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Conformational Studies by Dynamic NMR. 95.[1] Rotation around the Adamantyl−Alkyl Bond. Remote Substituent Effect on Conformational Equilibrium

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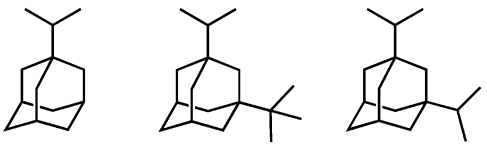
Restricted rotation has been observed by NMR spectroscopy at very low temperature in isopropyladamantane, 1-*tert*-butyl-3-isopropyladamantane, and 1,3-diisopropyladamantane. The barriers for the corresponding dynamic processes were also determined. In the case of the disubstituted adamantane derivatives, two and four conformers, respectively, were observed and they were assigned on the basis of the symmetry properties. The relative populations deviate from the statistical distribution.

Introduction

In contrast to rotation of a *tert*-butyl group as in **1**, which has been much studied,[2,3] rotation of an adamantyl group, its more rigid analogue **2**, has received little attention. Two pairs of relatively simple compounds, **1a**, **2a** and **1b**, **2b**, have been reported,[4a] and the adamantyl rotation barriers are about 1 kcal mol^{-1} lower than the corresponding *tert*-butyl barrier. More highly substituted molecules show less clear-cut effects.[4b,4c] We now want to consider studies of some further compounds, the isopropyladamantanes **3**−**5**, and to report how a substituent R in the relative 3-position in adamantane, that is, beyond the distance where it repels the isopropyl substituent, nonetheless perturbs its rotational equilibrium.

1a, 2a X = Y = Me, Z = Cl
1b, 2b X = *t*-Bu, Y = Me, Z = Cl



Results

Isopropyladamantane (3). The ^{1}H NMR spectrum of **3** at ambient temperature is essentially unchanged down to −100 °C, indicating fast isopropyl rotation on the NMR time scale. Below this temperature, the signal of the six equivalent hydrogens of the three CH_2 groups next to the isopropyl substituent broadens considerably and eventually splits into three sets of signals of equal intensity, as indicated in the spectrum at −166 °C (Figure 1, bottom).

Isopropyl−adamantyl bond rotation is slow, so there are three degenerate staggered conformations (Scheme 1) with two different kinds of methylene groups. The group *anti* to the isopropyl methine hydrogen has identical enantiotopic protons H_C and appears as a broad singlet at $\delta = 1.70$, while the two methylene groups *gauche* to the methine hydrogen are equivalent and have diastereotopic protons, see H_A and H_B in Scheme 1, and

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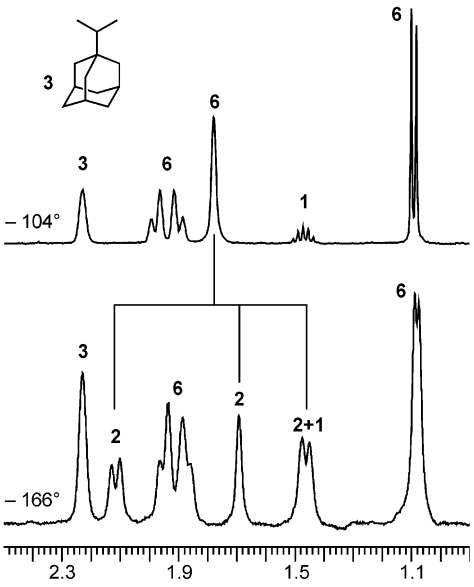
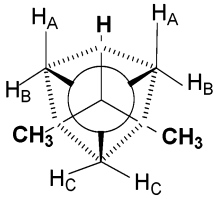


FIGURE 1. ^{1}H NMR spectrum (400 MHz) of compound **3** (in $CHF_2Cl/CHFCl_2$, 4:1 v/ v) obtained at −104 °C (top) and at −166 °C (bottom). The numbers indicate how many hydrogens correspond to the various signals. The single signal for the six methylene hydrogens (δ = 1.75) next to the isopropyl substituent splits into three signals (each corresponding to two hydrogens) below −150 °C (see the text).

SCHEME 1



appear as an AB-quartet J = −11.5 Hz at δ = 2.13 and 1.48 (the latter signal overlaps, in part, with the CH isopropyl signal at δ = 1.46). None of the other signals shows effects of this dynamic process, and in particular, the two methyl groups of the isopropyl substituent remain enantiotopic, appearing as a doublet (due to coupling with the isopropyl methine hydrogen).

Computer line shape simulation in the temperature range −127 to −150 °C provides a number of rate constants leading to a $\Delta G^{\ddagger}$ value of 6.1 ± 0.15 kcal mol^{-1}. As often observed in conformational processes, the free energy of activation is independent of temperature within the experimental uncertainty, indicating a negligible $\Delta S^{\ddagger}$.

1-*tert*-Butyl-3-isopropyladamantane (4). Introduction of a second substituent, such as a *tert*-butyl group, in the framework of isopropyladamantane **3** reduces the molecular symmetry, producing more than one type of conformer in the resulting derivative **4**, when isopropyl rotation is rendered slow on the NMR time scale. The corresponding rotation of the 3-fold symmetric *tert*-butyl group, even when slow, does not affect the overall symmetry of the molecule on the NMR time scale, but this rotation can be detected by dynamic NMR, since the isopropyl substituent itself desymmetrizes the otherwise symmetrical adamantyl group.

In the ^{13}C NMR spectrum of **4** the single line for the three methyls of the *tert*-butyl group broadens on cooling

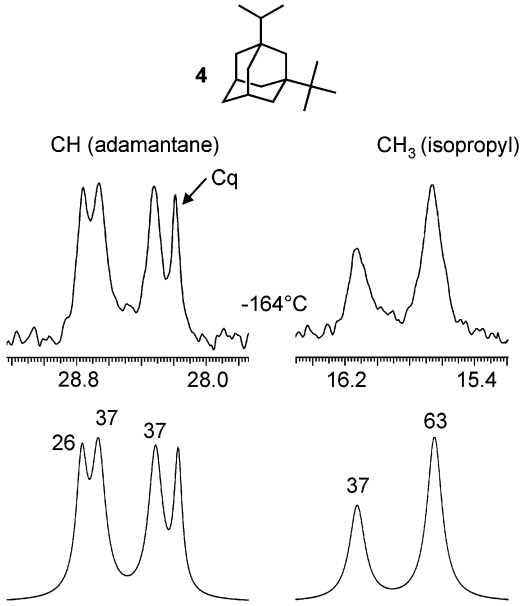
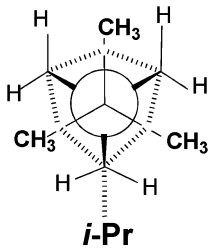


FIGURE 2. 100.5 MHz ^{13}C NMR signals (top) of the adamantyl CH carbon (left) and of the isopropyl methyl carbon (right) of compound **4** taken at −164 °C in $CHF_2Cl/CHFCl_2$ (4:1 v/v). Underneath are shown computer simulations obtained using the relative intensities (%) indicated (Cq is the singlet for the *tert*-butyl quaternary carbon, as determined via the HMBC sequence).

SCHEME 2

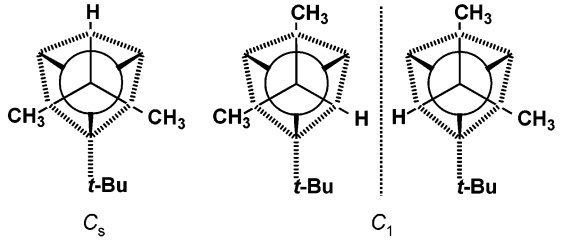


below −80 °C and eventually splits into a 1:2 pair of signals at −115 °C. The earlier results for **3** show that at this temperature, the isopropyl−adamantyl bond rotation is still fast on the NMR time scale, so the isopropyl behaves as a symmetric substituent. Thus, when the *tert*-butyl−adamantyl rotation is locked, presumably in a staggered arrangement, one methyl is diastereotopic with respect to the other two (enantiotopic) methyl groups (Scheme 2), so two rather than three methyl lines are observed at −115 °C. Line-shape simulation provided a barrier of 8.6_5 ± 0.15 kcal mol^{-1} for this rotational process.

When the temperature is further lowered below −140 °C, the isopropyl methyl signal and the adamantyl CH signal broaden and eventually split at −164 °C. As shown in Figure 2, the CH carbon appears as three signals with a relative intensity of 26:37:37, as deduced from computer simulation. At the same temperature the isopropyl methyl signal yields two lines with a relative intensity of 37: 63 (Figure 2).

Both of these observations can be explained from the existence of two types of conformer: an asymmetric one (C_1) in a 74% proportion (i.e. 2 × 37) and a symmetric one (C_s) in a 26% proportion. This straightforwardly

SCHEME 3. Representation of the C_1 and C_s Conformers Observed for 1-*tert*-Butyl-3-isopropyladamantane (4)[a]



[a] There are two enantiomeric forms of the more populated (C_1) conformer.

accounts for the three CH lines and also allows one to interpret the two methyl lines as due to the accidental coincidence (at 15.65 ppm) of two lines having the 37 and 26 relative intensity. Other signals showed less distinct changes as the temperature was lowered, which are in keeping with the above interpretation.

As shown in Scheme 3, the asymmetric C_1 conformer is 2-fold degenerate with enantiomeric forms and is therefore expected to be more populated than the symmetric companion C_s in a 66:33 proportion. Since the asymmetric conformer is slightly more favored than this, 74:26, the interaction between the two substituents cannot be completely negligible.

A full line-shape treatment of spectra in the range −150 to −160 °C shows that the barrier ($\Delta G^{\ddagger}$) for the rotation of the isopropyl substituent, which leads to the interconversion of the more into the less stable conformer, is 5.85 ± 0.15 kcal mol^{-1} (the barrier for the reverse process is obviously 5.7 kcal mol^{-1}). Within experimental errors, this value is equal to that found for the same rotation process in **3**, suggesting a negligible effect of the *tert*-butyl substituent.

1,3-Diisopropyladamantane (5). Having shown that it is possible to slow the isopropyl−adamantyl bond rotation and that the presence of a remote second group allows the direct observation of an equilibrium that deviates from the purely statistical, we investigated the case of the 1,3-diisopropyladamantane (**5**).

There are nine staggered conformations for the two isopropyl groups, and as shown in Scheme 4, there are four different types, each having a different symmetry and different versions (degeneracy). Below −100 °C most of the signals in the ^{13}C NMR spectrum broaden considerably and split into a number of signals at −165 °C. The most informative for understanding the conformational process are the signals of the adamantyl quaternary carbon and those of the adamantyl CH carbon (the assignment is the result of a DEPT sequence carried out at −165 °C).

As shown in Figure 3, the quaternary carbon displays five lines and only two of these lines are equally intense (19.1% each). This means that they must belong to the C_1 conformer, which is the only one having two diastereotopic quaternary carbons: accordingly its proportion is 38.2%. The other three single lines (35.2%, 14.1%, and 12.5%) thus belong to the C_2, C_s, and C_{2v} conformers, since each has a pair of homotopic (C_2) or enantiotopic (C_s and C_{2v}) quaternary carbons. It is not possible,

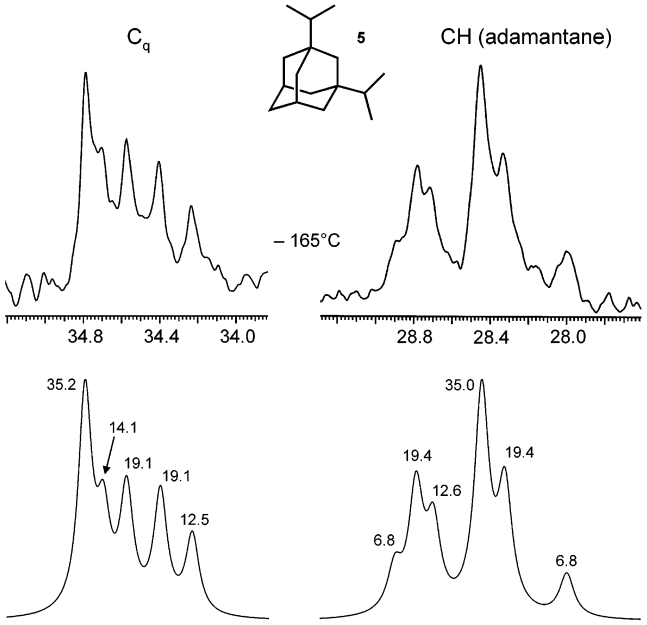
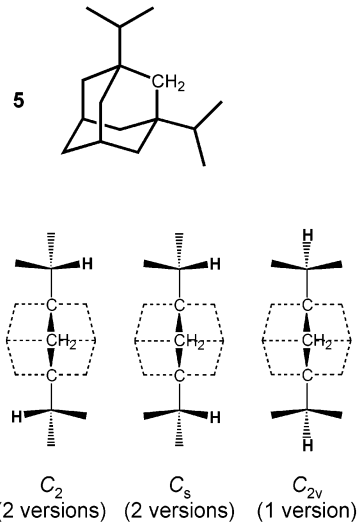


FIGURE 3. 100.5 MHz ^{13}C NMR signals (top) of the adamantyl quaternary carbon (left) and of the adamantyl CH carbon (right) of compound **5** taken at −165 °C in CHF_2Cl/$CHFCl_2$ (4:1 v/v). Underneath are shown computer simulations obtained using the relative intensities (%) indicated and a line width of 8.5 and 9 Hz, respectively.

SCHEME 4. Representation of the Four Conformers of 1,3-Diisopropyladamantane (5), with Indications of Degenerate Versions (Topomers or Enantiomers)



however, with only this information to link the remaining conformers with signals and thus with populations.

The CH adamantyl carbons appear as six lines, as in Figure 3. In this case there are two pairs of lines with equal intensity, i.e., 6.8% and 6.8% as well as 19.4% and 19.4%. The population of the latter conformer is equal, within experimental error, to that of the quaternary carbon signals above (38.8% ≅ 38.2%) and therefore is assigned to conformer C_1. The pair of lines of 6.8% intensity is consequently attributed to conformer C_s, the only other one having two diastereotopic CH carbons. The corresponding population is thus 13.6%, a value that

TABLE 1. Experimental Population (%) of the Conformers of 1,3-Diisopropyladamantane (5) Compared with the Statistical Distribution and with the Computed Relative Energies

	experimental population[a]				calcd rel energies[c]
degeneracy	from Cq	from CH_{Ad}	statistical distribution	relative stability[b]	MM3 (MMX)
4 (C_1)	38.2 (d)	38.8 (d)	44.4	9.6	0.06 (0.03)
2 (C_2)	35.2 (s)	35.0 (s)	22.2	17.55	0.04 (0.00)
2 (C_s)	14.1 (s)	13.6 (d)	22.2	6.9	0.08 (0.03)
1 (C_{2v})	12.5 (s)	12.6 (s)	11.2	12.55	0.00 (0.03)

[a] s, singlet; d, doublet. [b] (Experimental population)/(degeneracy). [c] kcal mol^{-1}.

matches the 14.1% population derived from the quaternary carbon spectrum.

The intensities of the two remaining single lines (35% and 12.6%) agree with those determined from the quaternary carbon spectrum (35.2% and 12.5%), and although they cannot be unambiguously assigned between conformers C_2 and C_{2v}, it appears reasonable to postulate that the less abundant conformer (12.6%) should have the C_{2v} symmetry, because it has no degenerate form, and thus a statistical population of 11.1%. In contrast, the C_2 conformer is doubly degenerate, so the signal of 35% population better fits this conformer.

The results of this interpretation are summarized in Table 1 where the terms s and d indicate, respectively, the observation of a single line or of a pair of equally intense lines. These results indicate that conformers C_1 and C_{2v} have proportions relatively close to the expectation of a statistical distribution, whereas C_2 has a higher and C_s a lower population than statistically predicted. The experimental trend for the relative stability of these conformations can be obtained by dividing the measured population of each conformer by the corresponding degeneracy.

Also in this case, line-shape simulation yields the value for the rotation barrier ($\Delta G^{\ddagger} = 6.1 \pm 0.15$ kcal mol^{-1}), which is equal to that measured for the monosubstituted derivative **3**.

Calculations. Molecular mechanics calculations[5] were carried out on the various rotational conformations of the substituted isopropyladamantanes **4** and **5**, but the differences in overall energy found were always small. The C_s conformer of **4** has the two isopropylmethyl groups as close as possible to the *tert*-butyl substituent and is calculated (MM3 force field) to be more stable than the C_1 conformer by 0.03 kcal mol^{-1}, but experimentally this C_s conformation is populated to *less* than the statistical amount, 26% rather than 33%.

From the NMR experiment the most stable conformer of **5** was found to be the C_2 (see the 5th column of Table 1), a result matched by MMX calculations that yielded essentially equal energy for the other three conformers (according to MM3, on the other hand, the most stable conformation of compound **5** is C_{2v} with the four isopropyl methyl groups nearest each other). The C_s conformation, with two methyl groups as far apart as possible, is calculated (MM3) to be the least stable, in agreement with the experimental observation (see the 5th column of Table 1). The two remaining conformations are of intermediate energy, and one shows more and the other shows less than the statistical proportion.

The *tert*-butyl−adamantyl bond in **4** is calculated (MM3) to be perfectly staggered as are the individual C-methyl bonds, and the significance of this will be discussed below.

The dihedral drive option in the MM3 program allows the calculation of rotational barriers when rotation is a simple process. Barriers are usually slightly lower than found by experiment,[5c] but within a series of similar compounds, the trend of values calculated follows the trend of experimental results.

The barrier calculated for isopropyl group rotation in adamantyl derivatives **3**, **4**, and **5** is 6.3 kcal mol^{-1}, while for pentamethylethane it is 6.2 kcal mol^{-1}. The barrier calculated for *tert*-butyl group rotation in **4** is 8.3 kcal mol^{-1}, while for hexamethylethane it is 8.1 kcal mol^{-1}. The rotational barrier calculated for 1-adamantyladamantane is 8.6 kcal mol^{-1}.

Discussion

The experimental rotational barrier of 6.1 kcal mol^{-1} in 1-isopropyladamantane **3** is markedly lower than that of 6.9 kcal mol^{-1} found[6,7] in the unbridged analogue, pentamethylethane. This is quite in keeping with previous comparisons in similar simple molecules reported in the Introduction. Such barriers are differences between the ground state and the eclipsed rotational conformations, and since strain produced by eclipsing of a rigid adamantyl group is expected to be higher than for a flexible *tert*-butyl group, the lower barrier for adamantyl compounds cannot be a transition-state effect. Rather, we conclude that pentamethylethane is able to relax to a markedly more stable ground state than is the more rigid compound **3**, so it has a higher rotational barrier.

In contrast, the experimental *tert*-butyl group rotational barrier in **4** (8.6 kcal mol^{-1}) is the same within experimental error as that inferred[8] and measured[9] for hexamethylethane, 8.4 kcal mol^{-1}. The fact that the adamantyl group has *not* lowered the barrier to rotation, as found in many examples for the isopropyl group, is probably linked to the different ground-state bond conformations in **4** and hexamethylethane, shown by calculations. The bond linking quaternary carbon atoms in **4** are perfectly staggered, while in hexamethylethane the Me−C−C−Me torsion angles are 5° from staggered, by experiment[10] (6.6° or 15° by calculation[11] by MM3 and MM2 respectively).

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(9) Anderson, J. E. unpublished results quoted in ref 3, Table 7. This experimental value, misquoted as 9.4 kcal mol^{-1} on page 104 of ref 3, was determined by a dynamic NMR experiment that was not described. The value was obtained for the isotopomer $(CH_3)_3C-C(CH_3)(CD_2)_2$, which was contaminated by other isotopomers, the ^{13}C signals of which almost coincide with that for the methyl carbons of the $(CH_3)_3C$-group. The latter signal broadens and then splits to give an overlapped 2:1 doublet at low temperatures, hence a barrier value of 8.4 ± 0.3 kcal mol^{-1} was obtained by computer simulation of the partially obscured spectral change.

We tried to observe the rotational barrier for an adamantyl−adamantyl bond, using (3-bromoadamantyl)-1-adamantane to introduce the necessary molecular dissymmetry, but we were frustrated by the insolubility of the compound, at even moderately low temperatures.

A substituent at position 3 clearly perturbs the isopropyl group rotational equilibrium in 1-isopropyladamantyl compounds. The two substituents, which are equivalent to 1,3-diequatorial on a six-membered ring, are too distant to have direct repulsive interactions (the separation of isopropyl methine carbons in **5** is calculated to be 5.1 Å). Their direct interaction must therefore be through van der Waals attractive interactions of pairs of atoms. This would suggest that the conformation with the isopropyl methyl groups near to the substituent should be more stable, but the results for compound **4** show that this is not the case. The conformation with both the isopropyl methyl groups near the 3-*tert*-butyl substituent has a lower than statistical population (26% vs 33%). The results for the four conformations of compound **5** are less clear-cut, for both the least and the most populated conformations have only two methyl groups (of a possible four) directed toward each other.

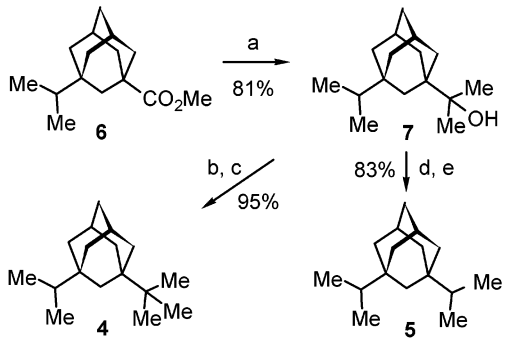
A similar observation about small but unpredictable population differences has been made previously in conformational studies of *sec*-alkylbenzenes with meta-substituents.[12] The two meta-substituents which should attract each other have the ortho C−H group in the space between them. Following that work, we conclude that the intervention of the adamantyl methylene group directly between the two interacting substituents leads to two sets of repulsive interactions with that methylene group. Buttressing of these repulsions by the second substituent counteracts the attraction between substituents. The equivocal results for **4** and **5** show that this buttressing is of a similar magnitude to the attractive interactions of the substituents.

Experimental Section

Preparation of Materials. 1-Isopropyladamantane (**3**)[13] was prepared according to the published procedure. 1-*tert*-Butyl-3-isopropyl- (**4**) and 1,3-diisopropyladamantane (**5**) were obtained in 77 and 67% overall yield, respectively, from the same synthetic precursor—methyl 3-isopropyladamantane-1-carboxylate (**6**)[14] (Scheme 5). This was transformed into the hydroxyisopropyl derivative **7** with an excess of methyllithium and then converted into hydrocarbons **4** or **5**, respectively, by applying Adcock's protocol[15] or an ionic hydrogenization procedure,[16] respectively.

Diethyl ether was dried by distillation from sodium benzophenone ketyl, and CH_2Cl_2 from P_4O_{10}. All other chemicals were used as commercially available. Organic extracts were dried over $MgSO_4$. NMR spectra were recorded at 250 MHz for ^1H and at 62.9 MHz for ^{13}C NMR. Multiplicities were determined by DEPT sequences. Chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shifts of residual $CHCl_3$ signals. TLC analyses were performed on precoated sheets, 0.25 mm Sil G/UV_{254}. Silica gel grade 60 (230−400 mesh) was used for column chromatography. All reactions were performed under an atmosphere of argon.

SCHEME 5[a]



[a] Reagents and conditions: (a) MeMgI (2.9 equiv), Et_2O, 34 °C, 1.5 h; (b) HCl, CH_2Cl_2, −50 °C, 15 min; (c) Me_3Al, CH_2Cl_2, −90 °C, 1 h, then −90 to 0 °C, 2 h; (d) Et_3SiH (2 equiv), TFA (1.95 equiv), CH_2Cl_2, 0 to 20 °C, 1 h; (e) H_2, Pd/C, EtOH/HOAc 50:1, 20 °C, 24 h.

2-(3-Isopropyladamantan-1-yl)propan-2-ol (7).[17] To the Grignard reagent solution prepared from MeI (21.434 g, 14.0 mL, 151 mmol) and magnesium turnings (3.8 g, 158 mmol) in anhydrous diethyl ether (150 mL) was added dropwise a solution of the ester **6** (12.27 g, 51.9 mmol) in Et_2O (50 mL) over a period of 45 min. The reaction mixture was stirred under reflux for an additional 1 h and cooled to 0 °C, and the reaction was quenched by careful addition of saturated aqueous NH_4Cl solution (50 mL). The aqueous layer was extracted with Et_2O (3 × 50 mL), and the combined extracts were washed with brine (100 mL), dried, and concentrated under reduced pressure. Column chromatography of the residue (250 g of silica gel, 25 × 6 cm column, hexane/Et_2O 2:1) gave alcohol **7** (9.86 g, 81%) as a colorless oil: $R_f = 0.41$; ^1H NMR ($CDCl_3$) δ 2.05 (m, 2 H), 1.61−1.16 (m, 14 H), 1.12 (s, 6 H), 0.80 0.80 (d, J = 7.0 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 74.8 (C), 39.4 (C), 38.5 (2 CH_2), 38.0 (CH_2), 37.8 (CH), 36.8 (CH_2), 36.0 (2 CH_2), 34.9 (C), 28.9 (2 CH), 24.3 (2 CH_3), 16.4 (2 CH_3).

1-*tert*-Butyl-3-isopropyladamantane (4). Dry HCl gas was bubbled into a vigorously stirred solution of the alcohol **7** (1.98 g, 8.44 mmol) in anhydrous CH_2Cl_2 (40 mL) at −50 °C for 0.5 h. The solvent was evaporated under reduced pressure, and the residue was dried in vacuo (0.1 Torr) for 10 min, taken up with anhydrous CH_2Cl_2 (40 mL), and cooled to −95 °C. To this solution was added dropwise Me_3Al (11.73 mmol, 5.87 mL of a 2 M solution in hexane) at such a rate that the temperature was maintained at −90 °C. The reaction mixture was allowed to warm to room temperature within 2 h and then cooled back to 0 °C, before a mixture of MeOH (5 mL) and CH_2Cl_2 (10 mL) was added, **very cautiously** followed by 5% H_2SO_4 solution (10 mL). The inorganic phase was extracted with CH_2Cl_2 (3 × 20 mL), the combined organic extracts were washed with 5% aqueous $NaHCO_3$ solution (50 mL) and brine (50 mL), dried, and concentrated under reduced pressure. Column chromatography of the residue (70 g of silica gel and 30 g of silica gel impregnated with 3% $AgNO_3$, 30 × 3 cm column, hexane) followed by distillation under reduced pressure gave the hydrocarbon **4** (1.88 g, 95%) as a colorless oil: $R_f = 0.66$, bp 72−73 °C (0.2 Torr); ^1H NMR ($CDCl_3$) δ 2.04 (t, J = 2.8 Hz, 2 H), 1.59−1.30 (m, 10 H), 1.27 (s, 2 H), 1.22 (sept, J = 6.8 Hz, 1 H), 0.82 (s, 9 H), 0.81 (d, J = 6.8 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 38.7 (2 CH_2), 38.2 (CH_2), 38.0 (CH) 37.1 (CH),

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37.0 (C), 36.0 (2 CH_2), 34.9 (2 C), 29.2 (2 CH), 24.8 (3 CH_3), 16.6 (2 CH_3). Anal. Calcd for $C_{17}H_{30}$ C, 87.10; H, 12.90. Found: C, 87.03; H, 12.66.

1,3-Diisopropyladamantane (5).[18] To a stirred solution of alcohol **7** (1.50 g, 6.42 mmol) in anhydrous dichloromethane (20 mL) at 0 °C were added in one portion triethylsilane (1.492 g, 2.05 mL, 12.83 mmol) and then trifluoroacetic acid (1.43 g, 0.96 mL, 12.51 mmol). The reaction mixture was stirred for 30 min at ambient temperature, poured into ice-cold 5% aqueous $NaHCO_3$ solution (80 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried, concentrated under reduced pressure, and purified by column chromatography (100 g of silica gel, 30 × 3 cm column, hexane) collecting a fraction with $R_f = 0.73-0.65$ which, according to its ^{1}H NMR spectrum, was a 4:1 mixture of diisopropyl and isopropylisopropenyl derivatives. This fraction was taken up with a mixture of EtOH and AcOH (30 mL, 50:1 per volume), Pd/C (Merck, 10% Pd, 683 mg, 0.64 mmol, 10 mol %) was added, and the mixture was vigorously stirred under an atmosphere of H_2 (1 bar) at 20 °C for 24 h. The catalyst was filtered off, the filtrate was concentrated under reduced pressure, and the product was isolated by column chromatography (60 g of silica gel impregnated with 3% $AgNO_3$, 15 × 3 cm column, hexane) followed by distillation under reduced pressure to give the hydrocarbon **5** (1.18 g, 83%) as a colorless oil: bp 68 °C (0.2 Torr) (lit.[18] bp 294−296 °C); ^{1}H NMR ($CDCl_3$) δ 2.03 (sept, $J = 2.9$ Hz, 2 H), 1.57 (narrow m, 2 H), 1.46 (br d, $J = 14.0$ Hz, 4 H), 1.35 (br d, $J = 14.0$ Hz, 4 H), 1.22 (sept, $J = 7.0$ Hz, 2 H), 1.19 (s, 2 H), 0.82 (d, $J = 7.0$ Hz, 12 H); ^{13}C NMR ($CDCl_3$) δ 41.4 (CH_2), 38.9 (4 CH_2), 37.8 (2 CH), 37.2 (CH_2), 35.0 (2 C), 29.1 (2 CH), 16.4 (4 CH_3).

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NMR Measurements. The samples for the ^{1}H and ^{13}C NMR low-temperature measurements were prepared by connecting to a vacuum line the NMR tubes containing the compound and some C_6D_6 for locking purpose and condensing therein the gaseous solvents (CHF_2Cl and $CHFCl_2$ in a 4:1 v/v ratio) under cooling with liquid nitrogen. The tubes were subsequently sealed in vacuo and introduced into the precooled probe of the spectrometer. The temperatures were calibrated by substituting the sample with a precision Cu/Ni thermocouple before the measurements. Complete fitting of dynamic NMR line shapes was carried out using a PC version of the DNMR-6 program.[19] We believe that estimates of conformer populations based on such fitting is accurate to ±2%, since such a change leads to a detectably poorer fit.

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Supporting Information Available: Fully optimized Cartesian coordinates of the various rotational conformations of **4** and **5** and their calculated total energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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