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Stereochemisty of 3,3-disubstituted 2-methoxy-1,2-oxazolidines†

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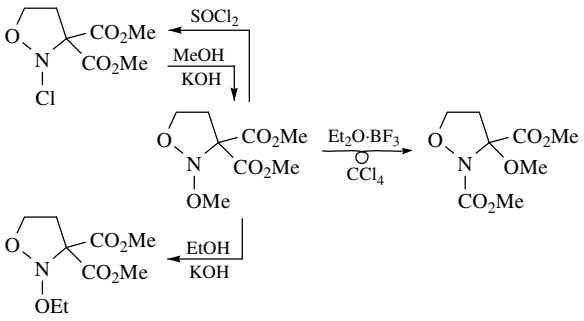
The conformations and anomeric effects for 1–3 in solution and for 3 in the solid state were investigated. The resolution of 1 by enantioselective gas chromatography was carried out and activation parameters of inversion in 1 were determined. The asymmetric transformation of the title compounds in an optically active solvent is discussed.

2-Alkoxy-1,2-oxazolidines are of particular interest in elucidating the phenomenon of asymmetric nitrogen. Complete resolution of 2-alkoxy-1,2-oxazolidines into enantiomers[2(a),(b)] has testified that a stable nitrogen pyramid is not restricted to three-membered rings like aziridines, diaziridines and oxaziridines. These data were incentives to obtain optically active dialkoxyamines containing an asymmetric centre at the nitrogen atom in an open chain,[2(c)–(e)] *e.g.*, diastereomeric NH dialkoxyamines,[2(f)] and a new class of configurationally stable open-chained trialkoxyamines.[2(g),(h)]

Formally, 2-alkoxy-1,2-oxazolidines can be considered as the acetals of corresponding nitrosoalkanes, and trialkoxyamines, as orthonitrites. In terms of chemical properties, they are similar to carbon analogues such as acetals and orthoesters, respectively (Scheme 1).[2(i)–(k)]

In many respects the chemical properties, as well as the molecular conformations and configurational stability, are determined by anomeric effects in the geminal systems ONO, ONCl and OCO, OCX of the carbon analogues. The structural data on the geminal systems ONO have been analysed, and the influence of anomeric effects on both the molecular geometry and pyramidal stability of the nitrogen atom in the systems XNY have been examined earlier.[3]

† Asymmetric nitrogen. Part 91, previous communication see ref. 1(*a*). Geminal Systems. Part 52, previous communication see ref. 1(*b*).



Scheme 1

Test compounds **1**–**3** were synthesised according the Scheme 2 and characterised by NMR spectra.‡

The activation parameters of nitrogen inversion in **1** were determined by dynamic chromatography.§ The molecular geometry of **1**–**3** was studied using NMR‡ and X-ray analysis of **3**.¶

The earlier reported data on 2-alkoxy-1,2-oxazolidines[2,3] indicate the presence of a significant anomeric effect [*n*(O-*endo*) → *σ**(NO-*exo*)]. On the basis of this fact and in view of the chemical behaviour of these compounds (Scheme 1), it was anticipated that the N–O-*exo* bond would be kinetically destabilised and thus prone to undergo reversible heterolysis. Therefore, the enantiomerization may not proceed *via* a planar transition state, which is typical of pyramidal nitrogen inversion, but by a dissociative mechanism through a tight ion pair. As it was shown earlier, such a process is observed for systems with a strong anomeric effect characterised by a large negative value of the activation entropy ($\Delta S^{\#}$).[5(a),(d),7] However, only the inversion barriers in **2** and 2-methoxy-3,3,5,5-tetracarbamoyl-1,2-oxazolidine (**A**) have been found previously from the kinetics of racemization of partly enriched samples ($\Delta G^{\#}$ = 114.5 and 119.1 kJ mol^{-1}, respectively) but no other activation parameters were determined.[2(m)]

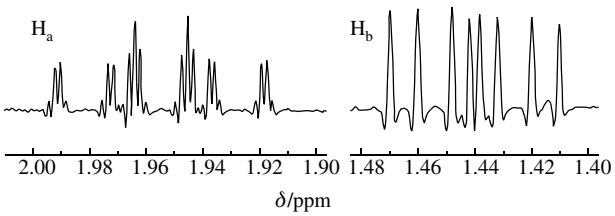
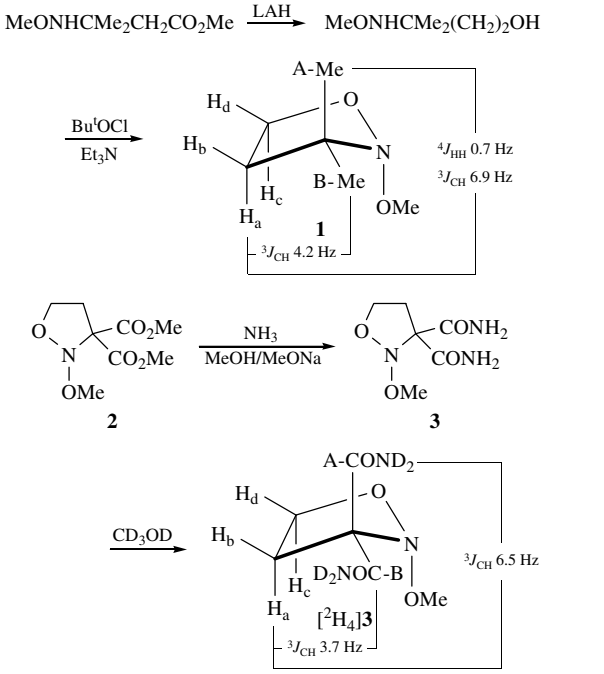


Figure 1 ^{1}H NMR spectrum of the protons H_a and H_b of **1** (400.14 MHz, [$^2H_6$]benzene at 20 °C, recorded with line narrowing); spin–spin coupling constant ^4J = 0.7 Hz of proton H_a with protons of A-Me group is observed.



Scheme 2

‡ NMR spectra were measured on a Bruker WM-400 spectrometer (400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C).

Compound **1** was obtained from the Michael adduct of $MeONH_2$ with methyl β,β-dimethylacrylate using a procedure described earlier[2(d)] (Scheme 2), the yield is 56.0% based on the starting $MeONH_2$, bp 30–31 °C (12 Torr).

^{1}H NMR ([$^2H_6$]benzene at 20 °C) δ: 0.99 (s, 3H, Me-A, width at half-height of 1.80 Hz), 1.26 (s, 3H, Me-B, width at half-height of 1.47 Hz), 1.44 (ddd, H_b, $^2J_{ba}$ –11.3 Hz, $^3J_{bc}$ 8.7 Hz, $^3J_{bd}$ 3.9 Hz), 1.955 (dddq, 1H, H_a, $^2J_{ab}$ –11.3 Hz, $^3J_{ad}$ 10.4 Hz, $^3J_{ac}$ 7.4 Hz, $^4J_{a,\,Me\text{-}A}$ 0.7 Hz), 3.57 (s, 3H, MeO), 3.73 (dt, 1H, H_c, $^3J_{cb}$ 8.7 Hz, $^3J_{ca}$ 7.4 Hz, $^2J_{cd}$ –7.4 Hz), 4.45 (ddd, 1H, H_d, $^3J_{da}$ 10.4 Hz, $^2J_{dc}$ –7.4 Hz, $^3J_{db}$ 3.9 Hz). ^{13}C NMR ([$^2H_6$]benzene at 20 °C) δ: 22.27 (qquint, Me-B, ^1J 126.2 Hz, ^3J 4.2 Hz, width at half-height of 9.6 Hz), 27.13 (qdquint, Me-A, ^1J 126.2 Hz, $^3J_{CH_a}$ 6.9 Hz, $^3J_{CH_b} = {}^3J_{CMe\text{-}B}$ = 4.2 Hz, width at half-height of 16.8 Hz), 37.42 (t, 4-CH_2, ^1J 133.2 Hz), 57.84 (q, MeO, ^1J 141.5 Hz), 67.71 (ddd, 5-CH_2, ^1J 150.0 Hz, ^1J 146.8 Hz, ^3J 3.2 Hz), 70.6 (br. s, 3-C).

2, obtained by the Tartakovskii reaction[4] as described in refs. 2(*l*),4(*b*) (Scheme 2), bp 95 °C (1.5 Torr). ^{1}H NMR ([$^2H_6$]benzene at 20 °C) δ: 2.56 (ddd, 1H, H_b, $^2J_{ba}$ –12.6 Hz, $^3J_{bc}$ 8.8 Hz, $^3J_{bd}$ 5.2 Hz), 3.11 (ddd, 1H, H_a, $^2J_{ab}$ –12.6 Hz, $^3J_{ad}$ 10.0 Hz, $^3J_{ac}$ 6.25 Hz), 3.25 and 3.34 (2s, 2×3H, 2CO_2Me), 3.52 (s, 3H, MeON), 3.69 (ddd, 1H, H_c, $^3J_{cb}$ 8.8 Hz, $^2J_{cd}$ –7.3 Hz, $^3J_{ca}$ 6.25 Hz), 3.94 (ddd, 1H, H_d, $^3J_{da}$ 10.0 Hz, $^2J_{dc}$ –7.3 Hz, $^3J_{db}$ 5.2 Hz).

3, obtained as described in refs. 2(*l*),4(*b*), 91% yield; triple crystallization from water gave crystals suitable for X-ray diffraction study, mp 171–173 °C [*cf.* for (±)-**3** mp 161–162 °C[2(l),4(b)] and for partly enriched (+)-**3** mp 170 °C[2(l)]].

Tetra-N-deuterated compound [$^2H_4$]**3**, obtained by dissolving **3** in an excess of [$^2H_4$]methanol followed by evaporation and vacuum treatment (1 Torr, 0.5 h, at 25 °C). ^{1}H NMR ([$^2H_6$]DMSO at 20 °C) δ: 2.52 (ddd, 1H, H_b, $^2J_{ba}$ –13.3 Hz, $^3J_{bd}$ 11.2 Hz, $^3J_{bc}$ 8.1 Hz), 2.76 (ddd, 1H, H_a, $^2J_{ab}$ –13.3 Hz, $^3J_{ac}$ 9.5 Hz, $^3J_{ad}$ 4.4 Hz), 3.54 (s, 3H, MeON), 3.84 (dt, 1H, H_c, $^3J_{ca}$ 9.5, $^3J_{cb}$ 8.1 Hz, $^2J_{cd}$ –8.1 Hz), 4.00 (ddd, 1H, H_d, $^3J_{db}$ 11.2 Hz, $^2J_{dc}$ –8.1 Hz, $^3J_{da}$ 4.4 Hz), 7.15, 7.23, 7.36 and 7.52 (br. s, 4H, 4HN). ^{1}H NMR (D_2O at 20 °C) δ: 3.00 (m, 2H, H_b and H_a, AB part of ABCD spectrum, $\Delta\nu$ 45.1 Hz, $^2J_{ab}$ –12.8 Hz, $^3J_{ad}$ 9.8 Hz, $^3J_{ac}$ 7.4 Hz, $^3J_{bc}$ 8.4 Hz, $^3J_{bd}$ 4.3 Hz), 3.83 (s, 3H, MeO), 4.28 (ddd, 1H, H_c, $^2J_{cd}$ –10.8 Hz, $^3J_{cb}$ 8.4 Hz, $^3J_{ca}$ 7.4 Hz), 4.46 (ddd, 1H, H_d, $^2J_{dc}$ –10.8 Hz, $^3J_{da}$ 9.8 Hz, $^3J_{db}$ 4.3 Hz). ^{1}H NMR ([$^2H_4$]methanol, 20 °C) δ: 2.85 (m, 2H, H_b and H_a, AB part of ABCD spectrum, $\Delta\nu$ 17.0 Hz, $^2J_{ab}$ –12.2 Hz, $^3J_{ac}$ 8.5 Hz, $^3J_{ad}$ 4.6 Hz, $^3J_{bd}$ 9.7 Hz, $^3J_{bc}$ 7.3 Hz), 3.63 (s, 3H, MeO), 3.97 (dt, 1H, H_c, $^2J_{cd}$ –7.3 Hz, $^3J_{ca}$ 8.5 Hz, $^3J_{cb}$ 7.3 Hz), 4.16 (ddd, 1H, H_d, $^2J_{dc}$ –7.3 Hz, $^3J_{db}$ 9.7 Hz, $^3J_{da}$ 4.6 Hz). ^{13}C NMR ([$^2H_6$]DMSO at 20 °C) δ: 29.19 (t, 4-CH_2, ^1J 137.4 Hz), 57.70 (q, MeO, ^1J 143.5 Hz), 68.10 (t, 5-CH_2, ^1J 151.9 Hz), 165.51 (d, B-CO, $^3J_{B\text{-}CH_a}$ 3.7 Hz, width at half-height of 6.6 Hz), 168.17 (dd, A-CO, $^3J_{A\text{-}CH_a}$ 6.5 Hz, $^3J_{A\text{-}CH_b}$ 4.5 Hz, width at half-height of 13.2 Hz).

§ *Stopped-flow multidimensional gas chromatography*[5] was performed on a Siemens Sichromat 2 gas chromatograph equipped with two ovens, a pneumatically controlled six-port valve (Valco), a cooling trap in oven 2 for use with liquid nitrogen, two flame-ionization detectors and a Shimadzu C-R 6A integrator. The whole process was monitored by a computer.

For separation of enantiomers of **1**, a fused-silica column coated with Chirasil-β-Dex[5(a)] (12.5 m × 0.25 mm i.d., 0.4 μm film thickness, 110 °C) was employed. Either the first or the second eluted (pure) enantiomer is trapped into the reactor column filled with deactivated fused silica and coated with dimethyl polysiloxane (1 m × 0.25 mm i.d., 0.002 μm film thickness). The reactor column is quickly heated to the temperature T whereby enantiomerization commences. After the contact time t the reactor column is rapidly cooled down with liquid nitrogen and the *de novo* enantiomeric mixture is transferred at the separation temperature into the second separation column where the enantiomers were separated. Helium was used as a carrier gas. The experiment was repeated three times at each temperature. The rate constant k of inversion was calculated from the observed enantiomeric ratio (*% er*) of the major peak area, the temperature T and the contact time according to the equation

$$k = \frac{1}{2t}\ln\frac{er+1}{er-1}. \qquad (1)$$

The mean values of ln(k/T) were plotted as a function of T^{-1} according to the Eyring equation. By a linear fit the values of $\Delta H^{\#}_{gas}$ and $\Delta S^{\#}_{gas}$ were obtained, and the activation parameters of inversion in **1** were calculated: $\Delta G^{\#}$ = 121.4±0.2 kJ mol^{-1} (at 25 °C), $\Delta H^{\#}$ = 98±2 kJ mol^{-1}, $\Delta S^{\#}$ = = –78±5 J mol^{-1} K^{-1}.

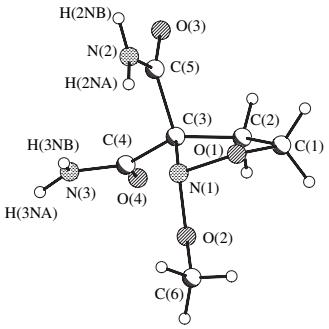


Figure 2 The general view of **3**. Selected bond lengths (Å): O(1)–N(1) 1.4151(8), O(1)–C(1) 1.462(1), N(1)–O(2) 1.4472(8), N(1)–C(3) 1.490(1); bond angles (°): N(1)–O(1)–C(1) 109.00(6), O(1)–N(1)–O(2) 107.64(6), O(1)–N(1)–C(3) 102.37(5), O(2)–N(1)–C(3) 102.06(5), C(6)–O(2)–N(1) 108.94(6).

In this work, the gas-chromatographic resolution of **1** using a chiral stationary phase has been carried out, and the activation parameters of enantiomerization have been determined by stopped-flow multidimensional gas chromatography.§ Indeed, a large negative value of the activation entropy ($\Delta S^{\#} = -78$ J mol^{-1} K^{-1}) points to a dissociative mechanism of nitrogen inversion. The values of $\Delta S^{\#}$ for 3,4-di-*tert*-butyl-1,3,4-oxadiazolidine[5(*d*)] and 2-chloro-3,3-pentamethylene oxaziridine[7(*b*)] are –93 and –182 J mol^{-1} K^{-1}, respectively, whereas in the case of pyramidal inversion the corresponding values are usually small, sometimes not exceeding ±48 J mol^{-1} K^{-1} (see ref. 8). Nevertheless, the barrier of enantiomerization in **1** ($\Delta G^{\#} = 121.4$ kJ mol^{-1}) is significantly higher than that in tetramethyl 2-methyl-1,2-oxazolidine-3,3-*trans*-4,5-tetracarboxylate ($\Delta G^{\#} = 47.8$ kJ mol^{-1}).[9] Note that in the latter compound the N-substituent has a pseudo-equatorial orientation both in solution and in a crystal,[9] whereas in **A** it has a pseudo-axial orientation, which is governed by the anomeric effect, and the enantiomerization barrier ($\Delta G^{\#} =$ = 119.1 kJ mol^{-1}) is close to those for **1** and **2**.

According to the NMR spectra, in solution, compounds **1**–**3** have a similar conformation, which is stabilised by the anomeric effect n(O-*endo*) → σ^*(NO-*exo*). It is evident from the high absolute values of the spin–spin coupling constants of proton H_a with protons of A-Me group ($^4J_{HH} = 0.7$ Hz) and carbon of A-Me group with proton H_a ($^3J_{CH} = 6.9$ Hz) in **1**, as well as carbon of A-COND$_2$ group with proton H_a ($^3J_{CH} = 6.5$ Hz) in [$^2H_4$]**3** (Scheme 2, Figure 1). An uncommon case of the less absolute value of $^2J_{HH}$ against $^3J_{HH}$ was observed earlier for protons of CH_2N group in perhydro-1,3,2-dioxazines[10(*a*)] and 1,3,2-dioxazolidine.[10(*b*)] A similar relation of these constants are valid for **1**–**3**;‡ however, for **3** in D_2O it is reversed that can be explained by a strong solvation of oxygen lone pairs in the ONO fragment.

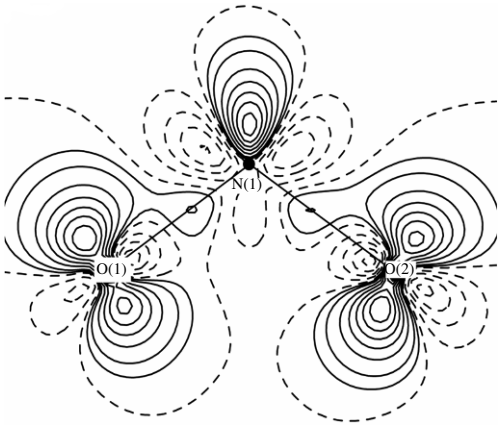


Figure 3 The distribution of the electron deformation electron density function in the plane O(1)N(1)O(2) in a crystal of **3**. The contours are drawn at a step of 0.1 eÅ^{-3}.

In the crystal of **3**, the conformation of the oxazolidine ring is an envelope [the deviation of N(1) atom is 0.557(1) Å] with the pseudoaxial position of the methoxy group (Figure 2). The torsion angles O(1)–N(1)–O(2)–C(6) and C(1)–O(1)–N(1)–O(2) characterising the mutual disposition of the N–O bonds are equal to 71.40(8)° and 70.23(8)°, respectively. It should be noted that the C(1)–O(1)–N(1)–O(2) torsion angle is quite stable and its value in the five known crystal structures of 2-alkoxy-1,2-oxazolidines[2(*b*),(*m*),14] vary in the narrow range 67.58–79.98°. It is also preserved in the isolated state of **3** (72.8°) according to B3LYP/6-31+G** calculations. In contrast, the C(1)–O(1)–N(1)–O(2) torsion angle is more dependent on the nature of alkoxy group and crystal packing effects. Thus, for example, in the isolated molecule of **3** it is equal to 89.2°.

The other common feature of 2-alkoxy-1,2-oxazolidines is the elongation of the *exo* N–O bond (1.407–1.429 Å) in comparison to the *endo* one (1.435–1.455 Å).[2(*b*),(*m*),14] For example, in **3** the N(1)–O(1) and N(1)–O(2) bond lengths in a crystal and isolated molecule are equal to 1.4151(8), 1.4472(8) Å and 1.4171, 1.4323 Å, respectively.

Clearly, such a stability of the conformation around *exo* and *endo* N–O bonds can be explained by charge transfer from the O(1) electron lone pair to the $\sigma^*_{N(1)-O(2)}$ and also from the O(2) electron lone pair to $\sigma^*_{N(1)-O(1)}$.

In order to obtain direct information on such stereoelectronic interactions, we performed the electron density analysis in the crystal of **3**.¶ The section of deformation electron density (DED) function in the O(1)N(1)O(2) plane clearly indicates that maximums related to the O(1) and O(2) electron lone pairs are parallel to the areas of DED depletion. Such a DED distribution undoubtedly indicates that both types of n–σ^*_{N-O} interactions occur in the crystal of **3**.

In addition to the visualisation of this effect, qualitative information on the n–σ^*_{N-O} interactions can be obtained from the topological analysis of an electron density function within Bader's 'Atom in Molecule' theory (AIM).[15] The ellipticity values (ε), which serve as a measure of the bond's π-component in the critical points (3, –1) of N(1)–O(1) and N(1)–O(2) bonds, are equal to 0.03 and 0.15, respectively. The same tendency is observed in the isolated molecule in which the ε values for

¶ *Crystallographic data for* **3**: at 153 K, crystals of $C_6H_{11}N_3O_4$ are monoclinic, space group $P2_1/c$, $a = 7.191(1)$, $b = 11.625(1)$ and $c =$ = 10.135(2) Å, $\beta = 103.53(3)°$, $V = 823.7(3)$ Å^3, $Z = 4$, $M = 189.18$, $d_{calc} =$ = 1.525 g cm^{-3}, μ(MoKα) = 0.129 mm^{-1}, $F(000) = 400$. Intensities of 7646 reflections were measured with a Syntex $P2_1$ diffractometer at 153 K [λ(MoKα) = 0.710712 Å, $\theta/2\theta$ scans, $2\theta_{max} = 92°$, and 7111 independent reflections ($R_{int} = 0.032$) were used in further refinement. The structure was solved by the direct method and refined by full-matrix least squares against F^2 in the anisotropic approximation for non-hydrogen atoms. All the hydrogen atoms were located from the electron density difference synthesis and included in the refinement in an isotropic approximation. The refinement converged to $wR_2 = 0.1515$ and GOF = = 1.027 for all independent reflections [$R_1 = 0.0511$ was calculated against F for 5359 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL 5.1 software.

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 number 256796. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2004.

The multipole refinement was carried out within the Hansen-Coppens formalism[13(*a*)] using the XD program package[13(*b*)] with the core and valence electron density derived from wave functions fitted to a relativistic Dirac–Fock solution.[13(*c*)] Before the refinement all C–H and N–H bond distances were normalised to the values obtained in B3LYp/6-31+G** calculation. The level of multipole expansion was octopole for carbon, nitrogen and oxygen atoms and dipole for hydrogens. The refinement was carried out against F. The multipole refinement converged to $R =$ = 0.02975, $wR = 0.0408$ and GOF = 1.0234 for 4404 merged reflections with $F > 3\sigma(F)$. All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria[13(*d*)] (difference of the mean square displacement amplitudes along the bond were not larger than 8×10^{-4} Å^2).

N(1)–O(1) and N(1)–O(2) bonds according to B3LYP/6-31+G** are equal to 0.03 and 0.06, respectively. As for the difference in ε for N(1)–O(2) in the crystal and isolated molecule, it can be explained by the variation of the C(1)–O(1)–N(1)–O(2) torsion angle. A detailed analysis of topological parameters, as well as the estimation of the specific solvation of the H-bonded pattern of **3**, will be published elsewhere.

It is well known that an optical enrichment observed upon crystallization of a racemate from an optically active solvent is a test for conglomerate formation.[11] However, it was shown earlier[12(a)] that racemic **A** is enriched with enantiomer (+)-**A** when crystallised from *l*-methyl lactate or with enantiomer (–)-**A** when crystallised from a mixture of *l*-methyl lactate and H_2O (1:1.7), and the optical purity is increased by a factor of three upon the subsequent single crystallization from water. This is surprising because (±)-**A** crystallises in achiral space group $P2_1/b$, $Z = 4$ [see ref. 2(*m*)]. We found that upon crystallization from *l*-methyl lactate (±)-**3** having the achiral space group $P2_1/c$, $Z = 4$, is enriched with (–)-**3** enantiomer {15% yield, mp 172–173 °C, $[\alpha]_{546}^{25} = +4.1°$ (*c* 3.0, H_2O)}. As it was shown earlier,[12(b)] partly enriched (+)-**3** {$[\alpha]_{546}^{25} = +1.36°$ (*c* 7.3, H_2O)} upon heating in *l*-methyl lactate (6 h at 100 °C) followed by removal of the solvent *in vacuo* gives (–)-**3** {mp 170 °C, $[\alpha]_{546}^{25} = -3.6°$ (*c* 1.1, H_2O)}. This phenomenon referred to as an asymmetric reaction of nitrogen inversion[12(b)] offers the following explanation for the above facts. Upon heating in a chiral solvent, the inversion equilibria are shifted to a more solvated enantiomer (invertomer) (–)-**3**, with which the residue after evacuation is enriched. Crystallization from a chiral solvent (with heating necessary for the preparation of a supersaturated solution) gives less solvated and, therefore, less soluble enantiomer (invertomer) (+)-**3**. Thus, the enantiomeric enrichment proceeds in solution and in no way connected with crystalline properties of the sample. The above test for conglomerate formation[11] cannot be applied to compounds capable of enantiomerization in solution, both thermally and catalytically induced.

Note that the closeness of the melting points of the racemate and enantiomers **3**,[2(b)] as well as the racemate and partly enriched samples of **A**[2(m)] can be explained by the thermally induced enantiomerization.

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