

CH/π Interaction on the Structure of *N*-Substituted-4-phenyltetrahydroisoquinoline Derivatives

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Rotational barriers about the C–N bonds and differences of ground state energies of *tert*-butyl 4-phenyltetrahydroisoquinoline-2-carboxylate derivatives were determined by NMR spectroscopy. The results are discussed assuming characteristic intramolecular CH/π interactions accompanied by results of X-ray structure analysis, ab initio MO, and DFT calculations. The calculated values with MP2/6-31G(d,p) level are in good agreement with the experimental results of X-ray structure analysis and NMR measurements.

Non-covalent interactions have been known to play important roles in understanding conformational preferences and behaviors of organic molecules. These interactions are very often attractive but far weaker than those of covalent bonds. Among weak attractive forces, the hydrogen bond[1] is one of the most significant.

An ordinary hydrogen bond, i.e., X–H···Y, is an interaction working between hard acid (XH) and hard base (Y), while a hydrogen bond such as CH/π interaction[2] can be regarded as weak interaction, which occurs between a soft acid (CH) and soft base (π-system). The enthalpy of CH/π interaction has been estimated by NMR to be at most 9 kJ mol^{-1} for intermolecular interacting CH-donor/aromatic π-base systems.[3] Although the CH/π interaction is weak, it can sometimes play an important role because many CH groups can participate simultaneously without considerable loss of entropy. Similarly, intramolecular CH/π interaction often affects conformational properties because it can interact without a large loss of entropy. Therefore the CH/π interaction is important factor in the fine tuning of organic and biochemical reactions and molecular recognition. Previously, we reported the CH/π interaction in determining the conformation of aromatic amides and ketones by spectroscopy,[4] and the crystal packing of clathrates,[5] the relative stability of diastereomeric salts[6] by using a crystallographic database (CSD), and the conformation of alcohols,[7] the diastereofacial selectivity in a reaction of chiral acyclic ketones[8] by ab initio MO calculation. Furthermore, high-level ab initio MO calculations supported the concept.[9]

On the other hand, dynamic nuclear magnetic resonance spectroscopy has supplied much useful information on the dynamic behaviors of molecules. Amides and related nitrogen compounds have been most extensively investigated by this method because their NMR spectra show coalescence phenomena near ambient temperature.[10–13] Rotational barriers about the C–N bonds of the amides are directly related to the partial double bond character. Therefore, these potential energy barriers are affected very sensitively by the conjugative properties of their hydrocarbon moieties with the carbonyl group. Previously we reported the rotational barriers about the C–N bonds of several arenecarboxamides[14,15] and *N*-acyl-*N*-alkylamino acids.[16]

During the course of a synthetic investigation of (6*S**,10b*R**)-6-phenyl-1,2,3,5,6,10b-hexahydrobenzo[*g*]indolidine,[17] we encountered an interesting structure of *tert*-butyl *trans*-1-allyl-4-phenyl-1,2,3,4-tetrahydroisoquinoline-2-carboxylate (***trans*-1**). Namely, an *N*-Boc group is directed to a phenyl group on C-4 of an isoquinoline ring and one of the methyl groups on *tert*-butyl is as close as possible to interact with the phenyl group by CH/π interaction. (Figure 1)

We then prepared some analogs of ***trans*-1** (X = allyl, Y = Ph, R = O^{t}Bu), ***trans*-1′** (X = allyl, Y = Ph, R = CH$_2$^{t}Bu), ***trans*-2** (X = allyl, Y = Ph, R = O^{i}Pr), ***trans*-3**[17] (X = allyl, Y = Ph, R = OEt), ***cis*-1**[17] (X = allyl, Y = Ph, R = O^{t}Bu), ***cis*-3**[17] (X = allyl, Y = Ph, R = OEt), **4** (X = H, Y = Ph, R = O^{t}Bu), **4′** (X = H, Y = Ph, R = CH$_2$^{t}Bu), **5** (X = H, Y = Ph, R = O^{i}Pr), **6** (X = H, Y = Ph, R = OEt), **6′** (X = H, Y = Ph, R = CH$_2$Et), **7** (X = H, Y = H, R = O^{t}Bu), and **7′** (X = H, Y = H, R = CH$_2$^{t}Bu) (Table 1), and measured the rotational barriers about their C–N bonds by NMR in order to clarify the effect of CH/π interaction on conformations of those compounds. Furthermore, we carried out quantum chemical calculations of these conformations.

Results and Discussion

In order to investigate the effect of CH/π interaction on the conformational preference and on the rotational barrier heights of *N*-substituted-4-phenyltetrahydroisoquinoline derivatives, their dynamic behaviors were examined by NMR. Changes in relative energies and structures during the process of rotation about the C–N bond of those compounds are illustrated in Figure 1. The rotational barriers ($\Delta G^{\ddagger}$), the conformational free

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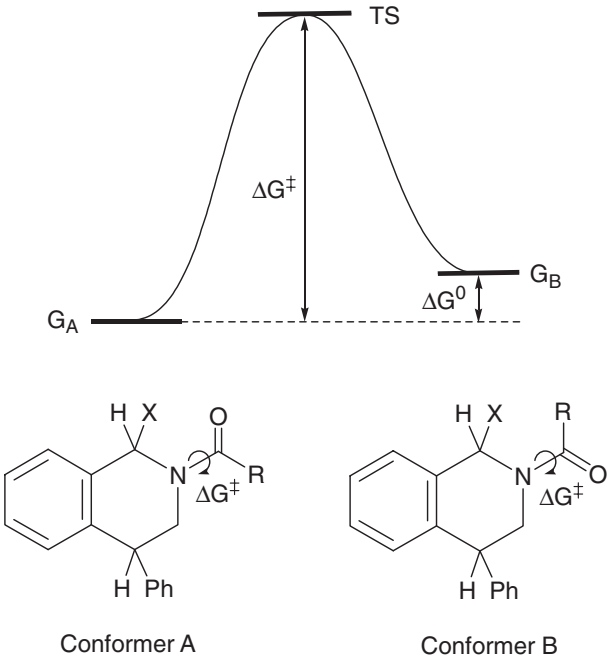


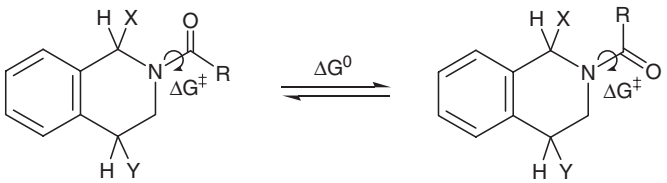
Figure 1. The rotational barrier and the conformational-energy difference between the conformers of *N*-substituted-4-phenyltetrahydroisoquinolines.

energy differences (ΔG^0) between the conformers about the C–N bond, the conformational population (P_A and P_B), and ^{1}H chemical shift (δ_A and δ_B) of R in *N*-COR are given in Table 1.

Effect of CH/π Interaction on ΔG^0. In a series of alkyl *trans*-1-allyl-4-phenyl-1,2,3,4-tetrahydroisoquinoline-2-carboxylate (***trans*-1**, **-2**, and **-3**), ^{1}H NMR signals (δ_A and δ_B) of the two conformers in ground state were observed unequivocally at room temperature. Conformer A is more stable than conformer B (about 2.5 kJ mol^{-1}) in the ground state (Table 1). The CH/π interaction between CH(CH_3) in *N*-COR and phenyl substituent of the isoquinoline ring is illustrated in Figure 2a. The CH/π interaction is assumed to stabilize conformer A, and the value of ΔG^0 is the same without regard to R (***trans*-1**, **-2**, and **-3**). In the case of ***trans*-1′**, ΔG^0 became larger (4.5 kJ mol^{-1}) than that of ***trans*-1** because CH/π interaction occurred between the 4-phenyl ring and CH_3 in ^{t}Bu as well as CH_2 in *N*-$COCH_2{}^t$Bu as shown in Figure 2b.

The CH/π interaction is supported also by chemical shifts; the ^{1}H chemical shift of CH_3 of R in conformer A revealed high-field shift of 0.30, 0.37, and 0.44 ppm corresponding to R = O^{t}Bu, O^{i}Pr, and OEt for ***trans*-1**, **-2**, and **-3**, respectively. These characteristic phenomena should originate from the phenyl ring magnetic anisotropy (π), which was not observed in conformer B. The high-field shift was more obvious for CH_2 in *N*-$COCH_2{}^t$Bu, that is, δ_A (δ in conformer A) was 1.36 ppm and δ_B (δ in conformer B) was 2.23 ppm. It meant that the CH/π interaction between CH in CH_2 of *N*-$COCH_2{}^t$Bu and the

Table 1. The Rotational Barrier ($\Delta G^‡$), the Conformational Free Energy Difference (ΔG^0), the Conformational Population (P), and ^{1}H Chemical Shift (δ) of *N*-Substituted-4-phenyltetrahydroisoquinolines in $CDCl_3$



Conformer A Conformer B

Compd.	X	Y	R	$\Delta G^‡$ /kJ mol^{-1}	ΔG^0 /kJ mol^{-1}	P_A /%	P_B /%	δ_A	δ_B	Obsd. ^{1}H (R)
***trans*-1**	allyl	Ph	O^{t}Bu	64.4	2.5	75	25	1.06	1.36	*Me* (^{t}Bu)
***trans*-1′**	allyl	Ph	$CH_2{}^t$Bu	73.5	4.5	88	12	0.76	1.00	*Me* (^{t}Bu)
								1.36	2.23	*CH_2*-^{t}Bu
***trans*-2**	allyl	Ph	O^{i}Pr	65.0	2.5	75	25	0.76	1.13	*Me* (^{i}Pr)
***trans*-3**	allyl	Ph	OEt	65.3	2.5	75	25	0.75	1.19	*Me* (Et)
***cis*-1**	allyl	Ph	O^{t}Bu	68.9	0	50	50	1.48		*Me* (^{t}Bu)
***cis*-3**	allyl	Ph	OEt	68.4	0	50	50	1.28		*Me* (Et)
4	H	Ph	O^{t}Bu	63.9	1.6	67	33	1.21	1.45	*Me* (^{t}Bu)
4′	H	Ph	$CH_2{}^t$Bu	72.5	1.9	70	30	0.93	1.01	*Me* (^{t}Bu)
								1.83	2.34	*CH_2*-^{t}Bu
5	H	Ph	O^{i}Pr	62.7	1.2	63	37	1.02	1.27	*Me* (^{i}Pr)
6	H	Ph	OEt	64.2	0.8	59	41	1.01	1.27	*Me* (Et)
6′[a)]	H	Ph	CH_2Et	72.6	1.9	70	30	0.66	0.86	*Me* (Et)
								2.22	2.90	*CH_2*-Et
7	H	H	O^{t}Bu	61.0	0	50	50	1.49		*Me* (^{t}Bu)
7′	H	H	$CH_2{}^t$Bu	70.5	0	50	50	1.08		*Me* (^{t}Bu)
								2.34		*CH_2*-^{t}Bu

a) Solvent: DMSO-d_6.

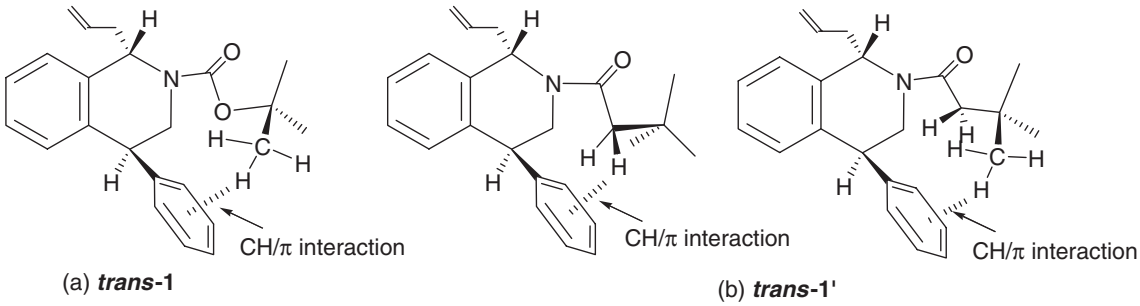


Figure 2. CH/π interactions in (a) ***trans*-1** and (b) ***trans*-1′**.

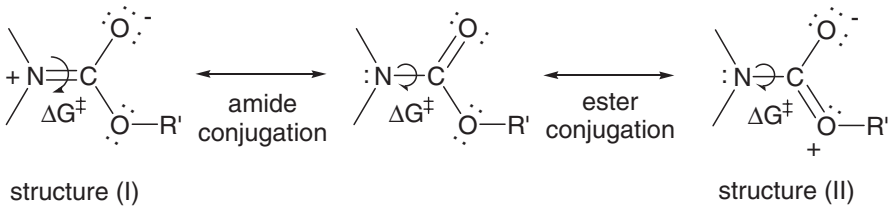


Figure 3. Cross conjugation in urethane.

4-phenyl ring was rather strong in conformer A of ***trans*-1′**. On the other hand, ^{1}H NMR signals of the two ground state conformers in ***cis*-1** and **-3** were observed equivalently ($\delta_A = \delta_B$). In *cis*-form, the two ground state energies are almost the same ($G_A = G_B$) and the stabilization by CH/π interaction in conformer A was not observed because CH(CH_3) in R could not be directed to and close to the phenyl ring due to the steric hindrance of the *cis*-1-allyl substituent. In the series of *N*-substituted-4-phenyl-1,2,3,4-tetrahydroisoquinoline **4**, **4′**, **5**, and **6**, with no substituent at C-2 of the isoquinoline ring, the predominant conformers were stabilized by 1.6 (R = O^{t}Bu), 1.9 (R = $CH_2{}^t$Bu), 1.2 (R = O^{i}Pr), and 0.8 (R = OEt) kJ mol^{-1} compared to the other conformer, respectively. All these results are explained similarly as in the case of ***trans*-1** by assuming CH/π interaction between CH(CH_3) in *N*-COR and 4-phenyl ring. High-field shift of CH_3 of R was also observed in those compounds. However, the strength of CH/π interaction in those compounds seemed to be weaker than those of ***trans*-1**, **-1′**, **-2**, and **-3** because values of both the differences of the ground state energies of the two conformers and high-field shifts were not as large as those of ***trans*-1**, **-1′**, **-2**, and **-3**.

Effect of Steric Hindrance on $\Delta G^{\ddagger}$. Since the rotational barrier was estimated as the energy difference between the more stable conformer A and the transition state (TS), steric effects on $\Delta G^{\ddagger}$ should originate from the steric congestion in the more stable conformer A. As the rotational barriers of ***cis*-1** and **-3** were higher by 5.0–4.2 kJ mol^{-1} than those of **4** and **6**, the transition state of ***cis*-1** and **-3** were labilized by steric hindrance of the *cis*-1-allyl substituent on the C–N bond rotation.

Effect of Resonance on $\Delta G^{\ddagger}$. Cross conjugation between amide and ester was permitted in compounds having urethane moiety, as shown in Figure 3. The relatively high rotational barrier in amides comes from the partial double bond character of the C–N bond due to the mesomeric contribution of the dipolar canonical structure (I).[18] As the structure (II) by ester conjugation has no influence on the rotational barrier about the C–N bond, the rotational barrier about the C–N bond becomes lower in urethane compared with the corresponding amide. Consequently, the rotational barriers of the *N*-COO^{t}Bu series (***trans*-1**, **-4**, and **-7**) were lower by about 9 kJ mol^{-1} than those of the corresponding *N*-COCH$_2{}^t$Bu series (***trans*-1′**, **-4′**, and **-7′**). The lowering of $\Delta G^{\ddagger}$ implies a decrease of the contribution of structure (I) in the amide conjugation.

CH/π Interaction as Evidenced Using X-ray Crystallographic Analysis. Crystal structures of ***trans*-1** and **4** are given in Figures 4 and 5. Hydrogen atoms of molecule **4** were located from difference Fourier maps and refined isotropically. Generally, the positions of hydrogen atoms obtained from neutron diffraction are more reliable than those from X-ray diffraction. However, it is assumed that the parameters of hydrogen atoms obtained from X-ray analysis can be equivalent to those from neutron data.[19] As is easily understood from Figures 4 and 5, the short CH–π(C(sp^2)) hydrogen bonds were observed in short intramolecular through space distances; 2.8813(18) and 2.9390(17) Å in ***trans*-1**, and 3.02(3) and 3.05(3) Å in **4** between the proton of CH donor group (^{t}Bu) and C(sp^2) (4-phenyl ring), in addition, 2.8277(16) Å in ***trans*-1** between CH (*cis*-1-allyl substituent) and C(sp^2) (isoquinoline) (Figure 4). As the difference of the intramolecular distance and a number of CH–π hydrogen bonds may relate to each ΔG^0, the stabilization of ***trans*-1** ($\Delta G^0 = 2.5$ kJ mol^{-1}) by CH/π interaction is larger than that of **4** ($\Delta G^0 = 1.6$ kJ mol^{-1}).

CH/π Interaction as Evidenced Using Ab Intio MO and DFT Calculations. At first, we carried out a full geometry optimization for the isolated ***trans*-1** and **4** molecules using MP2 (second-order Møller–Plesset perturbation) (Figures 6 and 7) in comparison with the experimental values as shown in Figures 4 and 5.

As seen by comparing the experimental data to the theoretical results at MP2/6-31G(d,p) level, the optimized CH/π hydrogen bond distances were in good agreement with experimental values of the crystalline state. However, there was a considerable difference in the optimized CH/π

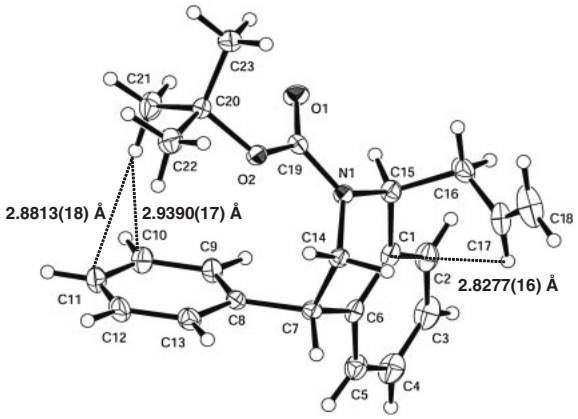


Figure 4. ORTEP drawing of ***trans*-1** with thermal ellipsoids drawn at the 30% probability level. Selected C···H distances are shown in the Figure and values in parentheses are estimated standard deviations.

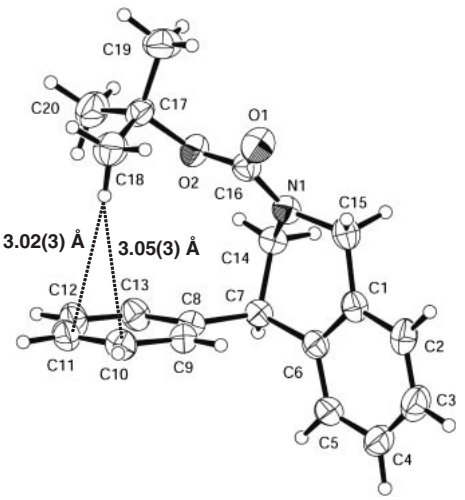


Figure 5. ORTEP drawing of **4** with thermal ellipsoids drawn at the 30% probability level. Selected C···H distances are shown in the Figure and values in parentheses are estimated standard deviations.

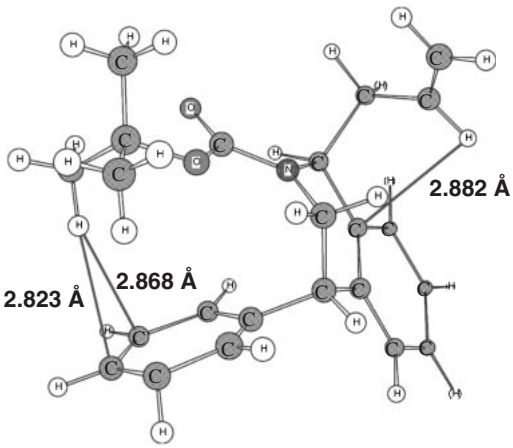


Figure 6. Optimized molecular structure of ***trans*-1** at MP2/6-31G(d,p) level.

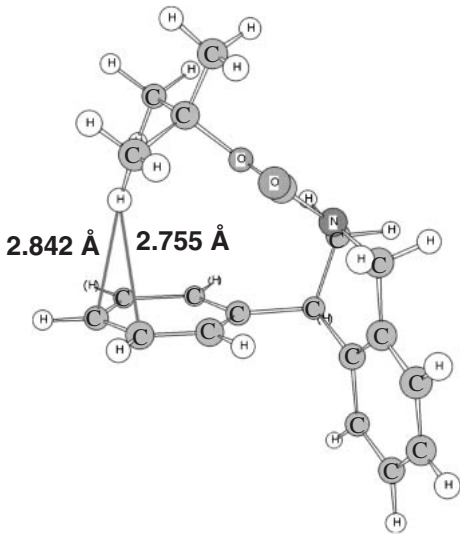


Figure 7. Optimized molecular structure of **4** at MP2/6-31G(d,p) level.

hydrogen bonds distances at HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels. These optimized CH/π hydrogen bonds distances were 4.056 and 3.758 Å in ***trans*-1**, and 4.253 and 3.881 Å in **4** at HF/6-311++G(d,p) level, and 4.045 and 3.739 Å in ***trans*-1**, and 4.196 and 3.772 Å in **4** at B3LYP/6-311++G(d,p) level. Thus, these methods are inappropriate for calculating the weak interactions such as CH/π hydrogen bonds in this paper. Weak intermolecular and intramolecular interactions such as the dispersion force and CH/π interaction cannot be precisely estimated by Hartree–Fock and density functional methods. Therefore, these computational results except Møller–Plesset perturbation bear poor implication in the field.

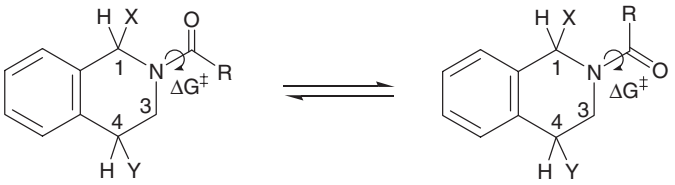
Conclusion

Both the effect of CH/π interaction on the conformational preference and the conformational free energy differences and the effect of resonance on the rotational barrier heights of *N*-substituted-4-phenyltetrahydroisoquinoline derivatives were estimated by NMR. The short CH/π hydrogen bond distances were observed in ***trans*-1** and **4** between the proton of CH donor (^{t}Bu) and C(sp^2) (4-phenyl ring) from X-ray structure analysis, and the experimental values were in good agreement with the theoretical results at MP2/6-31G(d,p) level, the optimized CH/π hydrogen bond distances.

Experimental

Materials. *tert*-Butyl *trans*-1-allyl-4-phenyl-1,2,3,4-tetrahydroisoquinoline-2-carboxylate (***trans*-1**), ethyl *trans*-1-allyl-4-phenyl-1,2,3,4-tetrahydroisoquinoline-2-carboxylate (***trans*-3**), *tert*-butyl *cis*-1-allyl-4-phenyl-1,2,3,4-tetrahydroisoquinoline-2-carboxylate (***cis*-1**), and ethyl *cis*-1-allyl-4-phenyl-1,2,3,4-tetrahydroisoquinoline-2-carboxylate (***cis*-3**) were prepared according to a reported method.[17] Isopropyl *trans*-1-allyl-4-phenyl-1,2,3,4-tetrahydroisoquinoline-2-carboxylate (***trans*-2**) was also prepared in a similar manner using isopropyl

Table 2. The Line-Shape-Analysis Parameters for Determining the Rotational Barrier ($\Delta G^{\ddagger}$) and the Calculated $\Delta G^{\ddagger}_{T_c}$ Values of *N*-Substituted-4-phenyltetrahydroisoquinolines in $CDCl_3$



Conformer A ⇌ Conformer B

Compd.	X	Y	R	P_A /%	P_B /%	$\Delta\nu$ /Hz	k /s^{-1}	T_c /°C	$\Delta G^{\ddagger}_{T_c}$ /kJ mol^{-1}	Obsd. ^1H
***trans*-1**	allyl	Ph	O^{t}Bu	75	25	51.3	99.5	37.7	64.4	1-H
***trans*-1′** [a]	allyl	Ph	$CH_2{}^t$Bu	88	12	12.2	22.2	60.8	73.5	1-H
***trans*-2**	allyl	Ph	O^{i}Pr	75	25	44.6	87.8	39.7	65.0	1-H
***trans*-3**	allyl	Ph	OEt	75	25	43.2	84.0	39.8	65.3	1-H
***cis*-1**	allyl	Ph	O^{t}Bu	50	50	46.0	99.5	58.8	68.9	1-H
***cis*-3**	allyl	Ph	OEt	50	50	35.7	77.1	53.0	68.4	1-H
4	H	Ph	O^{t}Bu	67	33	66.0	64.3	30.2	63.9	*Me* (^{t}Bu)
4′	H	Ph	$CH_2{}^t$Bu	70	30	22.0	18.3	54.0	72.5	*Me* (^{t}Bu)
5	H	Ph	O^{i}Pr	63	37	62.4	122.6	32.5	62.7	3-H
6	H	Ph	OEt	59	41	69.7	94.8	36.3	64.2	*Me* (Et)
6′ [a]	H	Ph	CH_2Et	70	30	41.6	35.0	61.7	72.6	4-H
7	H	H	O^{t}Bu	50	50	11.7	25.0	5.8	60.7	3-H
7′	H	H	$CH_2{}^t$Bu	50	50	12.0	25.7	49.5	70.5	4-H

a) Solvent: DMSO-d_6.

chloroformate. *tert*-Butyl 4-phenyl-1,2,3,4-tetrahydroisoquinoline-2-carboxylate (**4**), isopropyl 4-phenyl-1,2,3,4-tetrahydroisoquinoline-2-carboxylate (**5**), ethyl 4-phenyl-1,2,3,4-tetrahydroisoquinoline-2-carboxylate (**6**), and *tert*-butyl 1,2,3,4-tetrahydroisoquinoline-2-carboxylate (**7**) were prepared in a similar manner described above starting from 4-phenyl-1,2,3,4-tetrahydroisoquinoline[20] or commercially available 1,2,3,4-tetrahydroisoquinoline. *trans*-1-Allyl-2-(3,3-dimethylbutanoyl)-4-phenyl-1,2,3,4-tetrahydroisoquinoline (***trans*-1′**), 2-(3,3-dimethylbutanoyl)-4-phenyl-1,2,3,4-tetrahydroisoquinoline (**4′**), 2-butanoyl-4-phenyl-1,2,3,4-tetrahydroisoquinoline (**6′**), and 2-(3,3-dimethylbutanoyl)-1,2,3,4-tetrahydroisoquinoline (**7′**) were prepared by a reaction of the corresponding amines and 3,3-dimethylbutanoyl chloride (***trans*-1′**, **4′**, and **7′**) or butanoyl chloride (**6′**) in the presence of pyridine in a usual manner. In every case, the resulting crude product was purified by silica gel column chromatography or recrystallization, and the purified compound showed satisfactory NMR and IR spectra.

NMR Measurements. Variable-temperature NMR measurements were carried out by using a JEOL EX-270 NMR spectrometer. The value of ΔG^0 was calculated by the equations, $\Delta G^0 = -RT\ln K$, $K = P_B/P_A = \exp\{-\Delta G^0/RT\}$ at room temperature where P_A and P_B are the conformational population for conformer A and B, respectively. The peaks A and B in ^1H NMR spectra were separated at room temperature in most of the compounds. We adopted the coalescence temperature in order to determine $\Delta G^{\ddagger}_{T_c}$ values by using both temperature-dependant NMR experiments and computer simulation. This method requires the following parameters; T_c (the coalescence temperature), k (the rate of exchange between conformer A and B), $\Delta\nu$ in Hz (the difference in chemical shifts between the same proton of the two conformers). The coalescence temperature (T_c) was the temperature where two proton peaks of conformer A and B just coalesced to one peak, and was determined by measuring at several temperatures from low to high beyond T_c. The difference in chemical shifts ($\Delta\nu$ in Hz) was measured at low enough temperature where the conformer A and B exchanged very slowly. The rate of exchange between conformers (k) was computed by the simulation of NMR peak line shapes near T_c using DNMR3K (General NMR Line-Shape Program)[21] which needed $\Delta\nu$ in Hz and the population of two site protons (P_A and P_B). The value of $\Delta G^{\ddagger}_{T_c}$ was calculated by the equations, $\Delta G^{\ddagger}_{T_c} = -2.303RT_c\{10.32 + \log(T_c/k)\}$ at T_c. These parameters and the determined $\Delta G^{\ddagger}_{T_c}$ values are listed in Table 2.

Experimental Procedure for X-ray Crystallography. Crystallographic data of ***trans*-1** was already reported.[17] Suitable single crystal **4** was obtained by recrystallization from hexane and mounted on a glass fiber. Diffraction measurement of **4** was made on a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Cu Kα radiation ($\lambda = 1.54187$ Å). The data collections were carried out at 23 ± 2 °C to a maximum 2θ value of 136.5°. Indexing was performed from 3 oscillations that were exposed for 90 s. The crystal-to-detector distance was 127.40 mm. A total of 24 oscillation images were collected. A sweep of data was done using ω scans from 50.0 to 230.0° in 30.0° steps, at $\chi = 45.0°$ and $\phi = 0.0°$. The exposure rate was 90.0 [s/°]. A second sweep was performed using ω scans from 50.0 to 230.0° in 30.0° steps, at $\chi = 45.0°$ and $\phi = 90.0°$. The exposure rate was 90.0 [s/°]. Another sweep was performed using ω scans from 50.0 to 230.0° in 30.0° steps, at $\chi = 45.0°$ and $\phi = 180.0°$. The exposure rate was 90.0 [s/°]. Another sweep was performed using ω scans from 50.0 to 230.0° in 30.0° steps, at $\chi = 45.0°$

Table 3. Summary of Crystal Data for Compound **4**

Empirical formula	$C_{20}H_{23}NO_2$
Formula weight	309.41
Crystal color, habit	colorless, needle
Crystal size/mm^3	$0.55 \times 0.33 \times 0.25$
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
Lattice parameters	
a/Å	11.6624(17)
b/Å	25.017(4)
c/Å	6.1138(9)
β/°	102.713(13)
V/Å^3	1740.0(4)
Z	4
D_{calcd}/g cm^{-3}	1.181
F_{000}	664.00
μ(Cu Kα)/cm^{-1}	5.972
Reflections measured	9381
Independent reflections (R_{int})	2954 (0.050)
No. variables	300
Reflection/parameter ratio	9.82
Residuals: R; $wR2$ (All reflections)	0.0732; 0.1085
Residuals: $R1$ ($I > 2.0\sigma$ (I))	0.0457
No. of reflections to calc R, $R1$	2945, 1465
Goodness of fit Indicator	1.015
$\delta\rho_{max,\ min}$/e Å^{-3}	0.19, −0.33

and $\phi = 270.0°$. The exposure rate was 90.0 [s/°]. Readout was performed in the 0.100 mm pixel mode.

Crystallographic data and the results of measurements are summarized in Table 3. The structures were solved by direct methods (SIR 97),[22] and expanded using Fourier techniques.[22] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference Fourier maps and isotropically refined. All calculations were performed using the Crystal Structure crystallographic software package.[24,25]

Atomic coordinates, thermal parameters, and bond lengths and distances in CIF format have been deposited with Cambridge Crystallographic Data Center: Deposition number CCDC-744678 for compound **4**. Copies of the data can be obtained free of charge via http//www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Computational Method. The ab initio calculations were carried out with the Gaussian 03[26] program package. The basis sets implemented in the program were employed without modification. The geometry of ***trans*-1** and **4** were fully optimized without symmetry constraints by energy gradient method. All optimized geometries were obtained by using the HF (Hartree–Fock), MP2 (second-order Møller–Plesset perturbation) and the Becke 3LYP (B3LYP) hybrid density functional with the 6-311++G(d,p) and 6-31G(d,p). Vibrational frequencies were calculated by using the analytical second derivatives at the HF/6-311++G(d,p), the MP2/6-31G(d,p) and the B3LYP/6-311++G(d,p) levels to confirm the stationary structures.

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