 [*Dokl. Chem.* (*Engl. Transl.*), 1983, **269**, 126]; (*h*) A. V. Prosyanik, A. I. Mishchenko, O. V. Zelenskaya, A. Forni, I. Moretti, G. Torre, S. Brückner, L. Malpezzi, V. R. Kostyanovsky and R. G. Kostyanovsky, *Izv. Akad. Nauk, Ser. Khim*., 1998, 1398 (*Russ. Chem. Bull*., 1998, **47**, 1359); (*i*) R. G. Kostyanovsky, A. V. Prosyanik, A. I. Mishchenko, N. L. Zaichenko, I. I. Chervin and V. I. Markov, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1980, 882 (*Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1980, **29**, 632).

4 (*a*) R. G. Kostyanovsky, A. V. Prosyanik and V. I. Markov, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1974, 482 (*Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1974, **23**, 453); (*b*) R. G. Kostyanovsky, V. F. Rudchenko and V. I. Markov, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1975, 1685 (*Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1975, **24**, 1581); (*c*) R. G. Kostyanovsky, V. F. Rudchenko, A. V. Prosyanik, M. D. Isobaev, I. I. Chervin and V. I. Markov, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1977, 628 (*Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1977, **26**, 565); (*d*) R. G. Kostyanovsky and V. F. Rudchenko, *Dokl. Akad. Nauk SSSR*, 1976, **231**, 878 [*Dokl. Chem.* (*Engl. Transl.*), 1976, **231**, 712]; (*e*) R. G. Kostyanovsky, V. F. Rudchenko and G. V. Shustov, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1977, 1687 (*Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1977, **26**, 1560); (*f*) G. V. Shustov, N. B. Tavakalyan, N. L. Zaichenko and R. G. Kostyanovsky, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1980, 2183 (in Russian); (*g*) V. F. Rudchenko, O. A. D'yachenko, A. B. Zolotoi, L. O. Atovmyan, I. I. Chervin and R. G. Kostyanovsky, *Tetrahedron*, 1982, **38**, 961; (*h*) V. V. Rozhkov, I. I. Chervin, A. V. Prosyanik and R. G.

Kostyanovsky, *Izv. Akad. Nauk, Ser. Khim*., 1996, 3027 (*Russ. Chem. Bull*., 1996, **45**, 2876); (*i*) V. V. Rozhkov, I. I. Chervin, A. V. Prosyanik and R. G. Kostyanovsky, *Izv. Akad. Nauk, Ser. Khim*., 1998, 116 (*Russ. Chem. Bull*., 1998, **47**, 117); (*j*) A. V. Prosyanik, V. V. Rozhkov, A. S. Moskalenko, A. I. Mishchenko, A. Forni, I. Moretti, G. Torre, S. Brückner, L. Malpezzi and R. G. Kostyanovsky, *Izv. Akad. Nauk, Ser. Khim*., 1998, 120 (*Russ. Chem. Bull*., 1998, **47**, 119).

5 (*a*) S. Reich, O. Trapp and V. Schurig, *J. Chromatogr. A*, 2000, **892**, 487; (*b*) O. Trapp and V. Schurig, *J. Am. Chem. Soc*., 2000, **122**, 1424; (*c*) R. G. Kostyanovsky, G. K. Kadorkina, V. R. Kostyanovsky, V. Schurig, and O. Trapp, *Angew. Chem., Int. Ed. Engl*., 2000, **39**, 2938; (*d*) G. Schoetz, O. Trapp and V. Schurig, *Anal. Chem*., 2000, **72**, 2758; (*e*) O. Trapp and V. Schurig, *Comput. Chem*., 2001, **25**, 187; (*f*) O. Trapp and V. Schurig, *J. Chromatogr. A*, 2001, **911**, 167; (*g*) O. Trapp and V. Schurig, *Chem. Eur. J*., 2001, **7**, 1495; (*h*) O. Trapp, G. Schoetz and V. Schurig, *Chirality*, 2001, **13**, 403; (*i*) O. Trapp, G. Schoetz and V. Schurig, *J. Pharm. Biomed. Anal*., 2002, **27**, 497.

6 W. B. Jennings and D. R. Boyd, in *Cyclic Organonitrogen Stereodynamics*, eds. J. B. Lambert and Y. Takeuchi, VCH, New York, Weinheim, Cambridge, 1992, ch. 5, pp. 105–158.

7 (*a*) J. Jacques, A. Collet and S. H. Wilen, *Enantiomers, Racemates, and Resolutions*, Krieger Publ. Comp., Malabar, Florida, 1994; (*b*) R. G. Kostyanovsky, V. R. Kostyanovsky, G. K. Kadorkina and V. Yu. Torbeev, *Mendeleev Commun*., 2000, 83.

8 R. G. Kostyanovsky, P. E. Dormov, P. Trapencieris, B. Strumfs, G. K. Kadorkina, I. I. Chervin and I. Ya. Kalvin's, *Mendeleev Commun*., 1999, 26.

9 (*a*) R. G. Kostyanovsky and V. F. Rudchenko, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1976, 1903 (*Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1976, **25**, 1795); (*b*) V. F. Rudchenko, O. A. D'yachenko, I. I. Chervin, A. B. Zolotoi, L. O. Atovmyan and R. G. Kostyanovsky, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1978, 850 (*Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1978, **27**, 733).

10 R. G. Kostyanovsky, A. E. Polyakov, M. D. Isobaev, G. K. Kadorkina, and V. I. Markov, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1974, 1444 (*Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1974, **23**, 1373).

11 (*a*) R. G. Kostyanovsky, G. V. Shustov and N. L. Zaichenko, *Tetrahedron*, 1982, **38**, 949; (*b*) G. V. Shustov, A. B. Zolotoi, N. L. Zaichenko, O. A. D'yachenko, L. O. Atovmyan and R. G. Kostyanovsky, *Tetrahedron*, 1984, **40**, 2151.

12 F. Dufour, C. Gervais, M.-N. Petit, G. Perez and G. Coquerel, *J. Chem. Soc., Perkin Trans. 2*, 2001, 2022.

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