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Reductive Decyanation of Annulated Aminocyclopropane-*endo*-carbonitriles – a Way to Annulated Cyclopropane-*exo*-amines [1])

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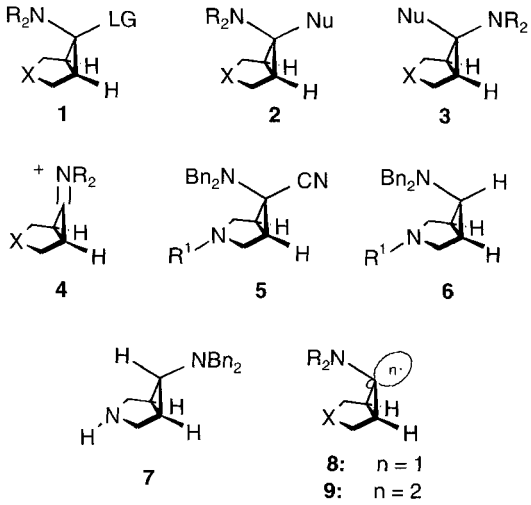
Abstract. Annulated Aminocyclopropane-*endo*-carbonitriles **11a,b** are reductively decyanated by sodium in liquid ammonia with complete retention of configuration. An additionally existing chlorine atom in the starting materials **12a,c–e**, thereby, is simultaneously replaced by hydrogen. The preparative advantage of this method is demonstrated by the selective access to 6α-*H*-isomers **13b** and **13e** as members of the ensemble of bicyclo[3.1.0]hexanediyl-dimorpholine diastereomers. A strong buckled bicyclohexane unit is present in 3α,6α-isomer **13e** as indicated by ^{1}H NMR spectroscopy and X-ray structural analysis.

Nucleophilic substitutions at aminocyclopropane derivatives are of preparative interest as they occur generally without opening [1, 2] of the three membered ring. Transfer of this reaction to annulated aminocyclopropanes **1** showed a very high selectivity [1–5] for removal of the *exo*-leaving group LG to give **2** by a substitution with retention of configuration due to less sterical shielding in the *exo* hemisphere both in starting material **1** and in cyclopropaniminium intermediate **4**.

The introduction of the attacking nucleophile Nu^- into the *endo*-position is much more difficult. Compounds **3** are obtained if either a subsequent isomerization of **2** takes place [3, 4, 6–9] or the attacking nucleophile is shifted to the inside of substrate **1** by complexation with X [10, 11]. Thus far, it was not possible to force hydride as attacking nucleophile into the *endo*-position in a considerable ratio. A partial solution of this problem was found recently in the substitution of the cyano moiety in annulated dibenzylaminocyclopiperidine-*exo*-carbonitriles **5** (R^1 = Bn, H) by hydrogen upon treatment with an alkali metal [12]: Sodium in liquid ammonia at low temperatures caused a substitution of the *exo*-nitrile moiety by hydrogen with retention of configuration [12] to give diamines **6**. On the other hand, reduction of **5** (R^1 = H) in an ammonia ethylamine mixture at 0 °C with lithium led mainly to isomerized diamine **7** [12]. The formation of **7** is assumed to be the consequence of an inversion of the intermediately generated aminocyclopiperidinyl *exo*-radical **8** or more likely of the *exo*-anion **9** (R = Bn, X = NH) to its *endo*-analogue at 0 °C. This isomerization, however, demands special substrates [12, 13] and requires strictly defined conditions in order to avoid too much products from side reactions [12].



It is known, that *endo*-bromide in an annulated bromo-chlorocyclopropane **10** [X = -$(CH_2)_2$-] can be substituted by hydrogen with predominant retention of configuration in a radical process when zinc is applied as reagent [14, 15].

It seems to be of interest, therefore, if the above mentioned reductive decyanation [12] allows the retentive displacement of the cyano group by hydrogen in annulated aminocyclopropane-*endo*-carbonitriles [16–18] **11** or **12** in order to create an easy access to annulated

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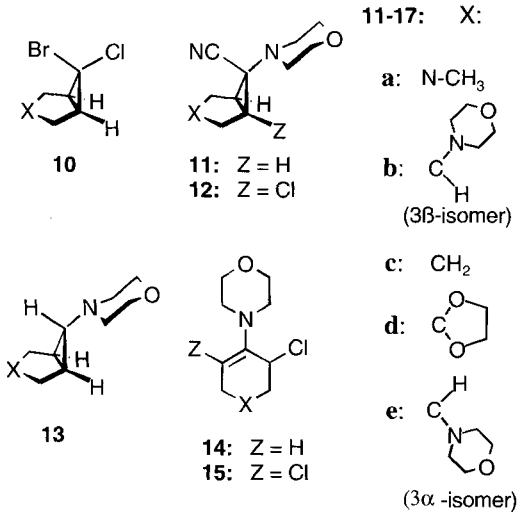
cyclopropane-*exo*-amines **13**. Compounds **12** are easily available by the reaction of dichloroenamines **15** with cyanide in water or in a mixture of water and acetonitrile [16–18]; reduction of **12** with sodium in THF/*tert*-butyl alcohol gives *endo*-nitriles **11** [16, 17]. As morpholine represents the best amino component for the synthesis of annulated aminocyclopropane-*endo*-carbonitriles we used these derivatives for our investigations.

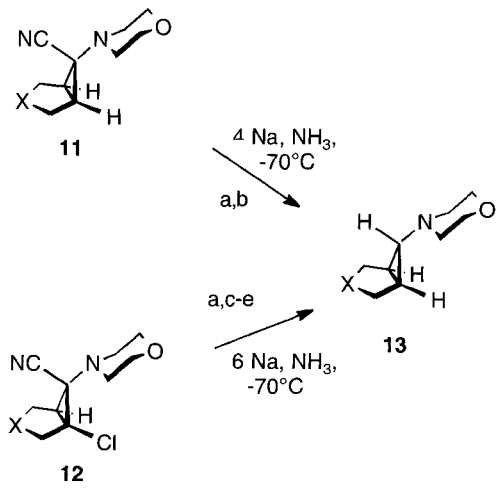


Results and Discussion

Reductive Decyanation of endo-Nitriles **11** *and* **12**

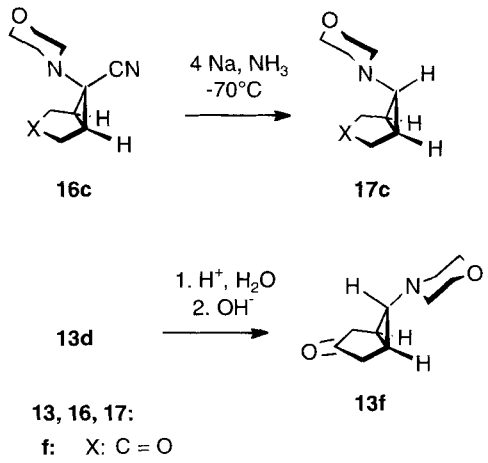
Treatment of annulated aminocyclopropane-*endo*-carbonitriles **11a,b** with 4 mole equivalents sodium in liquid ammonia at –70 °C, slowly heating up until the ammonia is evaporated and working up gave pure diamines **13a,b** in 88% and 82% yield, respectively. Chlorinated derivatives **12** which represent the precursors of compounds **11** can be applied in this reaction, too. In this case, both a reductive decyanation and a reductive dechlorination occurs. Thus, amino compounds **13a,c–e** were obtained from chlorinated *endo*-nitriles **12a,c–e** and 6 mole equivalents of sodium (yields of isolated products: **13a**: 76%; **13c**: 72%; **13d**: 89%; **13e**: 71%).

Reaction of **12a** with only 2 mole equivalents of sodium led mainly to dechlorinated product **11a** in a selectivity of at least 90%; this demonstrates that the reductive dechlorination precedes the reductive decyanation. Compound **13d** corresponds to a masked morpholinobicyclo[3.1.0]hexan-3-one **13f**; removal of the protecting group in **13d** by acidic hydrolysis generated ketone **13f**. The synthesis of the latter was tried without success [17] by isomerization of ketone **17f** *via* an enamine. The absence of *endo*-amines **17** or of products from decomposition [12] (*e.g.* ring opening or amine elimination) even in the crude reaction mixtures indicates a very clean reductive decyanation of **11** and



Scheme 1

12. The formation of annulated cyclopropane-*exo*-amines **13** is deduced from the small coupling of the hydrogen of the C_1-bridge with C(1/5)-H the ^{1}H NMR spectra ($^3J_{HH}$: 2.0 Hz for **13b,d,e**); the ^{1}H NMR spectra of **13a** and **13c** were identical with respect to published data [19, 20].



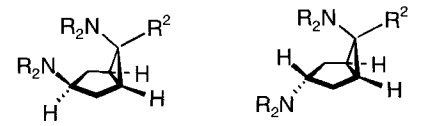
Scheme 2

The reductive decyanation of a nitrile R-C≡N by sodium in liquid ammonia is assumed [14, 21] to start with formation of a radical anion R-C≡N$^{\cdot -}$ and to give product R-H by passing the intermediates R$^{\cdot}$ and R$^-$. In the case of substrates **11** and **12**, this reaction leads to the stereochemical result of retention of configuration. The used reaction conditions – high concentration of sodium in ammonia and addition of the starting material as solid – are most opportune for retention of the configuration of the radicalic and anionic intermediates (see ref. [14]). The absence of isomerization steps (*e.g.* ref. [22]) in the process **11/12** → **13** was checked by the reductive decyanation of *exo*-nitrile **16c**. The formation

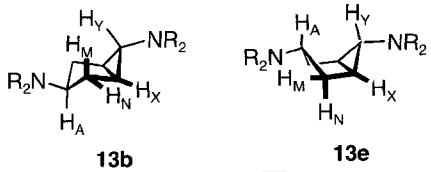
of *endo*-amine **17c** as main product (74% yield of isolated pure **17c**) in the analogous reaction and the absence of *endo*-amino products **17** from the reaction of nitriles **11/12** demonstrate that the removal of the cyano group in **11** occurs from the *endo*-position: Neither nitrile **11** nor the corresponding radical anion isomerized to the *exo*-analogue in order to allow a better removal of the cyanide leaving group. Thus, the reductive decyanation of **11** exclusively takes place in the inside hemisphere of the annulated aminocyclopropanecarbonitriles; this represents a strong contradiction to the results which are known from the substitution at annulated aminocyclopropanes *via* cationic intermediates. The difference may be understood in terms of the pyramidal geometry of the cyclopropyl radical [14] or -anion [14] on the one hand and the planar arrangement of the iminium ion on the other hand. In the latter case the necessary stabilization of the originating cation requires an inside movement of the *exo*-amino group which strongly hinders the simultaneous displacement of an *endo*-leaving group.

The "endo-Decyanation" as Important Step in Stereoselective Synthesis of the Members of the Ensemble of Diaminobicyclo[3.1.0]hexane Diastereomers.

All four diastereomeric diaminocarbonitriles **11b**, **11e**, **16b** and **16e** could be synthesized with high diastereoselectivity [17, 23] *via* chlorinated enamines **14/15**. The use of either mono- or dichloroenamines caused diastereoselection with respect to the configuration in C(6)-position. In the case of the parent diamines only diastereomers **17b** and **17e** were accessible [24] *via* chloroenamines **14**. Compounds **13b** and **13e** with 6α-configuration, however, could not be synthesized ana-logously from interaction of dichloroenamines **15b,e** with hydride due to formation of products from a ring opening (see reaction of **15a** with $NaBH_4$, ref. [19]). The new decyanation of *endo*-nitriles offers a solution of this problem and completes the selective accessibility



16b: R^2 = CN **16e:** R^2 = CN
17b: R^2 = H **17e:** R^2 = H



13b **13e**

NR_2 = —N O

of all four diastereomers of bicyclo[3.1.0]hexane-3,6-diyl-dimorpholines **13b**, **13e**, **17b** and **17e**, too.

Diastereomers **11b**, **11e**, **16b** and **16e** were proposed as constrained models for mimicking conformations of the corresponding cyclohexane species [17]. In this context, information about the conformation of the new diamines **13b** and **13e** is also of interest. The bicyclohexane unit in **13b** and **13e** appears as AMM'NN'XX'Y-system (chemical equivalent hydrogen atoms which are indicated by a prime are not shown in the drawn formulae above). The Calm-program [25] was used for simulation of the corresponding spectra and for refinement of the coupling constants. As expected [17, 23, 24], **13b** is present in a chair conformation and **13e** is found as boat conformer due to the equatorial anchoring effect of the C(3)-morpholine unit. High field shifting of $H(2)_M/H(4)_{M'}$ [**13b/13e**: $\Delta\delta$ = 0.78 ppm ($CDCl_3$)] and low field shifting of the C(3)-H unit [**13b/13e**: ^{13}C NMR: $\Delta\delta$= 10.3 ppm; ^1H NMR: $\Delta\delta$= 0.71 ppm ($CDCl_3$)] correspond to a chair conformation; the absence of a detectable coupling for $H_M H_X$ and $H_{M'}H_{X'}$ ($J < 0.8$ Hz) indicates a boat conformation (see ref. [17, 24]). The strong high field shifting for H_A (δ = 2.15 ppm; anisotropic effect of cyclopropane [24]) and the strong coupling for H_AH_N (^3J = 9.3 Hz) with respect to H_AH_M (^3J = 7.15 Hz) in the case of **13e** attract attention. Both data point to a much stronger buckling of the bicyclo[3.1.0]hexane skeleton in **13e** than in the compounds which were investigated thus far (*e.g.* ^3J for H_AH_M // H_AH_N in boat conformers: **11e**: 7.8//7.8 Hz [17]; **16e**: 7.5//7.5 Hz [26]; **17e**: 7.7//7.7 Hz [24]).

This strong ring buckling is confirmed by an X-ray structural analysis of **13e** as shown by the molecular plot in Fig. 1 and in Table 1. Additionally, selected dihedral angles are listed in Table 1; the observed values explain the higher coupling constant for $H_AH_N/H_AH_{N'}$ with respect to $H_AH_M/H_AH_{M'}$.

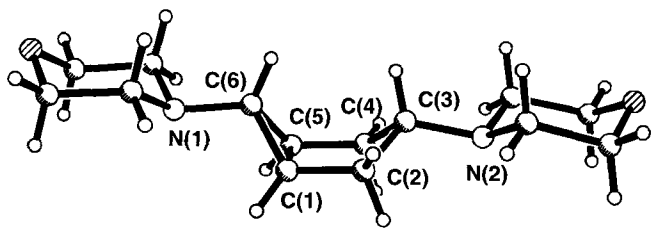


Fig. 1 X-Ray Structure of **13e**; Molecular Plot [27]

Thus, the new reductive decyanation of *endo*-nitriles **11** and **12** is not only of interest from a mechanistic point, it represents additionally one important step in a very easy access to annulated cyclopropane-*exo*-amine diastereomers **13** on the basis of dichloroenamines **15**.

Table 1 Selected Dihedral Angles [a] (°) and Interplanar Angles (°) of 4,4'-(3α,6α-Bicylo[3.1.0]hexane-3,6-diyl)-dimorpholine (**13e**)

H_A-C(3)–C(2)-H_M	−47(3)
H_A-C(3)–C(4)-$H_{M'}$	50(3)
H_A-C(3)–C(2)-H_N	−166(3)
H_A-C(3)–C(4)-$H_{N'}$	171(2)
H_X-C(1)–C(2)-H_M	−86(2)
$H_{X'}$-C(5)–C(4)-$H_{M'}$	79(3)
H_X-C(1)–C(2)-H_N	33(2)
$H_{X'}$-C(5)–C(4)-$H_{N'}$	−41(3)
C(1)C(5)C(6)/C(1)C(2)C(4)C(5)	61.0(2)
C(1)C(2)C(4)C(5)/C(2)C(3)C(4)	40.0(3)

[a] Hydrogen atoms are designated as depicted for compound **13e**; H_M and $H_{M'}$ are in the *endo*-position; H_N and $H_{N'}$ are in the *exo*-position.

We thank the Fonds der Chemischen Industrie for support of this work.

Experimental

^{1}H NMR and ^{13}C NMR spectra were obtained with a Bruker AMX 400 spectrometer (TMS as internal standard). Microanalyses were performed using a Perkin-Elmer 2400 Elemental Analyzer. Reactions in liquid ammonia were run with exclusion of moisture (nitrogen atmosphere).

Reductive Decyanation of *endo*-Nitriles 11a,b or Chloro-*endo*-nitriles 12a,c–e by Sodium in Liquid Ammonia (General Procedure)

Endo-nitrile **11** (5.0 mmol, **11a**: 1.04 g; **11b**: 1.39 g) or chloro-*endo*-nitrile **12** (5 mmol, **12a**: 1.21 g; **12c**: 1.13 g; **12d**: 1.42 g; **12e**: 1.56 g) was added to a "solution" of sodium (460 mg, 20 mmol in the case of **11**; 690 mg, 30 mmol in the case of **12**) in liquid ammonia (70 ml) at –70 °C. Then the cooling bath was removed and the mixture was stirred until the ammonia evaporated. Trituration of the residue with ether (3 × 30 ml) and distillation of the extract in a Kugelrohr apparatus gave pure amines **13a–e**.

4-(1α,5α,6α-3-Methyl-3-aza-bicyclo[3.1.0]hex-6-yl)-morpholine (**13a**)

Distillation at 95–120 °C/30 mbar; preparation from **11a** [16]: yield 0.81 g (88%), preparation from **12a** [18]: yield 0.69 g (76%), *m.p.* 39 °C (lit. [19]: 39 °C); identical ^{1}H NMR data with respect to published data [19]

$C_{10}H_{18}N_2O$	Calcd.:	C 65.90	H 9.95	N 15.37
(182.3)	Found:	C 66.1	H 9.9	N 15.3.

4,4'-(1α,3β,5α,6α-Bicyclo[3.1.0]hexane-3,6-diyl)-dimorpholine (**13b**)

Distillation at 90 °C/0.01 mbar; prepared from **11b** [17], yield 1.04 g (82%), *m.p.* 107 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.20 (H_M, $H_{M'}$, 2H), 1.38 (H_X, $H_{X'}$, 2H), 1.44 (H_Y, 1H), 2.22 (H_N, $H_{N'}$, 2H), 2.86 (H_A, 1H) (AMM'NN'XX'Y-system, $^3J_{AM} = {}^3J_{AM'} = 9.6$ Hz, $^3J_{AN} = {}^3J_{AN'} = 8.0$ Hz, $^4J_{MM'} = 1.2$ Hz, $^2J_{MN} = {}^2J_{M'N'} = 13.2$ Hz, $^4J_{NN'} = -1.0$ Hz, $^3J_{NX} = {}^3J_{N'X'} = 6.9$ Hz, $^3J_{XX'} = 8.3$ Hz, $^3J_{XY} = {}^3J_{X'Y} = 2.0$ Hz), 2.34 (m_c, 4H), 2.61 (m_c, 4H), 3.67 (m_c, 4H), 3.71 (m_c, 4H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 74.3 (d, $^1J_{CH} = 130$ Hz), 66.9 (t), 66.8 (t), 59.4 (d, $^1J_{CH} = 168$ Hz), 53.4 (t), 52.8 (t), 33.3 (t), 25.1 (d, $^1J_{CH} = 167$ Hz).

$C_{14}H_{24}N_2O_2$	Calcd.:	C 66.63	H 9.59	N 11.10
(252.4)	Found:	C 66.5	H 9.6	N 11.6.

4-(1α,5α,6α-Bicyclo[3.1.0]hex-6-yl)-morpholine (**13c**)

Distillation at 95–120 °C/30 mbar; prepared from **12c** [16], yield 0.61 g (72%), *b.p.* 90–95 °C/16 mbar (lit. [20]: 90–95 °C/12 Torr); identical ^{1}H NMR data with respect to published data [20].

$C_{10}H_{17}NO$	Calcd.:	C 71.81	H 10.25	N 8.37
(167.3)	Found:	C 71.8	H 10.3	N 8.3.

4-(1α,5α,6α-Spiro{bicyclo[3.1.0]hexane-3,2'-[1',3'-dioxolan]}-6-yl)-morpholine (**13d**)

Distillation at 80 °C/0.01 mbar; prepared from **12d** [17], yield 1.00 g (89%), *m.p.* 78 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.32 (H_X, $H_{X'}$, 2H), 1.71 (H_Y, 1H), 1.83 (H_M, $H_{M'}$, 2H), 2.12 (H_N, $H_{N'}$, 2H) (MM'NN'XX'Y-system, $^2J_{MN} = {}^2J_{M'N'} = 14.2$ Hz, $^3J_{NX} = {}^3J_{N'X'} = 5.7$ Hz, $^3J_{XX'} = 7.0$ Hz, $^3J_{XY} = {}^3J_{X'Y} = 2.0$ Hz), 2.57 (m_c, 4H), 3.63 (m_c, 4H), 3.78 (m_c, 2H), 3.89 (m_c, 2H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 117.6 (s), 66.9 (t), 64.2 (t), 64.1 (t), 53.5 (t), 49.4 (d, $^1J_{CH} = 168$ Hz), 38.1 (t), 22.2 ($^1J_{CH} = 171$ Hz).

$C_{12}H_{19}NO_3$	Calcd.:	C 63.98	H 8.50	N 6.22
(225.3)	Found:	C 64.1	H 8.6	N 6.3.

4,4'-(1α,3α,5α,6α-Bicyclo[3.1.0]hexane-3,6-diyl)-dimorpholine (**13e**)

Distillation at 115 °C/0.01 mbar; prepared from **12e** [17], yield 0.89 g (71%), *m.p.* 197 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.36 (H_X, $H_{X'}$, 2H), 1.41 (H_Y, 1H), 1.67 (H_N, $H_{N'}$, 2H), 1.98 (H_M, $H_{M'}$, 2H), 2.15 (H_A, 1H) (AMM'NN'XX'Y-system, $^3J_{AM} = {}^3J_{AM'} = 7.15$ Hz, $^3J_{AN} = {}^3J_{AN'} = 9.3$ Hz, $^4J_{MN'} = {}^4J_{M'N} = 0.6$ Hz, $^2J_{MN} = {}^2J_{M'N'} = 12.3$ Hz, $^3J_{NX} = {}^3J_{N'X'} = 5.0$ Hz, $^4J_{NX'} = {}^4J_{N'X} = -0.45$ Hz, $^3J_{XX'} = 7.3$ Hz, $^3J_{XY} = {}^3J_{X'Y} = 2.0$ Hz), 2.38 (m_c, 4H), 2.53 (m_c, 4H), 3.64 (m_c, 4H), 3.69 (m_c, 4H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 66.9 (t), 66.8 (t), 64.0 (d, $^1J_{CH} = 133$ Hz), 53.5 (t), 52.8 (t), 48.0 (d, $^1J_{CH} = 160$ Hz), 32.1 (t), 24.1 (d, $^1J_{CH} = 169$ Hz).

$C_{14}H_{24}N_2O_2$	Calcd.:	C 66.63	H 9.59	N 11.10
(252.4)	Found:	C 66.4	H 9.5	N 11.2.

1α,5α,6α-6-Morpholino-bicyclo[3.1.0]hexan-3-one (**13f**)

Aqueous hydrochloric acid (5M, 5 ml) was added to a solution of ketal **13d** (1.13 g, 5.0 mmol) in chloroform (20 ml) and stirred for 12 h at room temperature. Then aqueous sodium hydroxide solution (1M) was added under cooling until pH 14 was obtained. Extraction with chloroform (4 × 25 ml) and distillation of the extract in a Kugelrohr apparatus at 75–80 °C/0.01 mbar gave pure ketone **13f**. Yield 0.86g (95%), *m.p.* 115 °C. – ^{1}H NMR (C_6D_6): δ/ppm = 0.80 (H_Y, 1H), 1.17 (H_X, $H_{X'}$, 2H), 1.83 (H_M, $H_{M'}$, 2H), 2.09 (H_N, $H_{N'}$, 2H) (MM'NN' XX'Y-system, $^4J_{MN'} = {}^4J_{M'N} = 1.5$ Hz, $^2J_{MN} = {}^2J_{M'N'} = 18.8$ Hz, $^4J_{NN'} = 1.6$ Hz, $^3J_{NX} = {}^3J_{N'X'} = 6.3$ Hz, $^3J_{XX'} = 8.3$ Hz, $^3J_{XY} = {}^3J_{X'Y} = 2.3$ Hz), 2.24 (m_c, 4H), 2.54 (m_c, 4H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 217.5 (s), 66.6 (t), 53.2 (t), 53.0 (d, $^1J_{CH} = 164$ Hz), 39.9 (t), 20.3 (d, $^1J_{CH} = 174$ Hz).

$C_{10}H_{15}NO_2$	Calcd.:	C 66.27	H 8.34	N 7.73
(181.2)	Found:	C 66.1	H 8.2	N 7.6.

4-(1α,5α.6β-Bicyclo[3.1.0]hex-6-yl)-morpholine (**17c**)

Morpholinobicyclo[3.1.0]hexane-*exo*-carbonitrile **16c** [16] (0.96 g, 5.0 mmol) was decyanated as described for **11a** (460 mg, 20 mmol of sodium in liquid ammonia [70 ml] at −70 °C). The crude reaction product was distilled in a Kugelrohr apparatus at 95–120 °C/30 mbar; the distillate was dissolved in pentane (20 ml) and extracted with aqueous citrate buffer (pH 4.3; 3 × 10 ml) to remove small amounts of *exo*-amine **13c**. Evaporation of the pentane gave pure *endo*-amine **17c**. Yield 0.62 g (74%); *b.p.* 90–95 °C/16 mbar (lit. [20]: 90–95 °C/12 Torr); identical in the ^{1}H NMR data with respect to published data [20].

$C_{10}H_{17}NO$	Calcd.:	C 71.81	H 10.25	N 8.37
(167.3)	Found:	C 71.7	H 10.2	N 8.2.

X-Ray Crystal Structure Analysis [28] of 4,4'-(3α,6α-Bicylo[3.1.0]hexane-3,6-diyl)-dimorpholine (**13e**)

Single crystals of **13e** were obtained by crystallization from acetonitrile; only crystals of limited quality were available. Crystal data: $C_{14}H_{24}N_2O_2$, F. W. = 252.4; monoclinic, space group $P2_1/c$, a = 26.280(3), b = 6.2209(8), c = 8.4935(11) Å; $\alpha = \gamma = 90$, $\beta = 90.104(11)°$; V = 1388.6(3) Å^3; Z = 4; D_x = 1.207 g cm^{-3}; crystal size 0.25 × 0.35 × 0.50 mm; colorless prisms. The lattice constants were determined by least squares refinement on positions of 5000 reflections using the CELL routine implemented in the IPDS control program [29]. Data collection: Stoe Imaging Plate Diffraction System (IPDS), temperature: 293(2) K; graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å); 9324 reflections (2701 independent, R_{int} = 0.077) with 3.37 < Θ < 26.00°. No absorption and extinction corrections. Structure solution and refinement: The program SHELXS-86 [30] was used for primary structure solution by direct methods, the program SHELXL-97 [31] for secondary structure solution and refinement. Approximate positions for all the hydrogen atoms could be obtained from a ΔF map. The final full matrix least squares refinement on F^2 involved an anisotropic model for all atoms heavier than hydrogen. The H atoms at the morpholine rings were included in idealized positions and allowed to ride on the carbon atoms to which they are attached, additionally the orientations of the H atoms of the bicyclus were refined applying the rigid group model; the isotropic thermal displacement parameters were kept equal to 120% and 130% of the equivalent isotropic displacement parameters of the parent tertiary and secondary carbon atom, respectively. Twinning according to the index transformation matrix (100 0−10 00−1) was taken into account due to evidence from morphological aspects. The sum of the F_c^2 values of the individual twin components, each multiplied by its fractional contribution, was fitted to the F_o^2 values and the fractional contribution of the minor component refined to 0.061(4) [$(R(F)$ [$F_o^2 > 2\sigma(F_o^2)$], twin = 0.066; [$(R(F)$ [$F_o^2 > 2\sigma(F_o^2)$] = 0.072; $wR(F^2)$ [$F_o^2 > 0$], twin = 0.138 ; $wR(F^2)$ [$F_o^2 > 0$] = 0.148], S [all] = 1.151, $\Delta\rho_{max}/\Delta\rho_{min}$ = 0.31/ −0.28 e Å^{-3}, $(\Delta/\sigma)_{max}$ = 0.001.

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