to the gauche–gauche conformer, just the opposite occurs. The 1a level is the lowest of the four MO's and is 1–4 bonding. This level still emphasizes the central Si–Si bonds over the end Si–Si bonds. The 2a MO now has a node along the Si backbone at the Si2 positions and is therefore 1–4 antibonding. Neglecting the noncrossing rule temporarily, we note that the 1–4 bonding a level has fallen from −11.33 to −11.92 eV in going from anti–anti to gauche–gauche and that the 1–4 antibonding a level has risen from −11.54 to −10.74 eV. Because the 1–4 character in the two a levels reverses in energy order, an avoided crossing probably occurs in the middle of the process. We consider the 2b level, the highest occupied MO. In the anti–anti conformer, p orbitals aligned with the chain axis (i.e., perpendicular to the C_2 axis) along the Si backbone are in phase at every other Si position. Nearest neighbors have bonding relationships, but the Si1–Si2 and Si2–Si3 regions have opposite phase. This arrangement is preserved in the gauche–gauche form. As this orbital has b symmetry, the end bond region will interact favorably with the nonadjacent interior bond region. A stabilization of 0.35 eV in the gauche–gauche conformer versus the anti–anti conformer results.

As the chain length increases, the highest occupied MO will retain its bonding Si–Si nearest-neighbor quality and the out of phase relationship between adjacent bonding regions, implying that the 1–4 interactions will be in phase. As rotations about Si–Si single bonds occur, the highest occupied MO will be stabilized in the gauche versus anti conformation. This is compatible with the notion that the excitation energies in the anti form are shifted toward the red relative to those in the gauche form,[2,3] but a more definitive study would examine the conformational dependence of electron affinities (where Koopmans' theorem results are questionable) and excitation energies.

VII. Summary

We have carried out geometry optimizations at the SCF level using a 3-21G* basis for the unbranched forms of disilane, trisilane, tetrasilane, and pentasilane. Vertical ionization energies on these species are in excellent agreement with experiment. Total energy results for tetrasilane suggest no significant energy difference between the anti and gauche conformers. The trends of the EPT vertical ionization energies are consistent with MO concepts based on interactions of next nearest neighbors in a bond orbital model. If these ideas for tetrasilane and pentasilane can be extrapolated to longer polysilane chains, then we would expect the highest occupied states of the Si backbone to be stabilized with an increasing gauche population.

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Registry No. Si_2H_6, 1590-87-0; Si_3H_8, 7783-26-8; Si_4H_{10}, 7783-29-1; Si_5H_{12}, 14868-53-2.

Conformational Studies by Dynamic NMR. 35.[1] Structure, Conformation, and Stereodynamics of Hindered Naphthylamines

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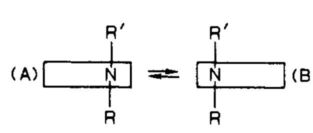
Abstract: The low-temperature ^1H and ^{13}C NMR spectra of a number of *N*-ethyl- and of *N*-isopropyl-*N*-alkyl-1-naphthylamines allowed the measurement of the interconversion barriers between the two twisted enantiomeric conformers. The free energies of activation increased substantially with the dimension of the N-alkyl groups (e.g., ΔG^{*}_{173} is 8.3 Kcal mol^{-1} when N-alkyl is a methyl group, and ΔG^{*}_{373} is 19.8$_5$ Kcal mol^{-1} when N-alkyl is a *tert*-butyl group in *N*-ethyl-*N*-alkyl-1-naphthylamines). Nuclear Overhauser enhancement (NOE) experiments confirmed that these molecules adopt a twist conformation and indicated that in *N*-methyl as well as in *N*-ethyl-*N*-isopropyl-1-naphthylamines the *N*-isopropyl moiety is closer to H-8 than to H-2. These results, obtained in solution, were confirmed by the X-ray investigation of an analogous derivative in the solid state. On the other hand, the less hindered secondary 1-naphthylamines turned out to be planar in solution (NOE experiments) as well as in the solid state (X-ray diffraction). Finally it was found that electron-releasing (e.g., -NH_2) and electron-attracting (e.g., -NO_2) substituents in position 4 increase and reduce, respectively, the interconversion barriers of the twisted tertiary 1-naphthylamines. As expected this trend is opposite to that reported in the case of planar *N*-methylanilines containing analogous substituents in position 4.

The 1-isomers of the *N,N*-dialkylnaphthylamines are sufficiently hindered as to have the dynamic plane containing the two alkyl groups and the rapidly inverting nitrogen atom significantly twisted with respect to the plane of the naphthalene ring. As a consequence, the torsional process that allows the interconversion between the pair of conformers indicated in Scheme I requires the passage through a transition state where the two planes become coplanar. On the contrary the less hindered 2-naphthylamines are known to have planar ground states and perpendicular transition states.[3,4]

Scheme I



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(1) Part 34. Casarini, D.; Lunazzi, L.; Macciantelli, D. *J. Org. Chem.* **1988**, *53*, 182–185.

(2) (a) Department of Organic Chemistry. (b) Department "G. Ciamician". (c) CNR, I.Co.C.E.A., Ozzano E.

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Table I. Free Energies of Activation ($\Delta G^{\ddagger}$ in Kcal mol^{-1}) for the Naphthyl–Nitrogen Rotational Process[c]

compd	$\Delta G^{\ddagger}$ (Kcal mol^{-1})	temp (°C)	solvent	difference of shifts (Hz)	resonance of nuclei (MHz)
1a	8.3[a]	−100	CD_2Cl_2	160 (−112°)	300 (^{1}H)
1b	8.9_5	−95	CD_2Cl_2/CHF_2Cl	25 (−115°)	300 (^{1}H)
1c (= **2c**)	11.2	−38	CD_2Cl_2	138 (−60°)	25.16 (^{13}C)
1d	10.6	−53	CD_2Cl_2	60 (−93°)	25.16 (^{13}C)
1e	19.8_5	+105	C_2Cl_4	15.7 (+25°)	100 (^{1}H)
2b	10.3[a]	−50	CD_2Cl_2	166 (−100°)	25.16 (^{13}C)
2d	15.3[b]	+29	$CDCl_3$	59 (+11°)	25.16 (^{13}C)
	15.5[b]	+17	$CDCl_3$	17.5 (−3°)	300 (^{1}H)
3	7.0	−120	CHF_2Cl	135 (−135°)	300 (^{1}H)
4a	12.4_5	−12	CD_2Cl_2	134 (−35°)	300 (^{1}H)
4b	8.1	−100	CHF_2Cl	85 (−125°)	25.16 (^{13}C)

[a] Reference 4. [b] Reference 3. [c] The temperatures (°C) at which the rotational barriers were measured are given in the third column together with the solvents employed (fourth column). The chemical shift differences (in Hz) between the appropriate anisochronous nuclei are reported in the fifth column where the temperatures at which they were observed are given in parenthesis (°C). The last column indicates the spectrometer frequency and the nucleus observed. The errors on $\Delta G^{\ddagger}$ are ±0.15 Kcal mol^{-1} with the exception of **1a** and **3** (±0.2 and ±0.3 Kcal mol^{-1}, respectively).

The dynamic process occurring in hindered 1-naphthylamines can thus be indicated, in a simplified manner, by the following equilibrium (Scheme I) where a rotation about the Ar–N bond interconverts the enantiomer A with its enantiomer B. Evidence that the structure of the conformational ground state in the 1-naphthylamines is not planar is offered by the NMR spectra of those derivatives where one of the two alkyl substituents (or both) is an ethyl, an isopropyl, or any other moiety having two geminal groups (e.g., the methylenic hydrogens if R = ethyl or the methyls if R = isopropyl). The geminal groups in the 1-isomers become anisochronous when the rotation is sufficently slow (usually at low temperature) owing to the fact that these molecules become chiral (if R ≠ R′) or prochiral (R = R′).[5] On the other hand, in the 2-naphthylamines the geminal groups remain isochronous at any temperature since the rotational ground state is planar.[3,4] Line shape analysis of the NMR spectra allows the determination of the rotational barrier: in the case of the 1-naphthylamines these values are expected to vary significantly with the bulkiness of R and R′.

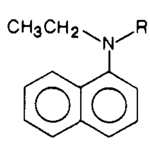
In the present work a number of tertiary 1-naphthylamines containing the ethyl or the isopropyl moieties were investigated and the corresponding barriers determined. Comparison between the low-temperature NMR spectra of tertiary 1-naphthylamines and analogous secondary 1-naphthylamines showed that the latter have a planar, rather than a twisted conformation. The information concerning the molecular arrangement of these derivatives were also substantiated by NOE experiments and X-ray diffraction studies.

It is also conceivable that the electronic properties of substituents in the naphthalene ring might affect the values of the rotational barrier. The trend of these barriers, however, should be opposite in the case of twisted (e.g., perpendicular) derivatives, such as the *N,N*-dialkyl-1-naphthylamines under investigation, with respect to analogous planar aromatic amines. To test this prediction the barriers of *N*-methyl-*N*-isopropyl-1-naphthylamines containing electron-withdrawing and electron-releasing substituents in position 4 were measured in order to be compared with those of the corresponding *N*-methylphenylamines that are known to have a coplanar conformation.[6a,b]

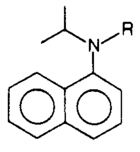
Results

The following *N*-alkyl- and *N,N*-dialkyl-1-naphthylamines were investigated in the present work.

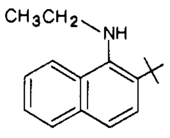
Chart I



1a, R = Me
1b, R = Et
1c = **2c**, R = CHMe$_2$
1d, R = CHEt$_2$
1e, R = CMe$_3$



2a, R = H
2b, R = Me
2c = **1c**, R = Et
2d, R = CHMe$_2$



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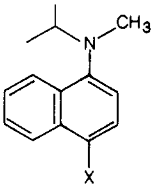
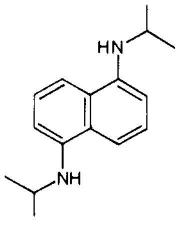


4a, X = NH$_2$
4b, X = NO$_2$



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Dynamic NMR. In the derivatives containing the ethyl group (**1a–e**) the proton signal of the methylenic hydrogens is a single line when the methyl hydrogens of the CH_3CH_2 moiety are decoupled at room temperature. At low temperature, on the other hand, the two methylenic hydrogens become anisochronous, and a typical AB spectrum is observed. For instance in the spectrum of **1b** (R = Et) the methylenic hydrogens have a chemical shift difference of 25 Hz (at 300 MHz) and a $J_{HH} = -13.5$ Hz when the temperature is −115° (in CD_2Cl_2/CHF_2Cl 1:1). Computer simulation of the line shape at different temperatures yields the rate constant for the exchange process indicated in Scheme I, hence the free energy of activation ($\Delta G^{\ddagger}_{178} = 8.9_5$ Kcal mol^{-1}). In the case of derivatives containing the *i*-Pr or the Et_2CH (3-pentyl) moiety the dynamic process can be also followed with C-13. For instance in derivative **1d** the pair of methylenic carbons of the 3-pentyl moiety displays two anisochronous ^{13}C signals, separated by 60 Hz (25.16 MHz) at −93° in CD_2Cl_2. These signals coalesce at −54° yielding a $\Delta G^{\ddagger}_{219} = 10.6$ Kcal mol^{-1}. The values of the free energies of activation for all the compounds are collected in Table I. The line shape simulation required to obtain the rate constant was usually performed at a single temperature. When simulations could be obtained at various temperatures (in the cases of **1a**, **1d**, **1c**, **2d**), the $\Delta G^{\ddagger}$ values were found equal within the errors, so that meaningful determinations of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ could not be achieved.

Secondary amines such as **2a** and **5** do not display, on the contrary, anisochronous signals even at the lowest attainable temperatures (−150 °C and −135 °C, respectively), thus suggesting that, contrary to the analogous *N,N*-dialkyl-1-naphthylamines, they adopt a planar conformation. This conclusion is supported by the experiment carried out on derivative **3** where the bulky *tert*-butyl group in position 2 is expected to force even a secondary amine into a nonplanar conformation. Indeed the ^{1}H NMR spectrum of **3** shows at −135° two anisochronous methylenic

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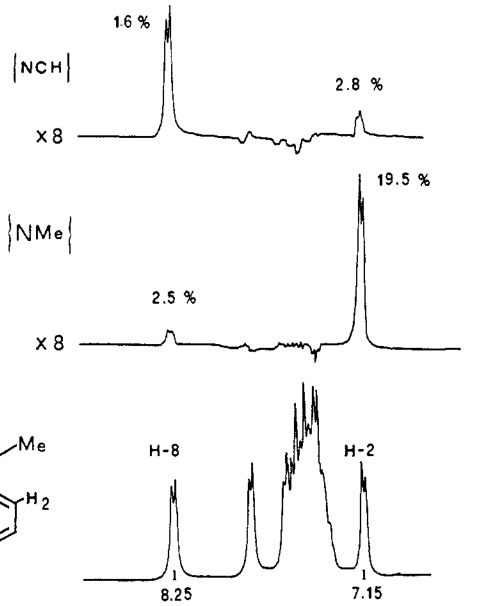


Figure 1. Aromatic region of the ^1H spectrum (300 MHz) of **2b**: the position of the signals for H-2 and H-8 is given in ppm (lower trace). The two upper traces (eight times amplified) are the results of the differential NOE spectra. The NOE values obtained irradiating NCH (top trace) and NMe (middle trace) are indicated for each signal.

Table II. Differential Nuclear Overhauser Enhancements[a]

compd	irradiated signal	NOE (H-8)	NOE (H-2)
2b	NCH_3	2.5	19.5
	NCH	16	2.8
1c	NCH_2	2	11
	NCH	10	2.5
2d	NCH	2	4
2a	NH	31	6
	NCH	8	18
4b	NCH_3	3	22.5
	NCH	16	3.5

[a] NOE (expressed as percent) detected on H-8 and H-2 when the protons of the NCH_n (n = 1, 2, 3) or of the NH groups are irradiated.

hydrogens, separated by 135 Hz (300 MHz in CHF_2Cl); the corresponding $\Delta G^{\ddagger}_{153}$ was found to be 7.0 Kcal mol^{-1} (Table I).

Nuclear Overhauser Enhancement. In derivatives **2a–d** differential NOE experiments[7] showed enhancement of the signals of protons in positions 2 and 8 when irradiating the CH hydrogen of the *N*-isopropyl group or the hydrogens of the various nitrogen-bonded R groups.

A typical experiment is shown in Figure 1 for derivative **2b**. Irradiation of the NCH hydrogen of the isopropyl group induces a large enhancement (16%) on H-8 but a much smaller one (2.8%) on H-2. The reverse occurs when the hydrogens of the NCH_3 group are irradiated in that the enhancement is much larger on H-2 (19.5%) than on H-8 (2.5%). All the results are collected in Table II where it can be also seen that the presence of substituents in the position 4 of the naphthalene ring (e.g., the nitro group in derivative **4b**) do not greatly affect the NOE values.

Solid-State NMR. The cross polarization (CP) magic angle spinning (MAS) ^{13}C NMR spectra were measured in the solid state for the two crystalline derivatives **4b** and **5**.

The spectrum of **5** is reported in Figure 2. The signals of the carbons directly bonded to nitrogen (i.e., the methine carbons of the isopropyl groups and the ring carbons 1,5) are split into two owing to the quadrupolar interactions with ^{14}N.[8] The other eight carbons of the naphthalene ring yield four signals, thus indicating that the center of molecular symmetry has been maintained also in the crystalline state. As observed in the great majority of cases the center of molecular symmetry is coincident with the center of crystallographic symmetry. Conversely the four methyl carbons, that were found equivalent in solution even at the lowest attainable temperature, yield in the solid a pair of signals. This means that the two methyls within each isopropyl group occupy two positions that are not symmetric with respect to the plane of the naphthalene: this feature has been also observed in the solid-state spectrum of **4b**. The existence of a center of symmetry in **5** also indicates that the asymmetric conformer **5b** (Chart II) is not populated. The choice between the other two symmetric conformers **5a** and **5c** cannot be unambiguously made only on the basis of the solid-state NMR spectrum, although **5a** seems to be more likely on a steric ground.

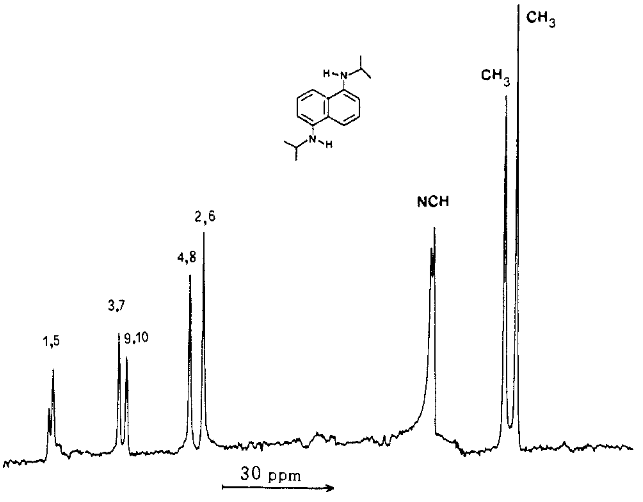
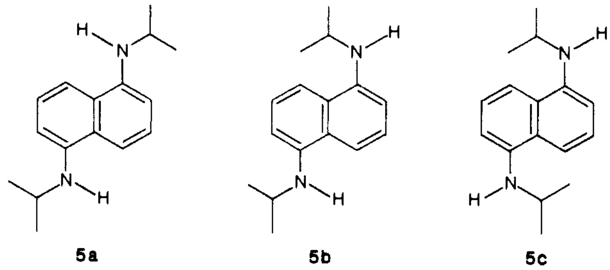


Figure 2. ^{13}C CP-MAS spectrum (75.46 MHz) of **5**. The carbons C1, C5 as well as the NCH carbons yield split signals owing to the incomplete elimination of their interactions with ^{14}N (see text). The four *N*-methyl carbons yield a pair of signals since the plane of naphthalene is not a plane of symmetry for the two equivalent isopropyl groups (see text). The pairs of remaining carbons (2 and 6, 3 and 7, 4 and 8, 9 and 10) yield single signals since **5** adopts in the solid the centrosymmetric conformation **5a**, and, in addition, the molecular and crystallographic centers are coincident.

Chart II



5a **5b** **5c**

X-ray Diffraction. The structure of the two solid derivatives **4b** and **5** was determined by X-ray diffraction. In Figure 3 (top) the structure of **4b** is reported. The most relevant structural features are hereafter summarized. The carbons of the naphthalene ring lie essentially on a plane, the maximum deviation from this average plane being –0.127 Å for C-3 and 0.115 Å for C-1. With respect to the plane containing the three carbons bonded to the nitrogen (i.e., C-1, C-12, C-13) the nitrogen atom deviates by –0.287 Å, thus indicating that the amino nitrogen is pyramidal. However this pyramid is relatively flat owing to the repulsion of the three substituents. The average ∠CNC angle is in fact 116.2° ± 1.2°, which is closer to the 120° expected for a planar arrangement than to the 109° of a tetrahedron. The "average plane" involving the atoms C-1, N-11, C-12, and C-13 (i.e., a plane parallel to the dynamic plane created in solution by the fast N-inversion) is twisted with respect to the plane of naphthalene by 45.2°. This obviously agrees with the low-tem-

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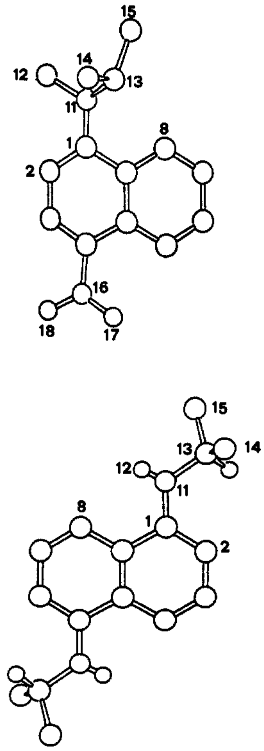

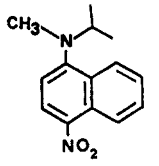

4b

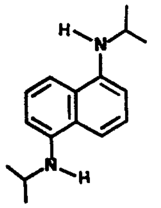

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Figure 3. Top: crystal structure of **4b** showing that the average plane related the atoms 1,11,12,13 is twisted (45°) with respect to the naphthalene ring. Bottom: crystal structure of **5** where, on the contrary, the average plane related to the atoms 1,11,12,13 is essentially coplanar to the naphthalene ring.

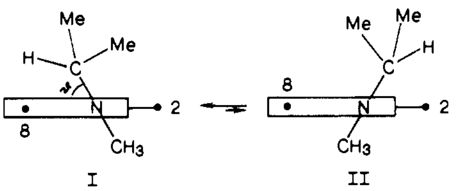
perature NMR observations that require a nonplanar conformation to account for the anisochronous methyls of the isopropyl moiety. The plane containing the NO_2 group is also twisted with respect to the naphthalene plane: the angle, however, is much smaller (20.9°). From Figure 3 it is also evident that the preferred conformation of **4b** features the isopropyl group close to C-8 and the methyl group close to C-2. The carbon–carbon distance between C-8 and C-13 (3.08 Å) is in fact shorter than that between C-8 and C-12 (4.26 Å), whereas the carbon–carbon distance between C-2 and C-13 (3.66 Å) is longer than that between C 2 and C-12 (2.78 Å). This result agrees with the conclusion derived from the interpretation of the NOE effect in solution (see the discussion section). The structure of derivative **5** (Figure 3, bottom) indicates that the molecule has a center of symmetry and that, contrary to the case of tertiary amines like **4b**, the secondary amines adopt a planar conformation. The N atom has an essentially planar arrangement since it deviates only by 0.07 Å from the plane containing C-1, H-12, and C-13. The average plane related to C-1, N-11, H-12, and C-13 is also coplanar to that of the naphthalene ring, the twist angle being only 1.3°. This feature thus explains why this secondary amine displays isochronous methyl signals at any temperature in solution.

Amongst the three possible conformations of Chart II, the less hindered centrosymmetric **5a** is the preferred one in the crystal. Finally the positions of the pair of methyls within each isopropyl group are not symmetrical with respect to the naphthalene ring, as predicted from the solid-state NMR spectrum. One of the two methyls (C-14) has in fact a distance of 1.37 Å from the plane of the naphthalene, the other (C-15) of −0.65 Å. An analogous feature had been observed in the case of **4b**, the two distances being 2.65 (C-14) and 1.17 (C-15) Å, respectively.

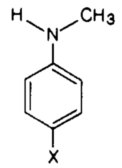
Discussion

The values of the free energies of activation (Table I) indicate that the rotational barriers increase with the increasing bulkiness of the substituents R within a homologous series. The ΔG^* values for the N-ethyl derivatives **1a–e** cover in fact the range 8.3–19.8$_5$ Kcal mol^{-1} when R changes from methyl (**1a**) to *tert*-butyl (**1e**). This is consistent with the existence of a twisted ground state less hindered than the planar transition state. An opposite trend would have been observed if the ground state had been planar and the transition state perpendicular as occurs, for instance, in the case of the planar *N*-alkylanilines.[6] A slight discrepancy in this trend is given by the value of **1d** which is smaller than that of **1c**, despite the fact that the substituent R in **1d** (i.e., $CHEt_2$) is apparently bulkier than in **1c** (i.e., $CHMe_2$). This reversal in the expected behavior has been also observed in other cases for the same[1] or for similar[9] groups and has not yet found a general explanation. The hypothesis of differences in the activation entropy has been suggested[9] in order to account for the reversal of this pair of ΔG^* values.

Scheme II



The effect of substituents in the naphthalene ring is also expected to have an opposite trend in these twisted naphthylamines with respect to other planar aromatic amines. Electron-attracting substituents in position 4 (e.g., NO_2 in derivative **4b**) would in fact stabilize the coplanar transition state by increasing the double bond character of the *N*-naphthyl bond. The twisted ground state, on the other hand, would be much less affected, and therefore the barrier of **4b** decreases with respect to that of the unsubstituted derivative **2b**. For the same reason the electron-releasing substituents (e.g., NH_2 in **4a**) increase the barrier. The ΔG^* values measured in **4b**, **2b**, and **4a** (Table I) display in fact an increasing trend (8.1, 10.3, and 12.4$_5$ Kcal mol^{-1}, respectively, at 173, 223, and 261 K), whereas the 4-substituted derivatives of the planar *N*-methylanilines **6** follow a decreasing trend for the rotational barriers (i.e., the ΔG^* values are 11.1, 7.2, and 5.7 Kcal mol^{-1} when X is, respectively, NO_2, H, and OMe).[6]



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In Scheme I the two enantiomeric conformers A and B, corresponding to the ground state of 1-naphthylamines, were represented, for simplicity, as perpendicular. The X-ray investigation has shown that this is not the case and that the angle ϑ can be different from 90°. When the two groups bonded to nitrogen are not equal, two different conformers (I and II) should be considered, as shown in Scheme II for the case of **2b**.

The activation energy for the exchange (libration) between these conformers is much lower than for the enantiomerization process of Scheme I and cannot be measured by low-temperature NMR. Nonetheless information concerning the conformational preference between the situations I and II can be obtained, in solution, by the analysis of the NOE experiments.

The large enhancement of the H-8 signal observed in **2b** when NCH is saturated indicates that conformer I is preferred with respect to conformer II: this is confirmed by the large enhancement of the H-2 signal observed when NCH_3 is saturated (Table II). The existence of a small, but not null effect on H-2 when NCH is saturated (and conversely on H-8 when NCH_3 is saturated) can be interpreted as due to the presence of conformer II in rapid equilibrium with I but with a much lower population. The very large differential NOE effects observed in **2a** also indicate that the angle should not be very close to 90°, thus allowing short distances between H-8 and the methine hydrogen of the isopropyl

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(9) Bechaus, H.-D.; Rüchardt, C.; Anderson, J. E. *Tetrahedron* **1982**, *38*, 2299.

Scheme III

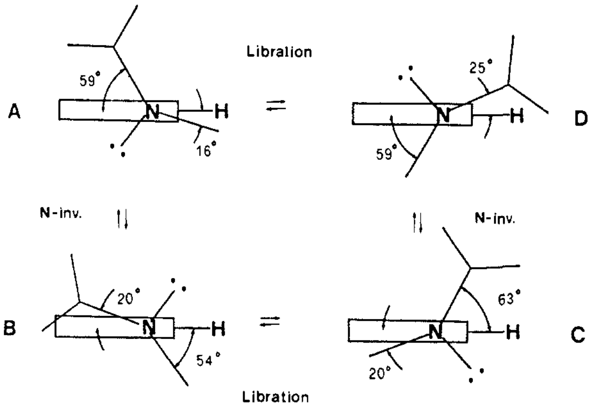


Table III. Dihedral Angles Obtained from the X-ray Structure of Derivative **4b** (Figure 3)[a]

C2	C1	N11	C12	-15.88°
C2	C1	N11	C13	125.69°
C9	C1	N11	C12	159.68°
C9	C1	N11	C13	-58.75°
C12	N11	C13	C1	142.02°

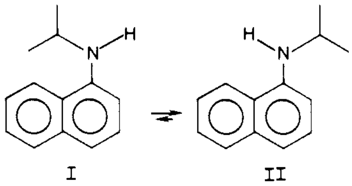
[a] These values correspond to that of conformer A in Scheme III.

groups as well as between H-2 and the methyl hydrogens of NCH_3. This conclusion agrees with the results of the X-ray investigations in the solid nitro derivative **4b**. In fact not only the isopropyl group was found to be closer to H-8 than to H-2 but also the angle turned out to be 45°, i.e., significantly different from 90°. In the crystal, however, only the more populated of the two conformers (i.e., conformer of type I) was observed. As often occurs, the less populated conformers disappear in the passage from the solution to the solid state. When R = Et (**2c**) the NOE values becomes significantly smaller than in **2b** (Table II), thus indicating that the corresponding interprotonic distances are larger, hence the angle ϑ closer to 90°. Indeed substitution of the methyl with the bulkier ethyl group can twist the conformation even more. This hypothesis is further supported by the even lower NOE effects observed when R is isopropyl (**2d**). Here the two conformers I and II must be equally populated, and the very low enhancements observed for both H-2 and H-8 upon irradiation of NCH indicate that the angle is much closer to 90°, in agreement with the fact that the isopropyl group is the most bulky amongst these three groups.

In order to understand why in Scheme II the conformation of type I is more populated than that of type II, the reader is reminded that both I and II are simplified graphic representations of the average between the "invertomers" **A**,**B** and **C**,**D** reported respectively, in Scheme III.

The X-ray structure of **4b** yields the geometry corresponding to A whose relevant dihedral angles are listed in Table III. By using the simplifying assumption that both the N-inversion (that exchanges A with **B** and C with **D**) and the libration (that exchanges A with **D** and **B** with C) processes occur via a fully symmetrical pathway, an estimate of the corresponding dihedral angles for **B**, **C**, and **D** could be deduced from the values of A. Under this assumption that N-inversion moves the two alkyl groups by 19° above and below the plane containing the planar transition state, and the libration rotates the direction of the lone pair (assumed to lie on the plane bisecting the C12,N11,C13 angle) by 101°. The pictures obtained in this way (Scheme III) clearly indicate that conformers **B** and **D**, having the bulkier *i*-Pr group close to the naphthalene, are more hindered, respectively, than **A** and **C**. As a consequence the species I and II of Scheme II mainly reflect the contribution of conformers **A** and **C**, respectively. Both of these conformers have the *i*-Pr group substantially tilted away from the plane of naphthalene (the dihedral angles C9,C1,N11,C13 and C2,C1,N11,C13 are equal to 61 ± 2°) so that the influence of the *i*-Pr moiety upon the conformational stability should essentially be the same in **A** and **C**, as far as the steric effects are concerned. On the contrary, the methyl group is much closer to the plane of naphthalene (C2,C1,N11,C12 and C9,C1,N11,C12 are equal to 18 ± 2°); therefore the corresponding steric interactions will have greater importance in determining the relative stability of the conformers. In conformer **A** the methyl group is close to C2 (which exerts little steric repulsion), whereas in **C** it is close to C9, where a larger steric hindrance is expected, owing to the proximity of C8 and H8. On this ground conformer **C** appears to be more hindered than **A**, thus explaining its lower abundance in solution (according to the analysis of the NOE effect) as well as its absence in the solid state (X-ray structure). The conclusion that the most abundant conformer is that of type A (where the NMe group is closer than the isopropyl group to the plane of naphthalene) is also in agreement with the fact that irradiation of NMe in **2b** yields an NOE effect on H-2 (19.5%) larger than that experienced by H-8 (16%) when NCH is irradiated (Figure 1 and Table II).

Scheme IV



When R is a hydrogen atom (**2a**) the trend of the NOE values previously observed in the tertiary amines **2b**–**d** is reversed. Irradiation of NCH gives a large enhancement (18%) of the H-2 signal, whereas irradiation of NH greatly enhances (31%) the signal of H-8. Such a result, combined with the absence of anisochronous methyl signals at any temperature, indicates that in solution the molecule is most likely planar and conformation II of Scheme IV is by far more important than conformation I.

Again the results of the NOE experiment on **2a** in solution agree with the planar structure obtained by X-ray diffraction for derivative **5** in the crystal. Once more the less populated conformer of type I of Scheme IV is present in solution (as indicated by the pair of smaller NOE effects detected in **2a**), but it is not observed in the solid state.

Experimental Section

Materials. Derivatives **1a**, **2a**, **2b**, **2d**, **3**, and **5** have been described elsewhere.[4,10,11] Derivatives **1b**–**e** were all prepared according to the same procedure, a typical example being the synthesis of ***N*-ethyl-*N*-*tert*-butyl-1-naphthylamine (1e)**. To a cold (−40 °C) solution of *N*-*tert*-butyl-1-naphthylamine[4] (3 g, 15 mmol) in anhydrous ether (10 mL) a 1.6 M *n*-hexane solution (10 mL) of *n*-butyllithium (15 mmol) was added dropwise. After 0.5 h EtI (1.8 mL, 22 mmol) was added, and, after having reached room temperature, the system was left overnight under stirring. After quenching with water the organic layer was separated, washed to neutrality, dried (Na_2SO_4), and concentrated. The residue (3.7 g) was passed through a SiO_2 column (eluent petroleum ether/ether, 95:5) to yield 1.7 g of pure product (yield 50%): ^{1}H NMR (CCl_4, 60 MHz) 0.75 (3 H, t, *Me*CH_2), 1.1 (9 H, s, Me), 3.2 (2 H, m, *CH_2* Me), 7–8 (6 H, m, Ar), 8.6 (1 H, m, H-8), MS, *m/e* 227 (M^+). Anal. Calcd for $C_{16}H_{21}N$: C, 84.58; H, 9.25; N, 6.17. Found: C, 83.9; H, 8.9; N, 6.5.

***N*,*N*-Diethyl-1-naphthylamine (1b).** ^{1}H NMR (CCl_4, 60 MHz) 1.0 (6 H, t, *Me* CH_2), 3.2 (4 H, q, *CH_2* Me), 7–8 (6 H, m, Ar), 8.3 (1 H, m, H-8), MS, *m/e* 199.1351 (calcd for $C_{14}H_{17}N$ 199.1361).

***N*-Ethyl-*N*-isopropyl-1-naphthylamine (1c = 2c).** ^{1}H NMR (CCl_4, 60 MHz) 0.95 (3 H, t, *Me*CH_3), 1.1 (6 H, d, *Me*$_2$CH), 3.2 (2 H, q, *CH_2*Me), 3.4 (1 H, sept, *CH*Me_2), 7–8 (6 H, m, Ar), 8.3 (1 H, m, H-8), MS, *m/e* 213 (M^+). Anal. Calcd for $C_{15}H_{19}N$: C, 84.51; H, 8.92; N, 6.57. Found: C, 83.9; H, 9.3; N, 6.2.

***N*-Ethyl-*N*-(3-pentyl)-1-naphthylamine (1d).** ^{1}H NMR (CCl_4, 60 MHz) 1.0 (9 H, m, *Me*CH_2), 1.5 (4 H, m, CH*CH_2*), 3.1 (3 H, m, NCH and NCH_2), 7–8 (6 H, m, Ar), 8.3 (1 H, m, H-8), MS, *m/e* 241.1820 (calcd for $C_{17}H_{23}N$ 241.1830).

***N*-methyl-*N*-isopropyl-1-(4-nitronaphthyl)amine (4b).** To an acetic acid solution (10 mL) of **2b** (2g, 10 mmol) kept at 10–15 °C was slowly

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added HNO_3 (2 g, 10 mmol). After 2 h the mixture was quenched with ice, extracted with ether, and neutralized ($NaHCO_3$). After removal of solvent the solid residue was purified on a silica column (eluent petroleum ether/benzene, 7:3) and crystallized from EtOH (mp 65–66 °C). The yield in **4b** was about 50% as the isomer nitrated in position 2 and the 2,4-dinitro derivative were also recovered. The presence of the nitro group in position 4 was unambiguously established by complete analysis of the aromatic region of the 300 MHz NMR spectrum of **4b** in acetone-d_6, carried out with the help of homo decoupling and NOE experiments. The following parameters were obtained: ^1H NMR 1.25 (6 H, d, *Me*$_2$CH), 2.92 (3 H, s, MeN), 3.93 (1 H, sept, *CH*Me$_2$), 7.13 (1 H, d, $J_{23} = 8.4$ Hz, H-2), 7.60 (1 H, ddd, $J_{75} = 1.3$ Hz, $J_{76} = 6.6$ Hz, $J_{78} = 8.3$ Hz, H-7), 7.71 (1 H, ddd, $J_{65} = 8.5$ Hz, $J_{67} = 6.6$ Hz, $J_{68} = 1.45$ Hz, H-6), 8.20 (1 H, dddd, $J_{83} = 0.3$ Hz, $J_{85} = 0.75$ Hz, $J_{86} = 1.45$ Hz, $J_{87} = 8.3$ Hz, H-8), 8.28 (1 H, d, $J_{32} = 8.4$ Hz, H-3), 8.66 (1 H, ddd, $J_{56} = 8.5$ Hz, $J_{57} = 1.3$ Hz, $J_{58} = 0.75$ Hz, H-5); MS, *m/e* 244 (M^+). Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.3; H, 6.3; N, 11.9.

***N*-Methyl-*N*-isopropyl-1-(4-aminonaphthyl)amine (4a)** was obtained by reduction of **4b** (2.44 g, 10 mmol) with a stoichiometric amount of hydrogen (Pd as catalyst) in a EtOH solution. The reaction was completed in 1 h with a 95% yield: ^1H NMR ($CDCl_3$, 300 MHz) 1.04 (6 H, d, *Me*$_2$CH) 2.63 (3 H, s, MeN), 3.35 (1 H, sept, *CH*Me$_2$), 3.87 (2 H, br s, NH_2), 6.66 (1 H, d, H-2), 6.91 (1 H, d, H-3), 7.36 (2 H, m, H-6 and H-7), 7.73 (1 H, m, H-5), 8.18 (1 H, m, H-8). Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.9; H, 8.8; N, 12.7.

NMR Spectra. In the variable temperature measurements carried out (Varian XL-100) at 25.16 MHz (^{13}C) and at 100 MHz (^1H), the temperature was determined by substituting the sample with a thermocouple or a thermistor. In the experiments at 300 MHz (Bruker CXP-300) the temperatures were monitored by substituting the samples with a tube containing methanol whose chemical shift difference is calibrated.[12] The values below the freezing point of methanol (−98 °C) were obtained by extrapolating below −98 °C the differences observed at higher temperatures between the real values and those indicated by the dial instrument of the spectrometer. Such a procedure resulted in a larger uncertainty on the temperature, particularly in the case of **3** whose $\Delta G^{\ddagger}$ has thus an error (±0.3 Kcal mol^{-1}) twice as large as that (±0.15) of the other values.

The samples containing the gaseous CHF_2Cl as a solvent were prepared by connecting the NMR tube to a vacuum line and condensing CHF_2Cl by means of liquid nitrogen. The samples were then sealed off and allowed to reach room temperature before being introduced in the precooled probes of the spectrometers.

Line shape analysis of the exchanging signals was performed with a computer program,[13] based on the Bloch equations, written for a personal computer. Sample outputs were cross checked with the standard DNMR program.[14] The nuclear Overhauser enhancement (NOE) experiments were performed at 300 MHz by preirradiating the desired signals for 15–20 s and acquiring the spectrum with the decoupler turned off, so that coupled spectra were obtained. The decoupler power was kept at the minimum value (40–50 db below 0.2 W) required to saturate the irradiated signals. A control experiment, where the irradiation was kept away from any signal, was also carried out. After two dummy scans, eight accumulations were collected for each irradiated signal and the control as well. The cycle was repeated 4–8 times thus resulting into 32–64 accumulations for each spectrum. The FID's, acquired with 16 K for 3 KHz sweep width, were Fourier transformed with 32 K (zero filling) and with a 4–5 Hz line broadening. Subtraction of the control from the various irradiated spectra yielded the differential NOE values reported in Table II. The samples (CCl_4 as solvent with some C_6D_6 for lock) were degassed with nitrogen, and the level of the liquid in the tube was kept at the minimum (0.3 mL) compatible with a reasonable resolution.

The solid-state CP-MAS spectra were obtained at 75.47 MHz (Bruker CXP-300) by using the TOSS sequence that suppresses the side bands. The cross polarization time was 1 ms, the repetition time 30 s, and the spinning rate 2.5 KHz.

X-ray Diffraction. Intensity data were collected by a CAD4 diffractometer by using $\omega/2\vartheta$ scan, ϑ range $2.5° \leqslant \vartheta \leqslant 25°$, Mo K$\alpha$ radiation λ 0.71069 Å. Diffraction intensities were measured with a 1.0 deg scan width and a scan speed variable between 0.7 and 8.0 deg min^{-1}. The unit cell parameters were determined by a least-squares refinement on 25 independent 2ϑ values: range $7° \leqslant \vartheta \leqslant 12.5°$ and $8° \leqslant \vartheta \leqslant 16.2°$ for **4b** and **5**, respectively.

Crystal data for **4b**: space group $P2_1/c$, $a = 10.341$ (7) Å, $b = 10.663$ (4) Å, $c = 11.651$ (4) Å, $\beta = 98.65$ (4)°, $Z = 4$, $V = 1270.1$ Å^3, $F(000) = 520$, $D_c = 1.28$ g cm^{-3}, μ(Mo Kα) = 0.81 cm^{-1}. Out of 2082 unique reflections, 1616 having $I > 2.5\sigma(I)$ were considered observed.

Crystal data for **5**: space group $P2_1/c$, $a = 6.766$ (4) Å, $b = 9.170$ (1) Å, $c = 11.723$ (1) Å, $\beta = 94.39$ (3)°, $Z = 2$, $V = 725.2$ Å^3, $F(000) = 264$, $D_c = 1.11$ g cm^{-3}, μ (Mo Kα) = 0.61 cm^{-1}. Out of 1149 unique reflections, 771 having $I > 2.5\ \sigma(I)$ were considered observed.

The structures were solved by direct methods with the SHELX-76 program packages.[15] Refinement proceeded by full-matrix least-squares methods by using anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were located geometrically (CH distance 1.08 Å) but not refined. The programs XANADU[16] and SCHAKAL[17] were used for geometrical calculations and graphics. The final agreement index was 0.073 and 0.055 for **4b** and **5**, respectively.

Acknowledgment. We thank A. Hasenhindl (Freiburg, FRG) for assistence in recording the CP-MAS NMR spectra, Dr. M. Möller (Freiburg, FRG) for illuminating comments on the solid-state NMR spectra, and Dr. G. A. Weisman (University of New Hampshire) for useful suggestions. Thanks are also due to Dr. J. E. Anderson (University College, London) for helpful discussions on the stereodynamical processes that were made possible by a N.A.T.O. Research Grants Program. This work was carried out with a financial support from the Italian Ministry of Public Education.

Registry No. 1a, 83777-94-0; **1b**, 84-95-7; **1c**, 114326-20-4; **1d**, 114326-21-5; **1e**, 114326-22-6; **2a**, 4960-23-0; **2b**, 110014-41-0; **2d**, 4960-24-1; **3**, 110014-57-8; **4a**, 114326-23-7; **4b**, 114326-24-8; **5**, 786-78-7; *N-tert*-butyl-1-naphthylamine, 54961-92-1.

Supplementary Material Available: A listing of fractional atomic coordinates and thermal parameters and relevant atomic distances for **4b** and **5** (7 pages); observed and calculated structure factors for derivatives **4b** and **5** (13 pages). Ordering information is given on any current masthead page.

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