nomer-dimer exchange rates. However, the monoester-monomer exchange and the dimer-derived ester-dimer exchange increase significantly. The exchange rate between monoester and dimer-derived ester decreased and became comparable with the diester and monoester exchange rate (Table IV). In summary, imidazole seems to increase some exchange rates, it affects the concentrations of monomer, tetramer, and pentamer, and it prevents reduction of vanadium(V) in solutions containing complex organic ligands. The two most likely possibilities explaining these observations include direct interaction between the vanadate derivatives and imidazole or that the imidazole acts as a general base catalyst. Although the presented results favor the former, studies appropriately testing the latter possibility are underway. Conclusive evidence for whether imidazole acts as a general base or via complex formation must therefore await further detailed studies of the vanadate ester system.

Conclusion

Formation of organic vanadate esters in solutions containing vanadate, alcohol, imidazole, and KCl were studied in order to determine how the nature of the alcohol affects the ^{51}V NMR chemical shift and the stability of the vanadate monoesters and diesters. Primary, secondary, tertiary, and substituted alcohols generate vanadate monoesters with a chemical shift defined mainly by the alcohol and possibly modified by the conditions under which the reaction is being observed. The ^{51}V NMR chemical shift of the vanadate monoester can, in general, be used to assign the organic vanadate monoester when several organic vanadate derivatives are present in solution. The formation constants of vanadate monoesters were found to decrease as follows: primary > secondary > tertiary > (primary with electronegative substituents). This stability order of equilibrium constants for vanadate monoesters differs from the results reported previously by Tracey et al.[15,16] and suggests that not only do the stability constants vary with respect to ionic strength and buffers but the relative order of the stability constants changes with conditions. It seems reasonable to expect that if steric bulk and hydrophobicity of the esters were to be important in the stability of mono- and diesters, such effects will be largest at high ionic strengths. Using relaxation times, 1D and 2D ^{51}V NMR, we show that imidazole affects both the equilibria and the kinetics of the vanadate reaction. Specifically, the presence of imidazole in the solution resulted in larger exchange rates between vanadate esters and other vanadate derivatives, whereas vanadate oligomer exchange decreased. It is possible that vanadate esters form a complex with imidazole that facilitates these exchange reactions and that such a complex contains coordinated imidazole. The studies presented in this paper presently support such a mechanism. It is also possible that imidazole acts as a general base catalyst, which facilitates the loss of alcohols as leaving groups. Detailed understanding of the ester formation reaction without imidazole is necessary before the role of imidazole can conclusively be determined. The work presented in this paper shows qualitative and quantitative results suggesting that apparently innocuous molecules in solutions containing vanadate have the potential to affect both equilibria and kinetics of vanadate reactions. It is possible the catalytic and biochemical properties of vanadates are closely linked to the variability in the reactivity and stability of vanadate derivatives.

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Thermodynamically Controlled 1,3-Asymmetric Induction in an Acyclic System: Equilibration of α-Amino Nitriles Derived from α-Alkylbenzylamines and Aldehydes

Takashi Inaba,† Makoto Fujita, and Katsuyuki Ogura*

Department of Synthetic Chemistry, Faculty of Engineering, Chiba University, 1-33 Yayoicho, Chiba 260, Japan

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Acyclic α-amino nitriles **1**, derived from α-alkylbenzylamines **3** and aldehydes **4** via a Strecker-type reaction, readily epimerize in MeOH at the newly emerged asymmetric center α to the cyano group. The equilibrium diastereomeric ratio [(*R**,*R**)-**1**]:[(*R**,*S**)-**1**] varies from 73:27 for **1e** to 90:10 for **1h**. The latter ratio is unprecedentedly high for thermodynamically controlled 1,3-asymmetric induction. The aromatic group and a bulky alkyl group (R^1) of the parent amine **3** are required to obtain high concentrations of (*R**,*R**)-**1**, whereas the bulkiness of the alkyl group (R^2) of the parent aldehyde **4** has little effect. The reasons for the thermodynamic predominance of (*R**,*R**)-**1** over (*R**,*S**)-**1** were addressed by MM2 calculations, which predicted the most stable conformers of (*R**,*R**)-**1** and (*R**,*S**)-**1**. The structures of these conformers were verified by ^1H NMR spectroscopy and X-ray crystallography.

Introduction

There have been few reports on the highly efficient thermodynamic control of 1,3-asymmetric induction in an acyclic system, probably because thermodynamic control does not achieve satsifactory selectivity in comparison with kinetic control. To study thermodynamically controlled 1,3-asymmetric induction, our attention was focused on the equilibrium between the two diastereomers of an α-amino nitrile (**1**) (eq 1). At equilibrium, (*R**,*R**)-**1** is known to be the major component of the mixture, with a diastereomeric excess of about 50% when R^1 is Me and

† Fellow of Graduate School of Science and Technology, Chiba University, 1-33 Yayoicho, Chiba 260, Japan.

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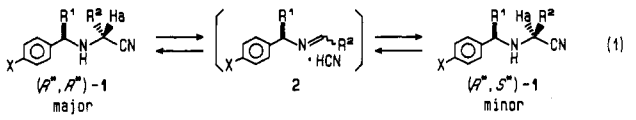
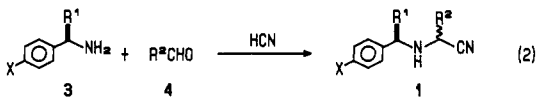


(1)

X is H.[1] Although α-amino nitriles, which are available from optically active α-methylbenzylamine (3: R^1 = Me, X = H) and aldehydes 4 (eq 2), are known to be good precursors of optically active α-amino acids,[2] neither are the factors controlling the position of equilibrium of 1 known nor have efforts to enhance the diastereomeric excess of (R*,R*)-1 been made.



(2)

We now report a method for controlling the ratio of (R*,R*)-1 and (R*,S*)-1 at equilibrium. Using this method, we synthesized acyclic α-amino nitriles with unprecedentedly high diastereomeric excesses.

Results and Discussion

According to a modified conventional procedure,[1f,3] α-amino nitriles 1 were prepared from α-alkylbenzylamine **3**, aldehydes **4**, and KCN, in the presence of $NaHSO_3$ (eq 2). The species 1 consists of two diastereomers (R*,R*)-1 and (R*,S*)-1. These epimerize in MeOH, and an equilibrium between (R*,R*)-1 and (R*,S*)-1, via the Schiff base **2**, is set up (eq 1).[1f] The diastereomers were first separated by preparative HPLC if possible[4] to obtain an accurate value for the equilibrium ratio. The isolated diasteromers were then separately dissolved in MeOH, and the solutions were heated at 80 °C in a sealed tube until the diastereomeric ratio in each tube reached a stable value according to HPLC. In general, complete equilibration was attained within 3 h. The ratio was then determined by ^1H NMR. The two diasteromers of **1b** and **1d** were not separable, so the ratios were determined after heating each mixture in MeOH for 3 h to complete equilibration. The equilibrium ratios are shown in Table I.

A significant enhancement of the diastereomeric ratio was observed when the alkyl group (R^1) of the parent amine became bulkier. Especially high ratios of 88:12 for **1g** and 90:10 for **1h** were obtained when R^1 was *t*-Bu. These values were unprecedentedly high for thermodynamically controlled 1,3-asymmetric induction in an acyclic system. However, the bulkiness of either R^2 of the parent aldehyde or the para substituent (X) of the parent benzylamine had little influence on the diastereomeric ratio of 1 (see Table I).

The relative stereochemistries of the new α-amino nitriles **1d–h** were estimated, by analogy, from their ^1H NMR spectra and those of **1a–c** and other known compounds.[1f,3] The signal due to the methine proton (H_a) of the major isomer, (R*,R*)-1, always appeared at a higher field than that of H_a of the minor isomer, (R*,S*)-1 (Table I). The structure of (R,R)-**1g** was confirmed by X-ray crystallography.[5] The structure of (R*,R*)-**1c** was also determined, and the same framework as that of (R*,R*)-**1g** was observed. Perspective drawings and atomic numbering schemes for these molecules are shown in Figure 1.

The stable conformers of each diastereomer were estimated by MM2 calculations[6] to gain insight into a possible method for controlling the diastereomeric ratio of **1**. For (R*,R*)-**1a** six energy-minimized conformers (A1–A6) were obtained (Figure 2). It was shown that two conformers (A1 and A2) must be taken into consideration. Analogous calculations were also performed for (R*,S*)-**1a** (R*,R*)-**1g**, (R*,S*)-**1g**, (R*,R*)-**1h**, and (R*,S*)-**1h**. The results are summarized in Figure 3.

For (R*,R*)-1, A1 and A2 were calculated to be relatively stable conformers, although the population of A2 was low.[9] The structures of (R,R)-**1g** and (R*,R*)-**1c** determined by X-ray crystallography (Figure 1) were in fair agreement with that of A1 (Figure 3). The predominance of A1 was confirmed by ^1H NMR spectroscopy. In the spectra of (R*,R*)-1, the signal due to the methine proton (H_a) at the α-position to the cyano group was always observed at higher field, by ca. 0.5 ppm, than that of the methine proton of (R*,S*)-1 (Table I).[10] This observation was consistent with the structure of A1, where H_a is located above the benzene ring and is magnetically shielded.

For (R*,S*)-1, the conformers B1 and B2 were shown by MM2 calculations to be relatively stable (Figure 3). When R^1 was bulky, the population of B2 was negligible, reflecting "1,3-diaxial repulsion"[11] between R^1 and H_a. In the ^1H NMR spectrum of (R*,S*)-**1h**, very sharp signals for H_a, H_b, and H_N were observed, with the coupling constants J_{HN-Ha} = 8.2 Hz and J_{HN-Hb} = 9.9 Hz,[12] suggesting that the dihedral angles H–N–C–H_a and H–N–C–H_b are close to 180°. This observation is consistent with the structure of B1.

The thermodynamic predominance of (R*,R*)-1 over (R*,S*)-1 is thus mainly due to the stability of A1 over that of B1 since A2 and B2 populations are low.[9] The difference in stability seems to be attributable to steric repulsion between the hydrogen on the amino nitrogen and the ortho

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(4) Each isomer was very stable in chloroform and showed a single peak under HPLC analysis.

(5) The analysis was performed with optically active (R,R)-**1g** (see Experimental Section).

(6) In the calculation, a stereoelectronic effect[7] that places the cyano group antiperiplanar to the lone pair of the amino nitrogen was considered. This was consistent with the X-ray crystal structures of (R*,R*)-**1c** and (R,R)-**1g**. Since the parameters of α-amino nitriles have never been reported, the framework (C_{sp^3} – HN_{sp^3} – C_{sp^3} – C_{sp}) of 1 was fixed at the coordinates that were obtained for $MeNHCH_2CN$ by AM1 calculation. As substitutes for the parameters of the lone pair on the nitrogen, those of α-alkoxy nitriles were used.[8]

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(9) At equilibrium, with >1.5 kcal/mol energy difference, the population of the minor conformer is less than 7%.

(10) This phenomenon was also observed with CD_3OD as solvent, as reported in ref 1f.

(11) The notation "1,3-diaxial", proper for a cyclic system, is here applied to an acyclic system.

(12) The sharp coupling constants could be rationalized by assuming a slow exchange rate of HN influenced by two bulky substituents on nitrogen. A similar phenomenon was observed in the spectrum of (R*,R*)-**1h**, in which J_{HN-Ha} = 1.0 Hz, J_{HN-Hb} = 12.9 Hz.

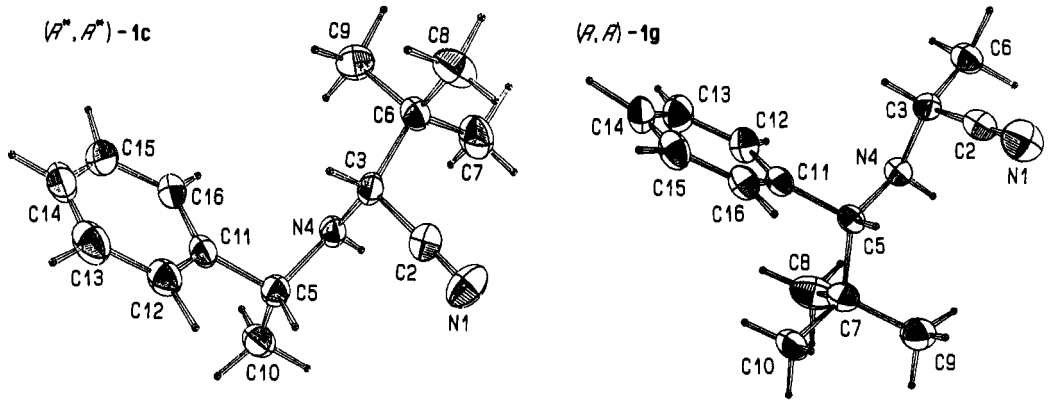


Figure 1. Molecular structures of (*R**,*R**)-1c and (*R*,*R*)-1g.

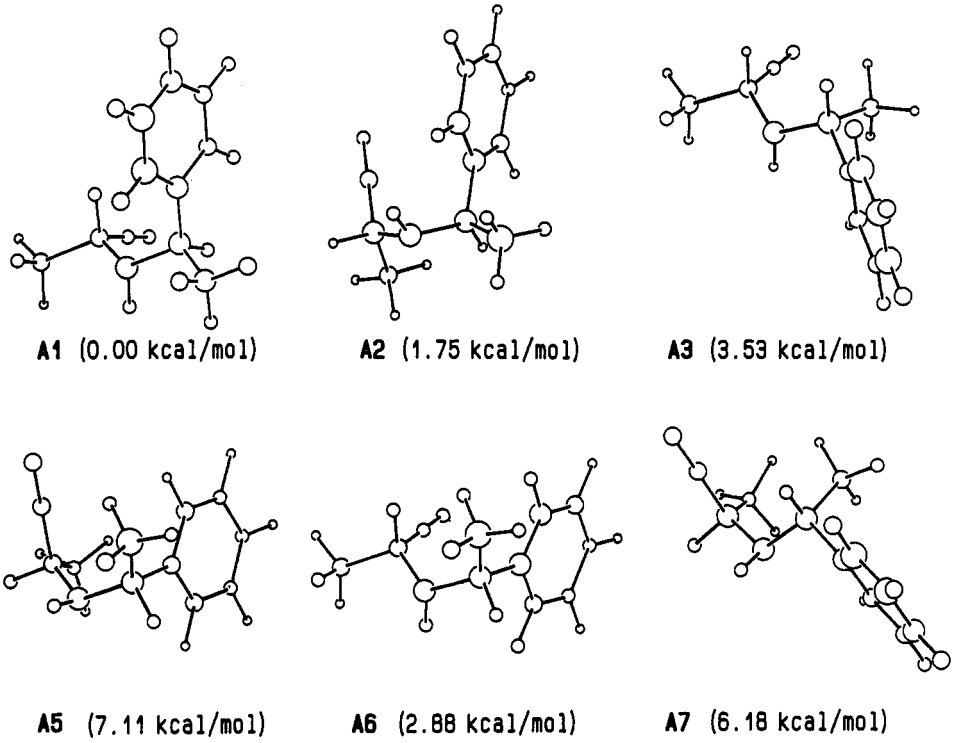
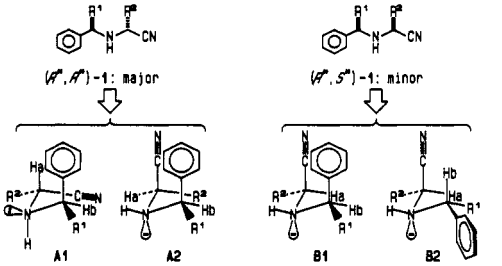


Figure 2. Structures and relative steric energies of stable conformers obtained by MM2 calculation of (*R**,*R**)-1a.



compounds	A1	A2	B1	B2
1a (R¹=R²=Me)	0.00 kcal/mol	1.75 kcal/mol	0.67 kcal/mol	1.53 kcal/mol
1g (R¹=t-Bu, R²=Me)	0.00 kcal/mol	1.57 kcal/mol	0.68 kcal/mol	5.57 kcal/mol
1h (R¹=R²=t-Bu)	0.00 kcal/mol	5.05 kcal/mol	0.85 kcal/mol	6.05 kcal/mol

Figure 3. Structures and relative steric energies of A1, A2, B1, and B2.

hydrogen of the benzene ring or an electrostatic repulsion between the aromatic ring and the cyano group of B1.

It was also noteworthy that, from the results of experiments and calculations, A1 was shown to be much more stable than B2. This implies that 1,3-repulsion of the benzene ring and hydrogen (H_a) in A1 of **1a** is less than that of the methyl group and the hydrogen in B2 of **1a**. The planar benzene ring can rotate so as to face H_a, as depicted in Figure 3, A1. Apparently, the benzene ring can be regarded as less bulky than a methyl group in this acyclic system.[13] Thus, the rotatable benzene ring, which

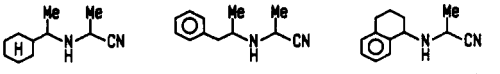


Figure 4. Structures and equilibrium ratios of **5**, **6**, and **7**.

(13) MM2 calculations were also carried out for *N*-ethyl-α-methylbenzylamine (**8**), whose conformers **8a** and **8b** correspond to A1 and B2, respectively. **8a** was shown to be thermodynamically more stable than **8b** by 1.34 kcal/mol. Hence, it was concluded that a benzene ring may be regarded as less bulky than a methyl group in some acyclic systems.

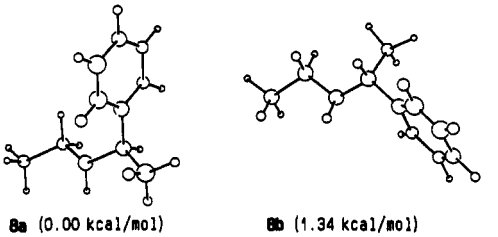


Table I. Equilibration of 1

compd	1 X	1 R^1	1 R^2	equilibrium ratio in MeOH[a] (R*,R*)-1:(R*,S*)-1	chemical shift of H_a (ppm)[b] (R*,R*)-1	(R*,S*)-1	chemical[c] yield (%)
1a	H	CH_3	CH_3	76:24	3.24	3.74	100
1b	H	CH_3	$(CH_3)_2CH$	76:24	2.99	3.46	90
1c	H	CH_3	$(CH_3)_3C$	80:20	2.84	3.28	99
1d	CH_3O	CH_3	CH_3	76:24	3.23	3.72	99
1e	NO_2	CH_3	CH_3	73:27	3.20	3.78	99
1f	H	$(CH_3)_2CH$	CH_3	81:19	3.23	3.64	96
1g	H	$(CH_3)_3C$	CH_3	88:12	3.23	3.56	98
1h	H	$(CH_3)_3C$	$(CH_3)_3C$	90:10	2.84	2.99	79

[a] The ratios were determined by 500 or 270 MHz ^1H NMR of $CDCl_3$ solutions. [b] In $CDCl_3$ solutions. [c] Yield of the Strecker reaction, based on amine 3.

can minimize the 1,3-repulsion of H_a, plays an important role in the stabilization of (R*,R*)-1.

With these points in mind, 5, 6, and 7 were prepared and the equilibrium ratios of their two diasteromers were determined (Figure 4). With 5 and 6, which have no benzene ring α to nitrogen, selectivity was poor (diastereomeric ratios of 55:45 and 59:41, respectively). The conformationally restricted compound 7 also exhibited low selectivity (diastereomeric ratio = 61:39).

As mentioned above, the equilibrium ratio of (R*,R*)-1 and (R*,S*)-1 can be approximated by [A1 + A2]:[B1 + B2]. The substituent (R^1) causes "1,3-diaxial" repulsion of H_a in B2, whereas it has little effect on the stability of A1, A2, and B1. Thus, introduction of a bulky R^1 should decrease the population of B2. In fact, it was observed that the bulkier the R^1 group of the parent benzylamine, the higher the concentration of (R*,R*)-1 was at equilibrium. MM2 calculations also showed that R^2 was placed at the least hindered site for all stable conformers except A2. Because the population of A2 must be very low even if R^2 is Me, it can be assumed that the bulkiness of R^2 has only a slight influence on the equilibrium ratio. This was also consistent with observation.

Thus, to obtain a high equilibrium ratio [(R*,R*)-1]:[(R*,S*)-1], it was necessary to employ parent benzylamines with a bulky alkyl (R^1) group. However, the bulkiness of the R^2 group of the parent aldehyde did not influence selectivity. On the basis of these observations, compounds **1g** and **1h**, which exhibited diastereomeric ratios of 88:12 and 90:10, respectively, were synthesized. These values were unprecedentedly high for thermodynamically controlled 1,3-asymmetric induction in an acyclic system.

Experimental Section

General Procedures. Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were determined with a JASCO-DIP-140 polarimeter. ^1H NMR spectra were recorded with a JEOL JNM-GSX 270 (270 MHz) or a JEOL JNM-GSX 500 (500 MHz) spectrometer. Tetramethylsilane served as an internal standard. Infrared (IR) spectra were recorded with a JASCO-A-200 spectrophotometer. 1-Phenylethylamine, racemic (Nakarai Tesque, Inc.) and optically active (Aldrich Chemical Co., Inc.), and 1,2,3,4-tetrahydro-1-naphthylamine hydrochloride (Aldrich Chemical Co., Inc.) were commercially available. 1-(4-Methoxyphenyl)ethylamine, 2-methyl-1-phenylpropylamine, 2,2-dimethyl-1-phenylpropylamine, 1-cyclohexylethylamine, and 1-methyl-2-phenylethylamine were prepared according to literature procedure.[14] (R)-1-Phenyl-2,2-dimethylpropylamine was obtained by recrystallization of its salt with *N*-acetyl-L-leucine.[15] 1-(4-Nitrophenyl)ethylamine was obtained by nitration of 1-phenylethylamine.[16]

2-[(1-Phenylethyl)amino]propanenitrile (1a). Typical Procedure. A modified literature procedure[1f] was employed. Thus, to a solution of acetaldehyde (440 mg, 10.0 mmol) in water (10 mL) were added $NaHSO_3$ (1.04 g, 10.0 mmol), KCN (650 mg, 10.0 mmol), and a solution of (R)-1-phenylethylamine (242 mg, 2.00 mmol) in MeOH (2 mL) under ice cooling. The mixture was then warmed to room temperature and was stirred for 4 h. The layers were separated and the oil formed was extracted with CH_2Cl_2 (20 mL). The aqueous layer, after addition of saturated aqueous $NaHCO_3$ (20 mL), was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Flash chromatography on silica gel (hexane/ethyl acetate, 6:1) afforded crude **1a** (370 mg). From an aliquot (152 mg) of the crude product, pure (R,R)-**1a** (96.3 mg) and a 27:73 mixture (46.8 mg) of (R,R)-**1a** and (R,S)-**1a** were obtained by preparative HPLC (SSC-Si-722 column, hexane/ethyl acetate, 1:1). The products were colorless oils. The yield of **1a** was calculated to be 100%. HPLC analysis[17] (hexane/ethyl acetate, 4:1, 1 mL/min): t_R = 11.1 min for (R,R)-**1a** and 11.7 min for (R,S)-**1a**. ^1H NMR ($CDCl_3$, 270 MHz): δ 7.38–7.26 (m, 5 H, Ar H), 4.09 (q, 1 H × 0.76, J = 6.6 Hz, PhC*H*N), 4.05 (q, 1 H × 0.24, J = 6.6 Hz, PhC*H*N), 3.74 (q, 1 H × 0.24, J = 6.9 Hz, NC*H*CN), 3.24 (q, 1 H × 0.76, J = 6.9 Hz, NC*H*CN), 1.50 (br s, 1 H, N*H*), 1.48 (d, 3 H × 0.24, J = 6.9 Hz, CH_3), 1.43 (d, 3 H × 0.76, J = 6.9 Hz, CH_3), 1.39 (d, 3 H × 0.76, J = 6.6 Hz, CH_3), 1.36 (d, 3 H × 0.24, J = 6.6 Hz, CH_3). These data agreed with those in the literature.[1f]

2-[(1-Phenylethyl)amino]-3-methylbutanenitrile (1b). A 69:31 mixture of (R*,R*)-**1b** and (R*,S*)-**1b** was obtained in 90% yield as a colorless oil. The diastereomers had the same retention time (t_R = 7.5 min) on HPLC analysis[18] (hexane/ethyl acetate, 10:1; 1 mL/min). ^1H NMR of the equilibrium mixture of diastereomers ($CDCl_3$, 270 MHz): δ 7.38–7.23 (m, 5 H, Ar H), 4.06 (q, 1 H × 0.76, J = 6.4 Hz, PhC*H*N), 4.02 (q, 1 H × 0.24, J = 6.3 Hz, PhC*H*N), 3.46 (d, 1 H × 0.24, J = 5.9 Hz, NC*H*CN), 2.98 (d, 1 H × 0.76, J = 6.3 Hz, NC*H*CN), 2.03–1.85 (m, 1 H, C*H*$(CH_3)_2$), 1.38 (d, 3 H × 0.76, J = 6.3 Hz, PhCHCH_3), 1.34 (d, 3 H × 0.24, J = 6.6 Hz, PhCHCH_3), 1.09 (d, 3 H × 0.24, J = 6.9 Hz, CH$(CH_3)_2$), 1.08 (d, 3 H × 0.24, J = 6.6 Hz, CH$(CH_3)_2$), 1.05 (d, 3 H × 0.76, J = 6.6 Hz, CH$(CH_3)_2$), 1.02 (d, 3 H × 0.76, J = 6.6 Hz, CH$(CH_3)_2$). These data agreed with those in the literature.[3]

2-[(1-Phenylethyl)amino]-3,3-dimethylbutanenitrile (1c). An 80:20 mixture of (R*,R*)-**1c** and (R*,S*)-**1c** was obtained in 99% yield as a colorless oil. The diastereomers were separated by preparative HPLC[19] (hexane/ethyl acetate, 15:1). (R*,R*)-**1c**: colorless crystals; mp 71 °C (hexane); HPLC analysis[18] (hexane/ethyl acetate, 25:1, 1 mL/min) t_R = 7.0 min; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.36–7.27 (m, 5 H, Ar H), 4.05 (q, 1 H, J = 6.6 Hz, PhC*H*N), 2.84 (br d, 1 H, J = 9.2 Hz, NC*H*CN), 1.38 (d, 3 H, J = 6.6 Hz, CHCH_3), 1.02 (s, 9 H, C$(H_3)_3$); IR (KBr) 3340, 2970,

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(17) 4.6 mm × 250 mm Finepak SIL (JAPAN SPECTROSCOPIC Co., Ltd.).
(18) 4.0 mm × 250 mm, 5 μm Hibarcolumn RT LiChrosorb Si60 (Merck).
(19) 30.0 mm × 250 mm D-SIL-5-06-B (S-5 60A SIL) (YMC Co., Ltd.).

2220, 1480, 1450, 1365, 1120, 945, 760, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95. Found: C, 77.88; H, 9.31; N, 12.94. (*R**,*S**)-**1c**: colorless crystals; mp 32 °C (hexane); HPLC analysis[18] (hexane/ethyl acetate; 25:1; 1 mL/min) t_R = 6.3 min; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.40–7.28 (m, 5 H, Ar H), 4.01 (q, 1 H, *J* = 6.3 Hz, PhC*H*N), 3.28 (br s, 1 H, NC*H*CN), 1.45 (br s, 1 H, N*H*), 1.32 (d, 3 H, *J* = 6.3 Hz, CHCH_3), 1.09 (s, 9 H, (CH_3)$_3$); IR (KBr) 3320, 2970, 2220, 1480, 1365, 1110, 760, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95. Found: C, 77.89; H, 9.31; N, 12.95.

2-[[1-(4-Methoxyphenyl)ethyl]amino]propanenitrile (1d). A 76:24 mixture of (*R**,*R**)-**1d** and (*R**,*S**)-**1d** was obtained in 99% yield as a colorless oil. The diastereomers could not be separated by preparative HPLC: HPLC analysis[18] (hexane/ethyl acetate, 4:1; 1 mL/min) t_R = 14.3 min [(*R**,*R**)-**1d**] and 17.0 min [(*R**,*S**)-**1d**]; ^1H NMR (mixture of diastereomers) ($CDCl_3$, 500 MHz) δ 7.28 (diffused d, 2 H × 0.76, *J* = 8.8 Hz, C*H*CHCOMe), 7.27 (diffused d, 2 H × 0.24, *J* = 8.3 Hz, C*H*CHCOMe), 6.87 (diffused d, 2 H, *J* = 8.8 Hz, C*H*COMe), 4.04 (q, 1 H × 0.76, *J* = 6.4 Hz, ArC*H*N), 4.01 (q, 1 H × 0.24, *J* = 6.9 Hz, ArC*H*N), 3.80 (s, 3 H, OCH_3), 3.72 (q, 1 H × 0.24, *J* = 7.2 Hz, NC*H*CN), 3.23 (q, 1 H × 0.76, *J* = 7.2 Hz, NC*H*CN), 1.47 (d, 3 H × 0.24, *J* = 7.2 Hz, CH_3), 1.42 (d, 3 H × 0.76, *J* = 7.2 Hz, CH_3), 1.36 (d, 3 H × 0.76, *J* = 6.4 Hz, CH_3), 1.34 (d, 3 H × 0.24, *J* = 6.6 Hz, CH_3); IR (neat) 3330, 2970, 2220, 1610, 1510, 1245, 1030, 835 cm^{-1}; high resolution mass spectrum calcd for $C_{12}H_{16}N_2O$ (M) 204.1262, found 204.1277.

2-[[1-(4-Nitrophenyl)ethyl]amino]propanenitrile (1e). A 58:42 mixture of (*R**,*R**)-**1e** and (*R**,*S**)-**1e** was obtained in 99% yield as a colorless solid. These diastereomers were separated by preparative HPLC[19] (hexane/ethyl acetate, 2:1). (*R**,*R**)-**1e**: colorless crystals; mp 136–137 °C (hexane–ethyl acetate); HPLC analysis[17] (hexane/ethyl acetate, 2:1; 1 mL/min) t_R = 10.85 min; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.21 (diffused d, 2 H, *J* = 8.8 Hz, C*H*CNO$_2$), 7.55 (diffused d, 2 H, *J* = 8.5 Hz, C*H*CHNO$_2$), 4.22 (q, 1 H, *J* = 6.6 Hz, ArC*H*N), 3.20 (dq, 1 H, *J* = 12.7, 7.2 Hz, NC*H*CN), 1.56 (br d, 1 H, *J* = 12.7 Hz, N*H*), 1.47 (d, 3 H, *J* = 7.2 Hz, CH_3), 1.41 (d, 3 H, *J* = 6.6 Hz, CH_3); IR (KBr) 3330, 2980, 2230, 1595, 1505, 1342, 1165, 1138, 1060, 853, 803, 750, 700 cm^{-1}. Anal. Calcd for $C_{11}H_{13}N_3O_2$: C 60.26; H, 5.98; N, 19.17. Found: C, 60.29; H, 6.01; N, 19.11. (*R**,*S**)-**1e**: colorless crystals; mp 109–110 °C (hexane–ethyl acetate); HPLC analysis[17] (hexane/ethyl acetate, 2:1; 1 mL/min) t_R = 13.5 min; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.20 (diffused d, 2 H, *J* = 8.8 Hz, C*H*CNO$_2$), 7.56 (diffused d, 2 H, *J* = 8.5 Hz, C*H*CHCNO$_2$), 4.18 (q, 1 H, *J* = 6.3 Hz, ArC*H*N), 3.78 (dq, 1 H, *J* = 8.3, 7.2 Hz, NC*H*CN), 1.53 (d, 1 H, *J* = 8.3 Hz, N*H*), 1.49 (d, 3 H, *J* = 7.2 Hz, CH_3), 1.38 (d, 3 H, *J* = 6.3 Hz, CH_3); IR (KBr) 3310, 2980, 2220, 1593, 1508, 1345, 1135, 1073, 850, 810, 750, 700 cm^{-1}. Anal. Calcd for $C_{11}H_{13}N_3O_2$: C, 60.26; H, 5.98; N, 19.17. Found: C, 60.21: H, 5.99; N, 19.12.

2-[(2-Methyl-1-phenylpropyl)amino]propanenitrile (1f). A 66:34 mixture of (*R**,*R**)-**1f** and (*R**,*S**)-**1f** was obtained in 96% yield as a colorless oil. The diastereomers were separated by preparative HPLC[19] (hexane/ethyl acetate, 5.7:1.0). (*R**,*R**)-**1f** colorless crystals; mp 54–55 °C (hexane): HPLC analysis[17] (hexane/ethyl acetate, 9:1; 1 mL/min) t_R = 13.9 min; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.34–7.24 (m, 5 H, Ar H), 3.63 (d, 1 H, *J* = 7.1 Hz, PhC*H*N), 3.23 (q, 1 H, *J* = 7.1 Hz, NC*H*CN), 1.87 (octet, 1 H, *J* = 6.8 Hz, C*H*Me$_2$), 1.57 (br s, 1 H, N*H*), 1.43 (d, 3 H, *J* = 7.1 Hz, CH_3), 0.99 (d, 3 H, *J* = 6.8 Hz, CH_3), 0.77 (d, 3 H, *J* = 6.8 Hz, CH_3); IR (KBr) 3340, 2970, 2230, 1500, 1488, 1450, 1365, 1160, 1130, 1068, 798, 755, 710, 650, 605 cm^{-1}. Anal. Calcd for $C_{13}H_{18}N_2$: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.28; H, 8.95; N, 13.85. (*R**,*S**)-**1f**: colorless oil; HPLC analysis[17] (hexane/ethyl acetate, 9:1: 1 mL/min) t_R = 13.1 min; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.35–7.26 (m, 5 H, Ar H), 3.64 (q, 1 H, *J* = 7.2 Hz, NC*H*CN), 3.57 (d, 1 H, *J* = 6.4 Hz, PhC*H*N), 1.93 (octet, 1 H, *J* = 6.8 Hz, C*H*Me$_2$), 1.55 (br s, 1 H, N*H*), 1.41 (d, 3 H, *J* = 7.2 Hz, CH_3), 0.93 (d, 3 H, *J* = 6.8 Hz, CH_3), 0.75 (d, 3 H, *J* = 6.8 Hz, CH_3); IR (neat) 3330, 2970, 2240, 1450, 1375, 1155, 1130, 760, 710 cm^{-1}; high resolution mass spectrum calcd for $C_{13}H_{19}N_2$ (M + H) 203.1547, found 203.1580.

2-[(2,2-Dimethyl-1-phenylpropyl)amino]propanenitrile (1g). A 77:23 mixture of (*R**,*R**)-**1g** and (*R**,*S**)-**1g** was obtained in 98% yield as a colorless solid. These diastereomers were separated by HPLC[19] (hexane/ethyl acetate, 5:1). (*R**,*R**)-**1g**: colorless crystals; mp 79–80 °C (hexane); HPLC analysis[18] (hexane/ethyl acetate, 10:1; 1 mL/min) t_R = 6.1 min; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.32–7.25 (m, 5 H, Ar H), 3.65 (s, 1 H, PhC*H*N), 3.23 (br dq, 1 H, *J* = 6.2, 7.3 Hz, NC*H*CN, signal changed to a quartet, *J* = 7.3 Hz, on treatment with D_2O), 1.60 (br s, 1 H, N*H*), 1.44 (d, 3 H, *J* = 7.3 Hz, CHCH_3), 0.92 (s, 9 H, C(CH_3)$_3$); IR (KBr) 3320, 2980, 2230, 1490, 1450, 1145, 1068, 707 cm^{-1}. Anal. Calcd for $C_{14}H_{20}N_2$: C, 77.73; H, 9.31; N, 12.95. Found: C, 77.58; H, 9.37; N, 12.94. (*R**,*S**)-**1g**: colorless crystals; mp 41 °C (hexane); HPLC analysis[18] (hexane/ethyl acetate, 10:1; 1 mL/min) t_R = 8.4 min; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.35–7.25 (m, 5 H, Ar H), 3.56 (q, 1 H, *J* = 7.3 Hz, NC*H*CH$_3$), 3.42 (s, 1 H, PhC*H*N), 1.68 (br s, 1 H, N*H*), 1.33 (d, 3 H, *J* = 7.3 Hz, CHCH_3), 0.90 (s, 9 H, C(CH_3)$_3$); IR (KBr) 3370, 2950, 2220, 1475, 1450, 1360, 1145, 730, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95. Found: C, 77.69; H, 9.39; N, 12.94.

Similarly, (*R*,*R*)-**2g** was prepared from (*R*)-2,2-dimethyl-1-phenylpropylamine:[15] mp 99–101 °C (hexane); $[\alpha]^{20}_D$ +196.0 (*c* 1.00, $CHCl_3$).

2-[(1-Cyclohexylethyl)amino]propanenitrile (5). A 61:39 mixture of the two diastereomers was obtained in 82% yield as a colorless oil. The diastereomers were separated by preparative HPLC[19] (hexane/ethyl acetate, 5.7:1.0; refractive index detection). **5** (less polar; minor product): colorless crystals; mp 35 °C (hexane); ^1H NMR ($CDCl_3$, 270 MHz) δ 3.62 (q, 1 H, *J* = 6.9 Hz, NC*H*CN), 2.75 (dq, 1 H, *J* = 10.9, 6.6 Hz, NC*H*-c-hex), 1.78-1.51 (m, 6 H, c-hex-*H*), 1.47 (d, 3 H, *J* = 6.9 Hz, CH_3), 1.42–0.93 (m, 6 H, c-hex-*H* + N*H*), 1.05 (d, 3 H, *J* = 6.6 Hz, CH_3); IR (KBr) 3320, 2920, 2220, 1442, 1158, 1138, 1059, 800 cm^{-1}. Anal. Calcd for $C_{11}H_{20}N_2$: C, 73.28; H, 11.18; N, 15.53. Found: C, 73.38; H, 11.10; N, 15.54. **5** (polar; major product): colorless crystals; mp 49 °C (hexane); ^1H NMR ($CDCl_3$, 270 MHz) δ 3.68 (q, 1 H, *J* = 6.9 Hz, NC*H*CN), 2.75 (dq, 1 H, *J* = 6.3, 6.6 Hz, NC*H*-c-hex), 1.78–1.66 (m, 6 H, cyclohexyl-*H*), 1.49 (d, 3 H, *J* = 6.9 Hz, CH_3), 1.39–1.00 (m, 6 H, cyclohexyl-*H* + N*H*), 0.99 (d, 3 H, *J* = 6.6 Hz, CH_3); IR (KBr) 3320, 2930, 2220, 1445, 1380, 1133, 1053, 803 cm^{-1}. Anal. Calcd for $C_{11}H_{20}N_2$: C, 73.28; H, 11.18; N, 15.53. Found: C, 73.02; H, 11.04; N, 15.54.

2-[(1-Methyl-2-phenylethyl)amino]propanenitrile (6). A 59:41 mixture of the two diastereomers was obtained in 100% yield as a colorless oil. These diastereomers could not be separated by preparative HPLC. HPLC analysis[18] (hexane/ethyl acetate, 2:1; 1 mL/min) t_R = 11.6 min (major diastereomer) and 12.1 min (minor diastereomer); ^1H NMR (mixture of diastereomers) ($CDCl_3$, 500 MHz) δ 7.34–7.18 (m, 5 H, Ar H), 3.70 (q, 1 H × 0.59, *J* = 7.2 Hz, NC*H*CN), 3.56 (q, 1 H × 0.41, *J* = 7.2 Hz, NC*H*CN), 3.26 (ddq, 1 H × 0.59, *J* = 5.5, 8.8, 6.1 Hz, PhCH$_2$C*H*N), 3.18 (dq, 1 H × 0.41, *J* = 7.2, 6.0 Hz, PhCH$_2$C*H*N), 2.80 (dd, 1 H × 0.59, *J* = 5.5, 13.8 Hz, PhCH_2), 2.79 (dd, 1 H × 0.41, *J* = 5.8, 13.2 Hz, PhCH_2), 2.61 (dd, 1 H × 0.59, *J* = 8.8, 13.8 Hz, PhCH_2), 2.51 (dd, 1 H × 0.41, *J* = 7.2, 13.2 Hz, PhCH_2), 1.43 (d, 3 H × 0.41, *J* = 6.9 Hz, CH_3), 1.41 (d, 3 H, *J* = 7.2 Hz, CH_3), 1.23 (br s, 1 H, N*H*), 1.10 (d, 3 H, *J* = 6.1 Hz, CH_3); IR (neat) 3330, 2980, 2230, 1450, 1375, 1140, 800, 745, 705 cm^{-1}; high resolution mass spectrum calcd for $C_{12}H_{15}N_2$ (M) 187.1234, found 187.1258.

2-[(2,2-Dimethyl-1-phenylpropyl)amino]-3,3-dimethylbutanenitrile (1h). To a suspension of pivalaldehyde (344 mg, 4.00 mmol) in water (10 mL) were added $NaHSO_3$ (1.04 g, 10.0 mmol), KCN (650 mg, 10.0 mmol), and a solution of 2,2-dimethyl-1-phenylpropylamine (326 mg, 2.00 mmol) in MeOH (3 mL) under ice cooling. The mixture was refluxed with stirring for 17 h. The oil formed was extracted with CH_2Cl_2 (10 mL × 1, 5 mL × 2). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated. Flash chromatography on silica gel (hexane/ethyl acetate, 8:1) afforded a 90:10 mixture of (*R**,*R**)-**1h** and (*R**,*S**)-**1h** (394 mg, 79%) as a pale yellow solid. The diastereomers were separated by preparative HPLC[19] (hexane/ethyl acetate, 15:1). (*R**,*R**)-**1h**: colorless crystals; mp 66 °C (hexane); HPLC analysis[18] (hexane/ethyl acetate, 100:1; 1 mL/min) t_R = 7.4 min; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.31–7.28 (m, 5 H, Ar H), 3.61 (d, 1 H, *J* = 1.0 Hz, PhC*H*N), 2.84 (d, 1 H, *J* = 12.9 Hz, NC*H*CN), 1.61 (br d, 1 H, *J* = 12.9 Hz, N*H*), 1.04 (s, 9 H, (CH_3)$_3$), 0.92 (s, 9 H, (CH_3)$_3$); IR (KBr) 3380, 2950, 2220, 1475, 1450, 1390, 1360, 1110, 740, 700 cm^{-1}. Anal. Calcd for $C_{17}H_{26}N_2$: C, 79.02; H, 10.14; N, 10.84. Found: C, 79.06; H, 10.24; N, 10.81. (*R**,*S**)-**1h**: colorless crystals; mp 102 °C (hexane); HPLC analysis[18]

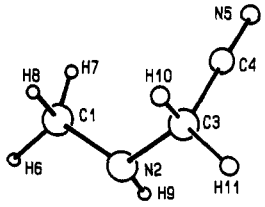

Figure 5. Structures and relative steric energies of **8a** and **8b**.

(hexane/ethyl acetate, 100:1; 1 mL/min) t_R = 16.7 min; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.37–7.21 (m, 5 H, Ar H), 3.32 (d, 1 H, J = 8.2 Hz, PhC*H*N), 2.99 (d, 1 H, J = 9.9 Hz, NC*H*CN), 1.67 (br t, 1 H, J = 9.6 Hz, N*H*), 1.05 (s, 9 H, (CH_3)$_3$), 0.91 (s, 9 H, (CH_3)$_3$); IR (KBr) 3340, 2950, 2220, 1475, 1390, 1360, 1110, 720, 700 cm^{-1}. Anal. Calcd for $C_{17}H_{26}N_2$: C, 79.02; H, 10.14; N, 10.84. Found: C, 79.20; H, 10.23; N, 10.84.

1,2,3,4-Tetrahydro-1-[(1-cyanoethyl)amino]naphthalene (7). To a solution of acetaldehyde (440 mg, 10.0 mmol) in water (10 mL) were added $NaHSO_3$ (1.04 g, 10 mmol), KCN (650 mg, 10.0 mmol), 1,2,3,4-tetrahydro-1-naphthylamine hydrochloride (367 mg, 2.00 mmol), $NaHCO_3$ (168 mg, 2.00 mmol), and methanol (2 mL) under ice cooling. The mixture was warmed to room temperature and was stirred for 4 h. The layers were separated and the oil formed was extracted with CH_2Cl_2 (20 mL). The aqueous layer, after addition of saturated aqueous $NaHCO_3$ (20 mL), was extracted with CH_2Cl_2 (10 mL × 2). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated. Flash chromatography (hexane/ethyl acetate, 6:1) afforded a 56:44 mixture of the two diastereomers (313 mg, 78%) as a colorless oil. The diastereomers were separated by preparative HPLC[19] (hexane/ethyl acetate, 5.7:1.0). **7** (major product): colorless crystals; mp 64 °C (hexane); HPLC analysis[18] (hexane/ethyl acetate, 5.7:1.0; 1 mL/min) t_R = 7.2 min; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.32–7.27 (m, 1 H, Ar H), 7.21–7.15 (m, 2 H, Ar H), 7.12–7.08 (m, 1 H, Ar H), 4.08 (t, 1 H, J = 3.6 Hz, ArC*H*N), 3.75 (q, 1 H, J = 6.9 Hz, NC*H*CN), 2.81 (dt, 1 H, J = 4.6, 16.5 Hz, ArCH_2), 2.72 (ddd, 1 H, J = 4.9, 9.2, 16.8 Hz, ArCH_2), 2.04–1.68 (m, 4 H, CH_2CH_2), 1.50 (d, 3 H, J = 6.9 Hz, CH_3), 1.27 (br s, 1 H, N*H*); IR (KBr) 3310, 2940, 2220, 1485, 1440, 1320, 1140, 1120, 1080, 1057, 810, 740 cm^{-1}. Anal. Calcd for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.98. Found: C, 78.06; H, 8.08; N, 13.98. **7** (minor product): a colorless oil; HPLC analysis[18] (hexane/ethyl acetate, 5.7:1.0; 1 mL/min) t_R = 8.2 min; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.31–7.28 (m, 1 H, Ar*H*), 7.22–7.09 (m, 3 H, Ar*H*), 3.98 (t, 1 H, J = 3.6 Hz, ArC*H*N), 3.65 (q, 1 H, J = 6.9 Hz, NC*H*CN), 2.86 (dt, 1 H, J = 16.5, 4.9 Hz, ArCH_2), 2.74 (dt, 1 H, J = 16.8, 8.2 Hz, ArCH_2), 2.14–1.71 (m, 4 H, CH_2CH_2), 1.48 (d, 3 H, J = 6.9 Hz, CH_3); IR (neat) 3330, 2940, 2220, 1488, 1445, 1150, 1010, 1060, 743 cm^{-1}; high resolution mass spectrum calcd for $C_{13}H_{15}N_2$ (M - H) 199.1234, found 199.1246.

Determination of Equilibrium Ratio of 1. Individual samples (10.0 mg) of (*R**,*R**)-**1** and (*R**,*S**)-**1**, obtained by preparative HPLC of **1a**, **1c**, **1e**, **1f**, **1g**, and **1h**, were dissolved in MeOH (0.5 mL) and heated at 80 °C in a sealed tube, until the diastereomeric ratio in each tube showed, by HPLC analysis, a stable value. The methanol was evaporated, and the sample was redissolved in $CDCl_3$. The final ratio was determined by ^{1}H NMR spectroscopy (500 or 270 MHz). When two diastereomers could not be separated, e.g., **1b** and **1d**, the ratio was determined by ^{1}H NMR spectroscopy after heating the isomeric mixtures (10.0 mg) in MeOH (0.5 mL) for 3 h. During evaporation of the solvent, the ratio of (*R**,*R**)-**1g** relative to (*R**,*S**)-**1g** increased because of preferential crystallization of (*R**,*R**)-**1g** and epimerization of (*R**,*S**)-**1g**. In this case, the ratio was determined from the ^{1}H NMR spectrum of the mixture in CD_3OD after 3 h of heating.

AM1 Calculation. The calculation for $MeNHCH_2CN$ was carried out with MOPAC Ver. 3.10 programs by J. J. P. Stewart.[20] The optimized structure is shown in Figure 5. Its Cartesian coordinates are in the supplementary section (Table II).

MM2 Calculations. The calculations were carried out with MM2(77).[21] The framework (C_{sp^3} - HN_{sp^3} - C_{sp^3} - C_{sp}) of **1** was fixed at the coordinates that were obtained for $MeNHCH_2CN$ by AM1 calculation. For the parameters of the lone pair on nitrogen, those of α-alkoxy nitriles[8] were used (see text).

X-ray Crystallography. The computer program UNICS III[22] PRG. MULTAN 80,[23] run on a HITACHI M680 computer at Tokyo University, was employed. The crystallographic data for (*R**,*R**)-**1c** and (*R*,*R*)-**1g** are in the supplementary section.

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Supplementary Material Available: Cartesian coordinates obtained for $MeNHCH_2CN$ by AM1 calculation (Table II), crystal data and experimental parameters for (*R**,*R**)-**1c** and (*R*,*R*)-**1g** (Table III), atomic parameters, bond distances and angles, and dihedral angles of (*R**,*R**)-**1c** (Tables IV–VII), atomic parameters, bond distances and angles, and dihedral angles of (*R*,*R*)-**1g** (Tables VIII–XI), and ^{1}H NMR spectra of **1d**, **1f**, **6**, and **7** (25 pages). Ordering information is given on any current masthead page.

(20) Revised by T. Hirano, University of Tokyo, for NEC PC machines.

(21) MM2(77) is the NEC PC version of QCMP004, converted by E. Ōsawa.

(22) Sakurai, T.; Kobayashi, K. *Rep. Inst. Phys. Chem. Res.* **1979**, *55*, 69.

(23) The following programs were modified: Main, P.; Woolfson, M. M.; Germain, G. LSAM "A System of Computer Programmers for the Automatic Solution of Centrosymmetric Crystal Structures;" University of York, York, England and Universite de Louvain, Louvain, Belgium, 1972. Main, P.; Woolfson, M. M.; German, G. MULTAN "A Computer Programmers for the Automatic Solution of Crystal Structure," University of York, York, England and Universite de Louvain, Louvain, Belgium, 1971. See also: Furusaki, A. *Acta Crystallogr., A* **1979**, *35*, 220.