proton spectra as indicated in the text and in the supplementary material. Because of spectral overlap, multiple processes taking place, and viscosity broadening, it was not always possible to measure rate constants over a wide range of temperature, so enthalpy and entropy of activation were determined from Eyring plots for only the phenyl group rotation.

Acknowledgment. We thank SERC (United Kingdom) for provision of the X-ray equipment, the Ministry of Public Education, Rome, for financial assistance, and NATO for a collaborative research grant.

Supplementary Material Available: Figures A1–A15 showing experimental and calculated spectra for phenyl and *tert*-butyl rotation at the same temperature used to determined the 3:1 ratio of rate constants for these processes and Eyring and Arrhenius plots for phenyl group rotation and tables showing parameters used for spectral simulation, of fractional coordinates, anisotropic thermal parameters, complete lists of bond lengths and interbond angles for X-ray analysis of **2**, and description of data collection and structure refinement (28 pages); observed and calculated structure factors for **2** (7 pages). Ordering information is given on any current masthead page.

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Conformational Studies by Dynamic NMR. 40.[1] Conformational Atropoisomerism in Highly Hindered Naphthylamines

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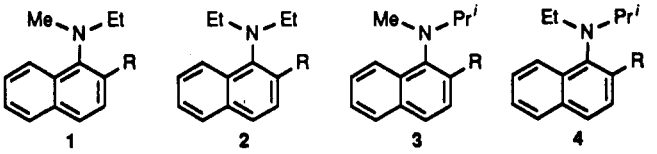
Received April 25, 1990

N,N-Dialkyl-1-naphthylamines substituted by alkyl groups R (R = Me, Et, *i*-Pr, *t*-Bu) in position 2 display anisochronous NMR signals owing to their twisted conformational arrangement. These conformers are enantiomerically related (conformational atropoisomers), and variable temperature NMR measurements allowed the enantiomerization barriers to be determined. The barriers increase with the increasing dimension of the substituents (covering the range 15.7–23.0 kcal mol^{-1}), and the observed trend was reproduced by Molecular Mechanics calculations. The calculations also gave indications upon the structure of the conformers that correspond to energy minima. The final choice among the possible conformations could be achieved by comparing the computed interprotonic distances with the results of NOE experiments.

Introduction

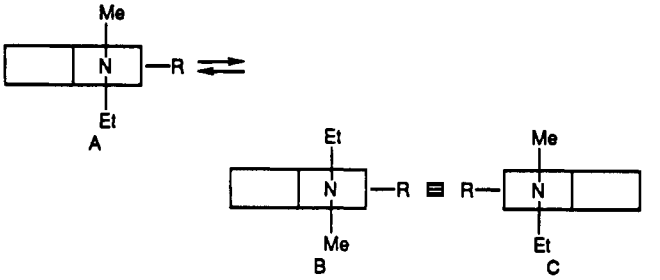
Hindered naphthylamines display conformational atropoisomerism owing to the restriction of the torsional process about the Ar–N bond.[3] It has been shown in fact that *NN*-dialkyl-1-naphthylamines adopt a twisted conformational arrangement both in solution[3] and in the solid state.[4] When two different groups are bonded to the nitrogen atom such a situation gives rise to a pair of conformational enantiomers.[4,5] Dynamic NMR investigations at variable temperature allow one to determine the corresponding free energies of activation for the enantiomerisation process, provided prochiral probes[6,7] (as for instance ethyl or isopropyl group) are introduced in appropriate positions. When such probes are not present, stereomutations can still be observed by NMR if the spectra are taken in the presence of a chiral auxiliary agent.[5,8] In the present study a number of highly hindered 1-naphthylamines were synthesized, and the dependence of their stereodynamics upon the bulkiness of the substituents were investigated by variable-temperature NMR. The conformational ground state of these molecule was also assigned by a combination of NOE (nuclear Overhauser enhancement) experiments and molecular mechanics calculations.

Chart I



a, R = Me; b, R = Et; c, R = *i*-Pr; d, R = *t*-Bu

Scheme I



Results

Dynamic NMR. Within the homogeneous groups of derivatives 1–4 the Ar–N torsional barriers were found to

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Table I. NMR Parameters for the Dynamic Processes of Naphthylamines 1a–4d, 6

compd	$\Delta G^{\ddagger}$,[a] kcal/mol	temp range, °C	observed group	$\Delta\nu$,[b] Hz	J, Hz, gem	solvent	spectrometer frequency
1a	15.7	16–37	NCH_2	10.8 (−40)	12.8	toluene	300
2a	17.5 (12.0)	55–71	NCH_2	17.5 (25)	12.8	toluene	300
3a	17.5	45–58	Me_2CHN	7.5 (25)	–	toluene	200
4a	19.6	75–89	Me_2CHN	8.0 (25)	–	ODCB/DMSO	300
1b	16.5	28–42	$ArCH_2$	11.0 (7)	13.7	CCl_4/Py	200
2b	18.6 (16.0)	80–85	NCH_2	6.0 (50)	12.7	toluene	200
3b	18.6	70–85	Me_2CHN	11.6 (25)	–	toluene	200
4b	21.1	109–114	Me_2CHN	8.4 (25)	–	toluene	200
1c	17.2	50–65	$ArCHMe_2$	23.0 (19)	–	DMSO	200
2c	19.3[c] (17.1)	–	NCH_2	4.5 (60)	12.5	toluene	200
3c	19.3	78–92	Me_2CHN	11.6 (25)	–	DMSO	300
4c	22.3	135–150	$ArCHMe_2$	11.9 (25)	–	DMSO	200
1d	19.6	108–125	NCH_2	61.0 (25)	12.8	ODCB/DMSO	100
2d	21.2 (22.3)	123–133	NCH_2	20.8 (80)	12.2	ODCB/DMSO	100
3d	21.3	125–165	Me_2CHN	125 (40)	–	DMSO	200
4d	23.0	137–150	Me_2CHN	104 (35)	–	DMSO	200
6	21.6	105–118	NCH_2	20 (25)	12.6	C_2Cl_4/C_6D_6	200

[a] The values in parentheses are the theoretical barriers computed by molecular mechanics (see text). [b] Chemical shift differences between the protons of the indicated groups used to monitor the line shape. In parenthesis are reported the temperatures (°C) where the shifts were measured. [c] This barrier could not be measured (see the Experimental Section) and it was assumed equal to that of **3c** by analogy with the pairs **2a**, **3a**; **2b**, **3b**; and **2d**, **3d** (see text).

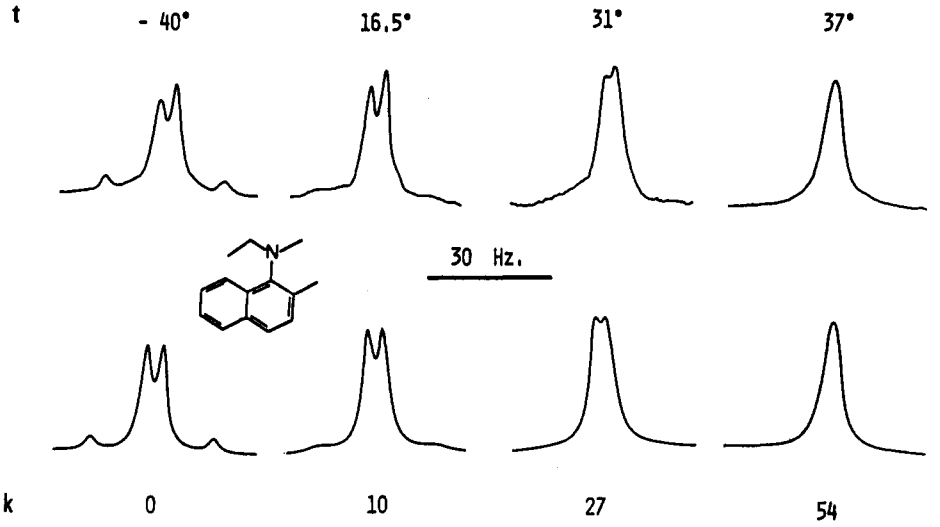

Figure 1. Top trace: 300-MHz signals of the NCH_2 hydrogens of **1a** (decoupled at the frequency of the methyl group of the *N*-ethyl moiety) recorded at four temperatures (t in °C). Lower trace: computer simulations obtained with the enantiomerization rate constants indicated (k in s^{-1}).

increase on increasing the bulkiness of the substituent R (Table I).

These barriers could be measured owing to the presence of prochiral probes (either ethyl or isopropyl groups) and to the existence of a nonplanar conformation where the dynamic plane containing the rapidly inverting nitrogen atom is twisted with respect to the plane of the naphthalene ring. The situation might be described in an approximate manner, as in Scheme I, for the case of **1a–d**.

The two *N*-alkyl groups were drawn for simplicity as staying in the plane where N-inversion occurs, and the dihedral angle formed with the naphthalene ring was considered equal to 90°. N-Inversion is known to have a quite small barrier in aromatic amines,[9] so that the interconversion of A into B via an Ar–N torsion can be considered independent of the inversion process. Owing to the twisted conformation adopted, the ethyl or the isopropyl groups of **1–4** display, respectively, diastereotopic methylene or methyl hydrogens at appropriate temperatures. On raising the temperature, line broadening of the NMR lines occurs and signals corresponding to homotopic CH_2 and CH_3 hydrogens were eventually obtained. In Figure 1 a typical example (derivative **1a**) is reported. The 300-MHz signals of the NCH_2 hydrogens (decoupled at the frequency of the methyl group to eliminate the CH_2–CH_3 coupling constant) display an AB pattern below 0 °C but a single line above 33 °C. The motion responsible for this behavior is the interconversion of A into B. The latter is actually identical with C, i.e. it is the enantiomer of A (Scheme I), so that the rate constants (reported in Figure 1) used to simulate the spectral patterns correspond to enantiomerisation rates. In the case of **2a–d**, however, a molecular plane of symmetry is present even in the twisted conformation, thus making A identical with B (topomers). Therefore, the dynamic process in this case is an enantiotopomerization[8,10] rather than an enantiomerization process.

The significative increasing of the measured $\Delta G^{\ddagger}$ values with the increasing bulkiness of R (Table I) excludes the possibility that N-inversion is responsible for the observed

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Table II. Differential NOE Values (η)[a] Experienced by H-8 (in 2a–d) or by H-2 (in 6) under Conditions of Maximum Enhancement on Irradiation of the Hydrogens of the *N*-Ethyl Moiety

compd	$\eta(NCH_2)$	$\eta(Me)$[b]
2a	18.5	5.0
2b	20.5	5.0
2c	20.0	4.5
2d	12.; 11.[c]	–[d]
6	9.4	1.8

[a] The η values (in $CDCl_3$ at 25 °C) are given as a percent of the original signal, with an estimated error not larger than ±1. [b] Methyl group of the *N*-ethyl moiety. [c] The methylene hydrogens (NCH_2) of **2d** are anisochronous at room temperature: the larger value (12.) refers to the irradiation of the downfield CH signal. The two NOE's remain different both at lower and higher temperatures, e.g. 7.5; 7 at −4 °C and 17; 16 at 50 °C. [d] Owing to the very little amount of available compound, small NOE values could not be detected in **2d**.

dynamic process. The rotational process of Scheme I requires in fact a quasi-planar transition state, more hindered than the ground state, a model which is consistent with an increasing of the barriers (steric deceleration), whereas an opposite trend (steric acceleration) would be expected for N-inversion.[11-15]

NOE Experiments. For the sake of simplicity the conformation of the ground state had been represented in Scheme I without taking into account the preference for one or the other of the possible arrangements available to the pyramidal nitrogen atom (invertomers). A better understanding of the conformational arrangement can be achieved by means of molecular mechanics calculations.[16] In Scheme II the four possible invertomers (I–IV) corresponding to a minimum energy (E in kcal mol^{-1}) are reported for the case of derivatives **2a** and **2d** (where R is, respectively, Me or *t*-Bu). All the invertomers have the plane of the naphthalene ring approximately bisecting the Et–N–Et angle, thus suggesting that the plane where N-inversion occurs is perpendicular to that of the ring, as it had been assumed in Scheme I. Although in the case of **2a** conformer I corresponds to the lowest energy, it seems dubious to conclude that it actually represents the preferred arrangement. This kind of calculations in fact do not allow one to unambiguously choose among conformers having energy differences as small as a few tenths of a kilocalorie per mole. However the interprotonic distances between H-8 and the hydrogens of the two ethyl groups differ significantly in I–IV. This is particularly evident for the pair of invertomers with the nitrogen lone pair directed toward H-8 (III and IV) with respect to those where the lone pair is directed toward the substituent R in position 2 (I and II). Differential nuclear Overhauser enhancement (NOE) can be helpful in determining which is the preferred conformer. In Table II the NOE's (η) experienced by H-8 when irradiating the methylene (NCH_2) and methyl (Me) hydrogens of the ethyl moieties in **2a–c** are reported. The values were obtained with experimental conditions that maximize the NOE and that were identical in the three samples.[4,17] In **2d**, contrary to the case of **2a–c**, the shifts of the diastereotopic methylene hydrogens are quite separated (53 Hz in $CDCl_3$ at 200 MHz). As a consequence each of the two NCH_2 hydrogens was individually irradiated. The resulting NOE on H-8 turns out to be, approximately, half of that observed in **2a–c** where, on the contrary, the methylene hydrogens have a small shift difference and they could be simultaneously irradiated. In derivatives of this type it is expected that the relaxation rate of H-8 is mainly determined by the interactions with the nearby aromatic hydrogens at fixed distances, the contributions due to the hydrogens of the *N*-alkyl groups being conceivably much smaller. According to the theory this implies that the larger the number of irradiated *N*-alkyl protons, the larger will be the NOE at H-8. In the limiting case of relaxations due to *N*-alkyl hydrogens really negligible with respect to other relaxation pathways, increasing n times the number of irradiated *N*-alkyl hydrogens will make the NOE experienced by H-8 exactly n times larger.[18] In order to confirm the observation that in these derivatives the NOE is apparently twice as large when twice as many hydrogens are saturated, one of the two ethyl groups of **2a** was substituted by a CD_2CD_3 group (compound **5**). As shown in Figure 2, the NOE values for H-8 are reduced, in **5**, to half of the value observed in **2a** (Table IV) either when the NCH_2 or the Me signals are irradiated in the same experimental conditions. Accordingly, to have a meaningful comparison with the molecular geometry, the experimental values of **2a–c** have to be divided by 6 or 4, depending on

Table III. Sixth Power of the Ratios (Computed) between the Averaged Distances H-8, Me (r_a) and H-8, NCH_2 (r_b) Calculated for the Invertomers I–IV of Compounds 2a–c[a]

		Computed			
compd	exp[b]	I	II	III	IV
2a	5.5	5.7	7.25	0.95	1.2
2b	6.2	6.7	9.35	0.9	1.0
2c	6.7	6.8	9.5	0.9	1.0
6	7.8	0.6	2.1	3.2	7.1

[a] In the case of **6** the distance are H-2, Me (r_a) and H-2, NCH_2 (r_b). The corresponding reciprocal ratios of the corrected NOE values (exp) are also reported. [b] Ratios between the $\eta(NCH_2)$ and $\eta(Me)$ values of Table II divided for the number of protons being irradiated, i.e. 4 for CH_2 and 6 for Me.

Table IV. Experimental NOE Values (η) Experienced[a] by the H-8 Signals of 1a, 2a, 4a, 5 on Irradiation of the Hydrogens of the Various Groups Indicated in Parentheses

compd	$\eta(NCH_3)$	$\eta(NCH_2)$	$\eta(Me)$[b]	$\eta(NCH)$	$\eta(Me_2)$[c]
1a	7.7	8.5	2.2		
2a		14.5[d]	4[d]		
4a		7.5	2.5	6	3.5
5		7.5	2		

[a] The values ($CDCl_3$ at 25 °C) are expressed as a percent of the original signal with an estimated error not exceeding ±1. [b] Methyl group of the *N*-ethyl moiety. [c] Methyl groups of the *N*-isopropyl moiety. [d] These values are smaller than those of Table II for the same compound (**2a**) as the need for selectivity in **1a** and **4a** required the use of an irradiating power lower than that yielding a maximum enhancement. The same lower power was also used for **2a** and **5** for meaningful comparison.

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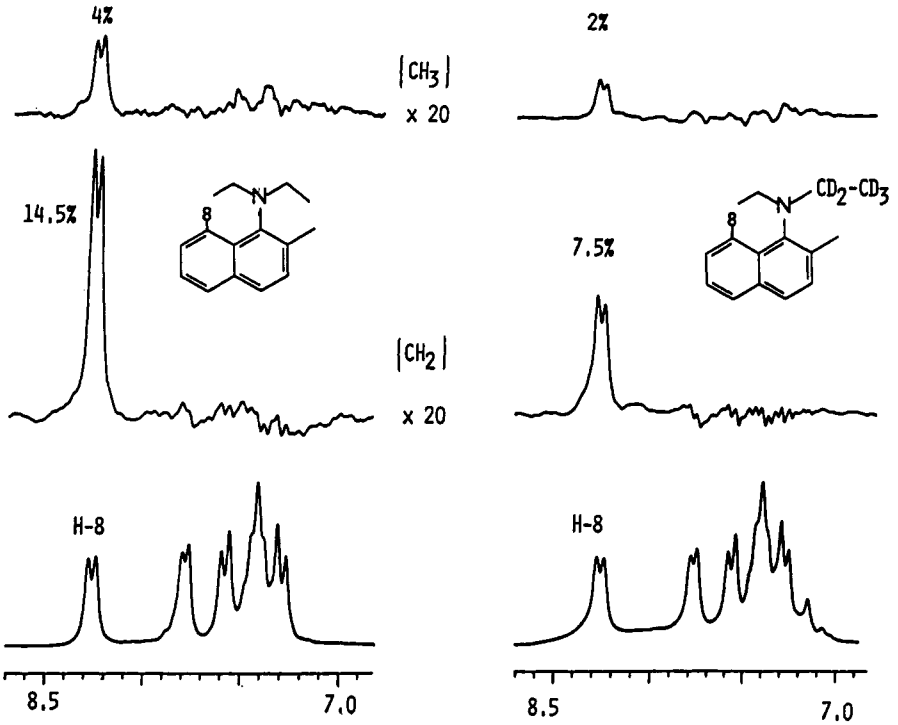
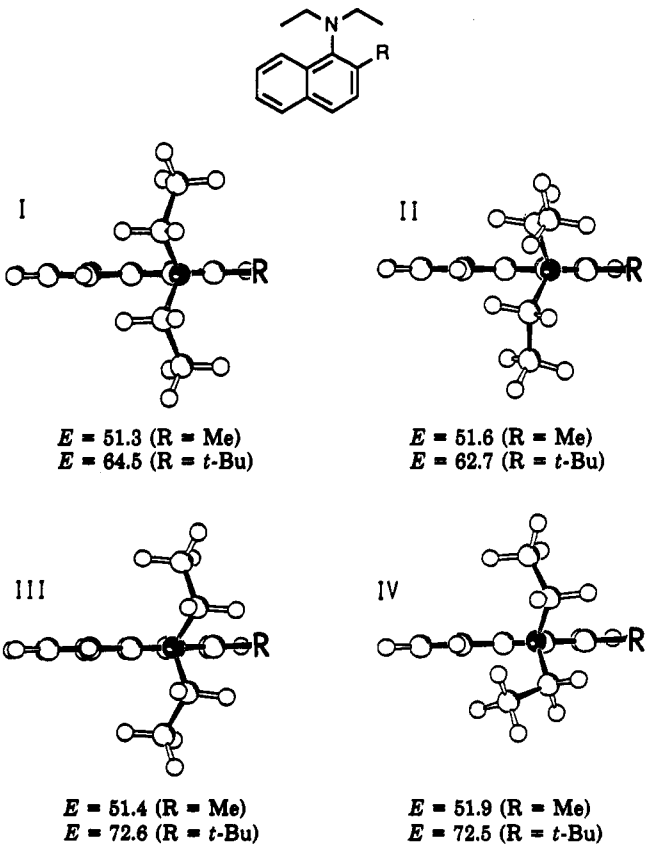


Figure 2. Left: aromatic region of the 200-MHz spectrum of **2a** in $CDCl_3$ (lowest trace). The differential NOE spectra obtained, respectively, on irradiation of the CH_2 and Me signals of the *N*-ethyl moiety are reported above with a 20-fold amplified vertical scale. The observed enhancement of the H-8 signal is indicated. Right: spectra of compound **5**, where one of the two ethyl moieties of **2a** has been replaced by a C_2D_5 group. They were obtained in the same experimental conditions and show that the NOE values are reduced to half those of **2a**, owing to the presence of half of the hydrogens being irradiated in the ethyl moiety.

Scheme II. Top View of the Conformers (I–IV) Corresponding to the Four Energy Minima (*E*, kcal mol^{-1}) as Obtained by MM2 Calculations for 2a (R = Me) and 2d (R = *t*-Bu)



E = 51.3 (R = Me)
E = 64.5 (R = *t*-Bu)

E = 51.6 (R = Me)
E = 62.7 (R = *t*-Bu)

E = 51.4 (R = Me)
E = 72.6 (R = *t*-Bu)

E = 51.9 (R = Me)
E = 72.5 (R = *t*-Bu)

whether the NOE is due to the irradiation of the Me (6 hydrogens) or of the NCH_2 (4 hydrogens) signals. From the MM calculations the averaged interprotonic distances can be obtained for each conformer: r_a represents the H_8,Me and r_b the H_8,NCH_2 distances. In Table III the sixth power of the r_a/r_b ratios in conformers I–IV are compared with the reciprocal ratios of the corrected NOE values obtained for derivatives **2a–c**. Owing to the sixth power relationship[17,18] between distances and NOE, the averages distances r_a and r_b were calculated according to the formula $[(\sum_i r_i^6)/n]^{1/6}$, where r_i corresponds to the individual distance from H-8 of a single hydrogen of the Me or of the NCH_2 moiety and n is equal to 6 in the case of r_a (six r_i distances) or to 4 in the case of r_b (four r_i distances). From Table III it is obvious that the geometries of the invertomers having the nitrogen lone pair directed toward H-8 (i.e. III and IV of Scheme II) are in disagreement with the experiment. On the contrary the geometries computed for the invertomers with the lone pair toward the substituent R in position 2 (i.e. I and II of Scheme II) substantially agree with the NOE experiment. In particular, the more symmetric invertomer I matches almost exactly the NOE values, thus indicating that **2a**, **2b**, **2c** seems to adopt preferentially this conformation.[19] In the case of the highly hindered *tert*-butyl derivative **2d** (where NOE due to saturation of the methyl hydrogens of the ethyl moiety is not available) the calculations indicate that, contrary to **2a–c**, the invertomers of type III, IV have exceedingly larger energies (Scheme II) with respect to the invertomers I, II, thus ruling out their presence on theoretical ground. In particular the less symmetric invertomer II is the most stable one, having an energy 2 kcal mol^{-1}

(19) As the differences between the computed ratios for conformers I, II (Table III) are not very large, it is quite possible that the apparent better agreement of the NOE results with the values computed for conformer I is fortuitous, due to the combination of experimental errors and theoretical approximations. The distinction between I and II is however uninteresting as the really important conclusion is that in **2a–c** the preferred invertomers are undoubtedly those with the N-lone pair electrons directed toward the substituent in position 2 (Scheme II).

Table V. Experimental vs Computed[a] Ratios of the NOE Values (Exp) Observed for the Signal of H-8 on Irradiation of the Pairs of Groups

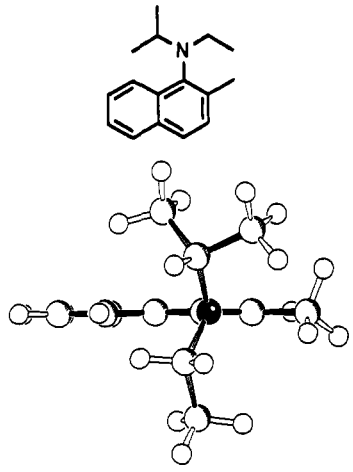
compd	groups[b]	exp[c]	computed
1a	NCH_2/NCH_3	1.65	1.3
	NCH_2/Me	5.8	5.2
	NCH_3/Me	3.5	4.0
4a	NCH_2/Me	4.5	4.2
	NCH/Me	7.2	6.2
	Me_2/Me	0.70	0.50
	NCH/NCH_2	1.6	1.5
	Me_2/NCH_2	0.15	0.12
	Me_2/NCH	0.097	0.082

[a] The sixth power of the reciprocal ratio of the corresponding averaged (see text) interprotonic distances, obtained for the preferred conformer of **1a** and **4a** (computed), are listed in column four. [b] Me represents the methyl group of the ethyl moiety and Me_2 the methyl groups of the isopropyl moiety. [c] These ratios were obtained by dividing the η values of Table IV by the number of protons being irradiated.

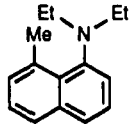
lower than that of I (Scheme II). Inspection of Table II indicates that the pair of NOE values due to the saturation of each of the two anisochronous NCH_2 signals are slightly different, the value corresponding to the saturation of the low-field CH signal being the larger one (12% vs 11%). To check that such a difference really exceeds the experimental errors, the measurements were repeated at different temperatures. Owing to the temperature dependence of the relaxation time T_1 the enhancements become smaller at lower (7.5% and 7%, respectively, at −4 °C) and larger at higher temperatures (17% and 16% at +50 °C). The same ratio is however maintained. The calculations indicate that in the case of **2d** the less stable symmetric invertomer (I in Scheme II) has equal interprotonic distances between H-8 and the two NCH hydrogens (the distance ratio thus being 1.000); this situation would entail two identical NOE's. On the contrary these distances are slightly different in the more stable asymmetric invertomer II (the sixth power ratio of distances being 1.2); two slightly different NOE's are, accordingly, expected. Little doubt seems thus left that, contrary to the case of **2a–c**, the NOE experiments assign to **2d** the arrangement corresponding to the invertomer II, in good agreement with the theoretical predictions.

The same type of investigation was carried out on **1a** and **4a** where one of the two ethyl groups of **2a** is replaced, respectively, by a methyl or an isopropyl group. Owing to the larger number of signals with respect to **2a–d**, the magnitude of the NOE effects had to be traded for selectivity,[17] and an irradiation power lower than in **2a–d** was thus employed. It can be observed (Table IV) that irradiation of the ethyl hydrogens of **1a** or **4a** gives NOE values at H-8 that are, approximately, half those of **2a** in the same experimental conditions. As previously discussed the presence of twice as many saturated ethyl hydrogens in **2a** with respect to either **1a** or **4a** accounts for this finding. Deuteration of one of the ethyl groups of **2a** brings in fact the NOE's of **5** to values analogous to those of **1a**, **4a**. Molecular mechanics calculations carried out on **1a** indicate again that the conformer with the lone pair toward the substituent (i.e. the methyl group in position 2) is more stable (by 0.3 kcal mol^{-1}) than the opposite invertomer. Comparison of computed distances and experimental NOE's (Table V) confirms that only the first of the two arrangements is acceptable. In the case of **4a** neither of the two invertomers has computed distances matching the experiment. This depends upon the fact that in the invertomer with the lone pair toward the substituent in position 2 (which is the most stable, as in **1a**) the distance between H-8 and NCH is too small. Rotation of the isopropyl group of this invertomer by 50° about the N–CH bond yields a conformer that, although not corresponding to a minimum of energy, agrees[20] satisfactorily with the experiment (Table V). The corresponding structure is given in Scheme III.

Scheme III. Conformation of Derivative 4a (Top View) as Obtained from NOE Experiments



All of these results indicate that in the 2-alkyl derivatives the most stable invertomers have the lone pair toward the bulkiest part of the molecule, so that the two *N*-alkyl groups can be accommodated into the less crowded part (in these cases toward H-8). If such an interpretation is correct, when the substituent is placed at position 8 rather than at position 2, the opposite situation would occur. One should therefore expect that the most stable invertomers become those with the lone pair directed toward position 8 (i.e. invertomers of type III, IV of Scheme II). To verify such a prediction the *N*,*N*-diethyl(8-methyl-1-naphthyl)-amine **6** was prepared.



6

The molecule is quite hindered having an Ar–N rotational barrier (21.6 kcal mol^{-1}) similar to that (21.2 kcal mol^{-1}) of the analogous *N*,*N*-diethyl derivative, with a *tert*-butyl in position 2 (**2d**). Therefore the two NCH_2 hydrogens of **6** are anisochronous at room temperature. Contrary to the case of **2d**, however, the shift difference is so small that both signals were simultaneously irradiated in the NOE experiments. The MM calculations indicate that the invertomers of type I, II (R = H in Scheme II for the case of **6**) have energy much higher (by as much as 15–16 kcal mol^{-1}) than those of invertomers of type III, IV where the lone pair is directed toward position 8. The latter ones have essentially the same computed energy, but only the asymmetric conformer of type IV has distances H-2,Me (r_a) and H-2,NCH_2 (r_b) that agree with the experimental NOE values measured for **6** (Table III). It is also worth mentioning that in the more crowded derivatives, such as **2d** and **6**, the less symmetric invertomers are

(20) It might seem a too easy explanation the suggestion that in solution the isopropyl moiety prefers a different arrangement with respect to that calculated for an isolated molecule. Nonetheless the barrier for the *i*-Pr–N rotation is expected to be so small that the population of the rotamers can easily be affected by the solvent.

apparently preferred with respect to the symmetric ones.

Discussion

Examination of the free energies of activation reported in Table I indicates that the steric effect is additive. The differences between the values of **2a–d** and the corresponding values of **1a–d** represent the effect due to the introduction of an additional methyl group, i.e. the effect observed in transforming a *N*-Me into a *N*-Et group. This value (average of four differences) is 1.9 ± 0.2 kcal mol^{-1} and it is equal to that obtained using the differences between the barriers of **4a–d** and those of **3a–d** (2.3 ± 0.4 kcal mol^{-1}) that are also a measure of the transformation of a *N*-Me into a *N*-Et group. The introduction of a second methyl group (i.e. the transformation of *N*-Et into a *N*-*i*-Pr moiety) also gives analogous values, as shown by the differences between the corresponding barriers of **4a–d** and those of **2a–d** (2.3 ± 0.4 kcal mol^{-1}) as well as between the barriers of **3a–d** and those of **1a–d** (1.9 ± 0.2 kcal mol^{-1}). It seems possible to conclude that each methyl group added to a carbon bonded to the nitrogen atom contributes to the increasing of the steric effect (as measured by the Ar–N rotational barrier) approximately by 2 kcal mol^{-1}. According to this conclusion it should be irrelevant whether the additional methyl group is introduced upon one or the other of the two N-bonded carbons. This nicely accounts for the fact that the barriers observed for the Et–N–Et moieties are equal to those observed for the Me–N–*i*-Pr moieties (the values of **2a,b,d** were found equal, respectively, to those of **3a,b,d**). Such an occurrence allows us to predict the barrier of **2c** that could not be directly measured (see the Experimental Section), owing to the extremely small shift difference of the *N*-CH_2 hydrogens: the same value as **3c** (19.3 kcal mol^{-1}) was thus assigned to **2c** on the basis of this analogy. The steric effects brought about by the substituents in position 2 of the naphthalene ring are smaller than those observed for the analogous variations at the N-substituents. For, when a methyl in position 2 is transformed into an ethyl group, the barrier increases by 1.1 ± 0.2 kcal mol^{-1}, as shown by the differences between the ΔG^* values of **1b–4b** and those, respectively, of **1a–4a**. Introduction of a second methyl group in position 2 (i.e. transformation of an ethyl into an isopropyl group) increases the barriers by 0.8 ± 0.2 kcal mol^{-1}, as shown by the differences between the ΔG^* values of **1c–4c** and those, respectively, of **1b–4b**. Apparently, introduction of each additional methyl group to the carbon in position 2 of a naphthalene ring increases the barrier by approximately 1 kcal mol^{-1}. This effect is about half that (≈2 kcal mol^{-1}) due to the introduction of an additional methyl group at the N-bonded carbon of the amino moieties. Such additivities for the steric effect had been indeed predicted[21] in the series Me, Et, *i*-Pr, *t*-Bu on the basis of molecular mechanics calculations. The parameter defining the hindrance (Ω_s) varies in steps of 0.044 ± 0.002 for each subsequent addition of a methyl group to a carbon atom. Thus the parameter defining the hindrance of a methyl group (0.288) becomes, respectively, 0.332 and 0.377 for an ethyl or an isopropyl group.[21] In our series however, the additivity breaks down when a *tert*-butyl moiety is involved. Transformation of an isopropyl into a *tert*-butyl group entails a larger steric effect in a not too crowded molecule (e.g. 2.4 kcal mol^{-1} going from **1c** to **1d**) but a much smaller one when the presence of bulkier N-substituents makes the molecule more crowded (e.g. the effect is only 0.7 kcal mol^{-1} going from **4c** to **4d**).

It is also worth mentioning that substitution of a hydrogen atom with a methyl group has an extremely larger effect. For instance the difference between the barriers reported in the literature[4,5] (the ΔG^* range being 8.3–11.2 kcal mol^{-1}) for naphthylamines without a substituent in position 2 (i.e. R = H in Chart I) and the corresponding (2-methylnaphthyl)amines (i.e. **1a–4a**) is 7.8 ± 0.6 kcal mol^{-1}. If the methyl is in position 8, as for instance in derivative **6**, the difference with the corresponding unsubstituted naphthylamine (i.e. *N*,*N*-diethyl-1-naphthylamine having a ΔG^* = 8.95 kcal mol^{-1})[4] is even larger, being equal to 12.65 kcal mol^{-1}. Substitution of a N–H hydrogen with an Me group also produces an equally large effect; the difference between the barrier of **1d** (19.6 kcal mol^{-1}) and that reported[4] (7.0 kcal mol^{-1}) for the corresponding secondary amine [i.e. *N*-ethyl(2-*tert*-butyl-1-naphthyl)amine] is again 12.6 kcal mol^{-1}.

Molecular mechanics calculations are also helpful in describing the dynamics of the enantiomerization (or enantiotopomerization) process. Thus, in addition to the energies of the twisted rotational ground states, also the energies corresponding to the quasi-planar rotational transition states were calculated for compounds **2a–d**. Only in the twisted ground state (see Scheme II) the lone pair electrons were explicitly localized upon the nitrogen orbital in order to obtain a better description of the electrostatic and nonbonded interactions associated with the sp^3 hybridization. The energy differences computed with this model are reported in parenthess in Table I, beside the experimental values of **2a–d**. The observed trend is well reproduced by the theoretical model and also the computed values are in reasonable agreement with the experiment, the average deviation being about 15%. A study of the energy profile as function of the Ar–N torsion (i.e. the dependence of the energy upon the C2–C1–N–CH_2 dihedral angle) indicates that the rotational transition state with the highest energy correspond to the situation whereby one of the two *N*-ethyl groups passes over the carbon (C2) bearing the substituent R (i.e. the C2–C1–N–CH_2 dihedral angle is 0°) rather than the situation where the same ethyl group passes over H-8. Owing to the extreme crowding the nitrogen atom, although in conjugation with the ring in the transition state, is not perfectly planar, so that when one ethyl group passes over C2 the other is not yet over H-8 and vice versa. The difference between the energies of the two situations is quite small for **2a**, when R = Me, (≈1 kcal mol^{-1}) but increases significantly (3 kcal mol^{-1}) for **2d** (R = *t*-Bu).

Experimental Section

Materials. The tertiary *N*,*N*-dialkyl(2-alkyl-1-naphthyl)amines were prepared according to a general method which is described in detail for the case of **4c**.

***N*-Ethyl-*N*-isopropyl(2-isopropyl-1-naphthyl)amine (4c).** To a cold (−40 °C) solution of *N*-isopropyl(2-isopropyl-1-naphthyl)amine (645 mg, 2.8 mmol) in anhydrous ether (50 mL) an ethereal 1.5 M solution of methyllithium (2 mL, 3.1 mmol) was added dropwise. After 2 h ethyl iodide (0.34 mL, 4.3 mmol) was added and, after having reached room temperature, the system was allowed to reflux for 100 h. The cooled mixture was treated with water and left for 1 h under stirring. Two phases were separated, and the organic layer was washed many times, dried, and concentrated. The residue was chromatographed on a silica gel column (eluent petroleum ether/ether, 100:2) to yield 300 mg of **4c**.

The others derivatives **1a–4a**, **1b–4b**, **1c–3c**, **1d–4d**, were also obtained by preparing the lithium salt of the appropriate secondary *N*-alkyl(2-alkyl-1-naphthyl)amine (where *N*-alkyl is an ethyl or an isopropyl group) which subsequently reacted with

(21) Kamatsuzaki, T.; Sakakibara, K.; Hirota, M. *Tetrahedron Lett.* **1989**, *30*, 3309.

methyl or ethyl iodide. In every reaction the molar ratio amine/iodide was 1.0–1.5. In the case of derivatives **1a–d** and **2a–d** the reactions were carried out at room temperature for 24–70 h. In the case of derivatives **3a–c** and **4a–b** the reactions were refluxed for 100 h. In order to obtain compounds **3d** and **4d**, the mixture had to be transferred into an autoclave and allowed to react for 100 h at 120 °C under nitrogen pressure (60 atm). In every case the raw materials were chromatographed on a silica gel column using petroleum ether or petroleum ether/ether, 100:2, as eluent.

***N*-(Ethyl-d_5)-*N*-ethyl(2-methyl-1-naphthyl)amine (5)** was obtained in the same way as the other tertiary amines by reacting at −40 °C *N*-ethyl(2-methyl-1-naphthyl)amine with methyllithium and then with CD_3CD_2I. The reaction was completed in 15 h at room temperature with a 63% yield.

The tertiary amines were identified as follow:

***N*-Ethyl-*N*-methyl(2-methyl-1-naphthyl)amine (1a)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.10 (3 H, t, CH_3CH_2N), 2.46 (3 H, s, CH_3Ar), 2.98 (3 H, s, CH_3N), 3.29 (2 H, m, CH_2N), 7.26 (1 H, d, H-3), 7.33–7.51 (2 H, br m, H-6, H-7), 7.57 (1 H, d, H-4), 7.78 (1 H, d, H-5), 8.24 (1 H, m, H-8); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.90 (CH_3CH_2N), 19.84 (CH_3Ar), 41.49 (CH_3N), 50.87 (CH_2N), 125.39, 125.60, 126.14, 126.33, 128.91, 130.77, 134.57 (quat), 137.21 (quat), two quaternary carbons were not detected; MS, molecular ion at *m/e* 199.13628, calcd 199.13610 (0.91 ppm). Anal. Calcd for $C_{14}H_{17}N$: C, 84.42; H, 8.54; N, 7.04. Found: C, 83.9; H, 8.7; N, 7.3.

***N*,*N*-Diethyl(2-methyl-1-naphthyl)amine (2a)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.00 (6 H, t, CH_3CH_2N), 2.44 (3 H, s, CH_3Ar), 3.19–3.38 (4 H, m, CH_2N), 7.26 (1 H, d, H-3), 7.33–7.46 (2 H, m, H-6, H-7), 7.55 (1 H, d, H-4), 7.75 (1 H, m, H-5), 8.23 (1 H, d, H-8); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 15.42 (CH_3CH_2N), 19.95 (CH_3Ar) 49.08 (CH_2N), 125.48, 125.84, 126.09 (2 C), 128.88, 130.55, 134.58 (quat), 135.50 (quat), two quaternary carbons were not detected; MS, molecular ion at *m/e* 213.15209, calcd 213.15175 (1.60 ppm). Anal. Calcd for $C_{15}H_{19}N$: C, 84.51; H, 8.92; N, 6.57. Found: C, 84.2; H, 9.2; N, 6.8.

***N*-Methyl-*N*-isopropyl(2-methyl-1-naphthyl)amine (3a)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.07–1.25 (6 H, m, $(CH_3)_2CHN$), 2.5 (3 H, s, CH_3Ar), 2.98 (3 H, s, CH_3N), 3.65 (1 H, sept, CHN), 7.30 (1 H, d, H-3), 7.35–7.55 (2 H, br m, H-6, H-7), 7.60 (1 H, d, H-4), 7.8 (1 H, d, H-5), 8.25 (1 H, d, H-8). Anal. Calcd for $C_{15}H_{19}N$: C, 84.50; H, 8.93; N, 6.57. Found: C, 85.1; H, 8.5; H, 6.2.

***N*-Ethyl-*N*-isopropyl(2-methyl-1-naphthyl)amine (4a)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.91 (3 H, t, CH_3CH_2N), 1.01–1.14 (6 H, m, $(CH_3)_2CHN$), 2.47 (3 H, s, CH_3Ar), 3.17–3.44 (2 H, m, CH_2N), 3.52–3.74 (1 H, sept, CHN), 7.28 (1 H, d, H-3), 7.35–7.65 (3 H, br m, H-4, H-6, H-7), 7.80 (1 H, d, H-5), 8.25 (1 H, d, H-8). Anal. Calcd for $C_{16}H_{21}N$: C, 84.58; H, 9.25; N, 6.17. Found: C, 84.2; H, 9.1; H, 6.5.

***N*-Ethyl-*N*-methyl(2-ethyl-1-naphthyl)amine (1b)**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10 (3 H, t, CH_3CH_2N), 1.26 (3 H, t, CH_3CH_2Ar), 2.83 (2 H, m, CH_2Ar), 2.96 (3 H, s, CH_3N), 3.26 (2 H, q, CH_2N), 7.31 (1 H, d, H-3), 7.34–7.48 (2 H, br m, H-6, H-7), 7.60 (1 H, d, H-4), 7.77 (1 H, d, H-5), 8.17 (1 H, d, H-8); MS, molecular ion at *m/e* 213.15147, calcd 213.15175 (1.31 ppm). Anal. Calcd for $C_{15}H_{19}N$: C, 84.51; H, 8.92; N, 6.57. Found: C, 85.0; H, 8.5; N, 6.3.

***N*,*N*-Diethyl(2-ethyl-1-naphthyl)amine (2b)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.03 (6 H, t, CH_3CH_2N), 1.26 (3 H, t, CH_3CH_2Ar), 2.88 (2 H, q, CH_2Ar), 3.29 (4 H, q, CH_2N), 7.35–7.48 (3 H, m, H-3, H-6, H-7), 7.62 (1 H, d, H-4), 7.77 (1 H, d, H-5), 8.22 (1 H, d, H-8); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 15.53 (CH_3CH_2Ar), 15.86 (CH_3CH_2N), 25.26 (CH_2Ar), 49.84 (CH_2N), 125.64, 126.12, 126.62, 128.57 (2 C), 128.91, 134.44 (quat), 142 (quat), 145 (quat), one quaternary carbon was not detected. Anal. Calcd for $C_{16}H_{21}N$: C, 84.58; H, 9.25; N, 6.17. Found: C, 84.2; H, 9.6; N, 5.17.

***N*-Methyl-*N*-isopropyl(2-ethyl-1-naphthyl)amine (3b)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.1 (6 H, m, $(CH_3)_2CHN$), 1.3 (3 H, t, CH_3CH_2Ar), 2.80 and 2.95 (2 H, m, CH_2Ar), 3.00 (3 H, s, CH_3N), 3.63 (1 H, sept, CHN), 7.30–7.50 (3 H, m, H-3, H-6, H-7), 7.65 (1 H, d, H-4), 7.80 (1 H, dd, H-5), 8.20 (1 H, dd, H-8). Anal. Calcd for $C_{16}H_{21}N$: C; 84.58; H, 9.25; N, 6.17. Found: C, 84.1; 9.5; N, 6.3.

***N*-Ethyl-*N*-isopropyl(2-ethyl-1-naphthyl)amine (4b)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.91 (3 H, t, CH_3CH_2N), 1.06 (6 H, 2 d, $(CH_3)_2CHN$), 1.29 (3 H, t, CH_3CH_2Ar), 2.91 (2 H, m, CH_2Ar), 3.32 (2 H, m, CH_2N), 3.63 (1 H, sept, CHN), 7.33–7.50 (3 H, br m, H-3, H-6, H-7), 7.65 (1 H, d, H-4), 7.78 (1 H, dd, H-5), 8.23 (1 H, dd, H-8); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 15.43 (CH_3CH_2Ar), 16.60 (CH_3CH_2N), 23.21 and 23.47 ($(CH_3)_2CHN$), 30.27 (CH_2Ar), 47.18 (CH_2N), 54.34 (CHN), 125.45, 126.02, 126.33, 126.58, 128.21, 128.85, quaternary carbons were not detected. Anal. Calcd for $C_{17}H_{23}N$: C, 84.65; H, 9.54; N, 5.81. Found: C, 84.9; H, 9.1; N, 5.9.

***N*-Ethyl-*N*-methyl(2-isopropyl-1-naphthyl)amine (1c)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.97 (3 H, t, CH_3CH_2N), 1.17 (6 H, d, $(CH_3)_2CHAr$), 2.87 (3 H, s, CH_3N), 3.16 (2 H, q, CH_2N), 3.57 (1 H, sept, CHAr), 7.29–7.48 (3 H, br m, H-3, H-6, H-7), 7.65 (1 H, d, H-4), 7.78 (1 H, d, H-5), 8.08 (1 H, d, H-8); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 14.82 (CH_3CH_2N), 23.71 and 24.15 ($(CH_3)_2CHAr$), 28.05 (CHAr), 41.83 (CH_3N), 50.87 (CH_2N), 124.80 (2 C), 124.94, 125.38, 126.09, 128.10, 133.43 (quat), 133.59 (quat), 144.35 (quat), 145.28 (quat). Anal. Calcd for $C_{16}H_{21}N$: C, 84.58; H, 9.25; N, 6.17. Found: C, 84.7; H, 9.0; N, 6.4.

***N*,*N*-Diethyl(2-isopropyl-1-naphthyl)amine (2c)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.98 (6 H, t, CH_3CH_2N), 1.23 (6 H, d, $(CH_3)_2CHAr$), 3.25 (4 H, q, CH_2N), 3.70 (1 H, sept, CHAr) 7.33–7.45 (3 H, br m, H-3, H-6, H-7), 7.65 (1 H, d, H-4), 7.78 (1 H, d, H-5), 8.20 (1 H, d, H-8). Anal. Calcd for $C_{17}H_{23}N$: C, 84.65; H, 9.54; N, 5.81. Found: C, 84.1; H, 9.8; N, 6.1.

***N*-Methyl-*N*-isopropyl(2-isopropyl-1-naphthyl)amine (3c)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.10 (6 H, 2 d, $(CH_3)_2CHAr$), 1.27 (6 H, m, $(CH_3)_2CHN$), 2.99 (3 H, s, CH_3N), 3.68 (2 H, m, CHAr and CHN), 7.30–7.52 (3 H, br m, H-3, H-6, H-7), 7.69 (1 H, d, H-4), 7.78 (1 H, br d, H-5), 8.19 (1 H, d, H-8); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.03, 22.42, 23.07, 24.34 ($(CH_3)_2CH$), 28.03 (CHAr), 39.80 (CH_3N), 53.41 (CHN), 124.78, 124.91, 125.34, 125.55, 126.42, 128.30, 133.66 (quat), 134.69 (quat), 144.17 (quat), 145.91 (quat). Anal. Calcd for $C_{17}H_{23}N$: C, 84.65; H, 9.54; N, 5.81. Found: C, 85.1; H, 9.2; N, 5.5.

***N*-Ethyl-*N*-isopropyl(2-isopropyl-1-naphthyl)amine (4c)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.93 (3 H, t, CH_3CH_2N), 1.06 (6 H, m, $(CH_3)_2CHAr$), 1.26 (6 H, d, $(CH_3)_2CHN$), 3.16–3.46 (2 H, m, CH_2N), 3.64 (1 H, sept, CHAr), 3.75 (1 H, sept, CHN), 7.35–7.50 (3 H, m, H-3, H-6, H-7), 7.67 (1 H, d, H-4), 7.76 (1 H, dd, H-5), 8.21 (1 H, d, H-8); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 16.46 (CH_3CH_2N), 22.71, 23.30, 23.74, 24.03 ($(CH_3)_2CH$), 27.86 (CHAr), 46.97 (CH_2N), 53.86 (CHN), 124.65 (2 C), 125.18, 125.60, 126.17, 128.00, 133.15 (quat), 135.16 (quat), 146.50 (quat), one quaternary carbon was not detected. Anal. Calcd for $C_{18}H_{25}N$: C, 84.71; H, 9.80; N, 5.49. Found: C, 84.3; H, 10.2; N, 5.7.

***N*-Ethyl-*N*-methyl(2-*tert*-butyl-1-naphthyl)amine (1d)**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.20 (3 H, t, CH_3CH_2N), 1.51 (9 H, s, $(CH_3)_3C$), 2.96 (3 H, s, CH_3N), 3.03 and 3.62 (2 H, m, CH_2N), 7.34 (2 H, m, H-6, H-7), 7.57 (2 H, s, H-3, H-4), 7.75 (1 H, m, H-5), 7.95 (1 H, m, H-8); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.143 (CH_3CH_2N), 32.446 ($(CH_3)_3C$), 36.700 ($C(CH_3)_3$), 42.371 (CH_3N), 51.585 (CH_2N), 125.395, 125.625, 126.054, 126.869, 126.964, 129.453, 135.132 (quat), 147.302 (quat), two quaternary carbons were not detected. Anal. Calcd for $C_{17}H_{23}N$: C, 84.65; H, 9.45; N, 5.81. Found: C, 85.1; H, 9.2; N, 5.6.

***N*,*N*-Diethyl(2-*tert*-butyl-1-naphthyl)amine (2d)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.06 (3 H, t, CH_3CH_2N), 1.53 (9 H, s, $(CH_3)_3C$), 3.27 and 3.63 (4 H, m, CH_2N), 7.38 (2 H, br m, H-6, H-7), 7.62 (2 H, s, H-3, H-4), 7.78 (1 H, m, H-5), 7.92 (1 H, m, H-8). Anal. Calcd for $C_{18}H_{25}N$: C, 84.71; H, 9.80; N, 5.49. Found: C, 84.3; H, 10.3; N, 5.3.

***N*-Methyl-*N*-isopropyl(2-*tert*-butyl-1-naphthyl)amine (3d)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.74 and 1.33 (6 H, 2 d, $(CH_3)_2CHN$), 1.55 (9 H, s, $(CH_3)_3C$), 3.0 (3 H, s, CH_3N), 3.85 (1 H, sept, CHN), 7.30–7.40 (2 H, br m, H-6, H-7), 7.60 (2 H, H-3, H-4), 7.78 (1 H, m, H-5), 7.95 (1 H, m, H-8); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.00 and 22.40 ($(CH_3)_2CHN$), 33.32 ($(CH_3)_3C$), 36.99 ($C(CH_3)_3$), 44.32 (CH_3N), 55.82 (CHN), 125.45, 125.78, 125.96, 126.67, 127.50, 129.28, 134.61 (quat), 136.61 (quat), 146.70 (quat), 148.00 (quat). Anal. Calcd for $C_{18}H_{25}N$: C, 84.71; H, 9.80; N, 5.49. Found: C, 84.9, H, 10.1; N, 5.1.

***N*-Ethyl-*N*-isopropyl(2-*tert*-butyl-1-naphthyl)amine (4d)**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.90 (3 H, t, CH_3CH_2N), 0.80 and

1.30 (6 H, 2 d, $(CH_3)_2CHN$), 1.55 (9 H, s, $(CH_3)_3C$), 3.4 (2 H, m, CH_2N), 3.85 (1 H, sept, CHN), 7.4 (2 H, br m, H-6, H-7), 7.60 (2 H, s, H-3, H-4), 7.75 (1 H, m, H-5), 7.95 (1 H, m, H-8). Anal. Calcd for $C_{19}H_{27}N$: C, 84.76; H, 10.04; N, 5.20. Found: C, 85.0; H, 10.2; N, 4.8.

***N*-(Ethyl-d_5)-*N*-ethyl(2-methyl-1-naphthyl)amine (5)**: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.03 (3 H, t, CH_3CH_2N), 2.45 (3 H, s, CH_3Ar) 3.28 (2 H, m, CH_2N), 7.27 (1 H, d, H-3), 7.32–7.48 (2 H, m, H-6, H-7), 7.56 (1 H, d, H-4), 7.77 (1 H, m, H-5), 8.25 (1 H, d, H-8).

The secondary *N*-alkyl(2-alkyl-1-naphthyl)amines (*N*-alkyl = Et, *i*-Pr) used as precursors of the tertiary amines were all prepared according to the same procedure, a typical example being the synthesis of *N*-isopropyl(2-isopropyl-1-naphthyl)amine required to obtain 4c. To a cold (−40 °C) solution of (2-isopropyl-1-naphthyl)amine (2.20 g, 12 mmol) in anhydrous ether (50 mL) was added dropwise an ethereal 1.5 M solution of methyllithium (8.8 mL, 13.2 mmol). After 2 h isopropyl iodide (1.8 mL, 18 mmol) was added, and the system was allowed to reflux for 24 h. The cooled mixture was treated with water and left for 1 h with stirring. Two phases were separated, and the organic layer was washed many times, dried, and concentrated. The residue was purified on a silica gel column (eluent petroleum ether/ether, 10:1) to yield 1.4 g of pure compound: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.09 (6 H, d, $(CH_3)_2CHN$), 1.19 (6 H, d, $(CH_3)_2CHAr$), 3.04 (1 H, br s, NH), 3.33 (1 H, sept, CHAr), 3.45 (1 H, sept, CHN), 7.22–7.46 (4 H, br m, Ar) 7.65 (1 H, d, H-5), 8.01 (1 H, d, H-8); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 24.25 (4 C, CH_3), 28.15 (CHAr), 51.75 (CHN), 123.94, 124.78 (2 C), 125.64, 125.85, 128.95, 134.0 (quat), 137.50 (quat), 140.48 (quat), one quaternary carbon was not detected.

The (2-alkyl-1-naphthyl)amines (where the 2-alkyl group is a methyl, ethyl, or isopropyl) were obtained by reducing the appropriate 2-alkyl-1-nitronaphthalene with a stoichiometric amount of hydrogen (Pd as catalyst) in a EtOH solution.

On the other hand the (2-*tert*-butyl-1-naphthyl)amine was obtained by reacting 1-naphthylamine with *tert*-butyl alcohol in an autoclave at high temperature (130–150 °C) for 24 h under nitrogen pressure (20 atm). The NMR values matches those reported in ref 5.

2-Methyl-1-nitronaphthalene (fp 70–72 °C), 2-ethyl-1-nitronaphthalene (fp 51–53 °C), and 2-isopropyl-1-nitronaphthalene (fp 48–50 °C) were obtained by reacting the appropriate 2-alkylnaphthalene with a 65% solution of nitric acid for 6 h at 70 °C, for 48 h at room temperature, and for 15 h at room temperature, respectively. The raw material was purified on a silica gel column using petroleum ether as eluent.

2-Methylnaphthalene and 2-ethylnaphthalene are commercially available whereas 2-isopropylnaphthalene was prepared according to the literature.[22]

***N*,*N*-Diethyl(8-methyl-1-naphthyl)amine (6).** To a cold (−40 °C) solution of (8-methyl-1-naphthyl)amine (420 mg, 2.7 mmol) in anhydrous ether (50 mL) an ethereal 1.5 M solution of methyllithium (2.0 mL, 3.0 mmol) was added dropwise. After 2 h ethyl iodide (0.32 mL, 4.0 mmol) was added. Subsequently the mixture was transferred at room temperature into an autoclave and allowed to react for 60 h at 120 °C under nitrogen pressure (60 atm). The cooled mixture was treated with water and left for 1 h under stirring. Two phases were separated, and the organic layer was washed many times, dried, and concentrated. The residue was purified on a silica gel column, using petroleum ether as eluent, to yield 20 mg of 6. In addition *N*-ethyl(8-methyl-1-naphthyl)amine (200 mg) was also recovered. Derivative 6 had the following: ^1H NMR ($CDCl_3$, 200 MHz) δ 0.99 (6 H, t, CH_3CH_2N), 2.98 (3 H, s, CH_3Ar), 3.12 (4 H, m, CH_2N), 7.2–7.4 (4 H, br m, Ar), 7.57 (1 H, dd, H-4), 7.66 (1 H, dd, H-5). Anal. Calcd for $C_{15}H_{19}N$: C, 84.51; H, 8.92; N, 6.57. Found: C, 84.8; H, 8.6; N, 6.4.

(8-Methyl-1-naphthyl)amine was obtained by reducing 1-methyl-8-nitronaphthalene (1.63 g, 8.70 mmol) with a stoichiometric amount of hydrogen (Pd as catalyst) in an EtOH solution. The reaction was completed in 48 h with a 73% yield: ^1H NMR ($CDCl_3$, 200 MHz) δ 3.0 (3 H, s, CH_3Ar), 4.3 (2 H, br s, NH_2), 6.67 (1 H, dd, H-2), 7.1 (1 H, d, H-7), 7.18–7.30 (3 H, br m, H-3, H-6, H-4), 7.58 (1 H, d, H-5); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 25.7 (CH_3), 112.7, 120.8, 126.1, 126.8, 128.3, 129.0, quaternary carbons were not detected.

1-Methyl-8-nitronaphthalene[23,24] was obtained by reacting a solution of 1-methylnaphthalene (14.2 g, 0.1 mol) in acetic acid (50 mL) with a 90% solution of nitric acid (6.0 mL, 0.1 mol). After 180 h at room temperature the mixture was quenched with ice, extracted with ether, and neutralized ($NaHCO_3$). After removal of the solvent the residue was distilled in vacuo to remove 1-methylnaphthalene as well as 1-methyl-4-nitronaphthalene (which is the main reaction product). After chromatography on a silica gel column (petroleum ether as eluent) 1.8 g of pure product was obtained. The presence of the nitro group in position 8 was unambiguously established by complete analysis of the aromatic region of the 200-MHz spectrum in benzene-d_6, carried out with the help of homodecoupling and NOE experiments. The following parameters were obtained: ^1H NMR (C_6D_6, 200 MHz) δ 2.45 (3 H, s, CH_3), 6.73 (1 H, dd, H-6), 6.94 (1 H, br d, H-2), 7.04 (1 H, dd, H-3), 7.10 (1 H, dd, H-5), 7.32 (1 H, br d, H-4), 7.37 (1 H, dd, H-7); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 20.64 (CH_3), 122.80, 124.72, 127.98, 128.04, 132.45, 133.51, quaternary carbons were not detected; mass spectrum, *m/e* 187 (M^+), 170 (M − OH), 142 (M − NO_2 + 1), 141 (M − NO_2), 140 (M − HNO_2), 129 (M − NOCO); the relatives intensities of the fragmentation peaks are consistent with those reported in ref 24.

Spectral Measurements. the variable-temperature NMR spectra were recorded by decoupling either the methyl of the ethyl group or the methine of the isopropyl group when, respectively, the anisochronous signals of the methylene or of the methyl groups were monitored. The temperature was calibrated by substituting the samples with standard NMR thermometers (methanol or ethylene glycol depending on temperature range). Computer line shape simulation was carried out in all cases in the temperature range indicated in Table I: the various ΔG^* values were averaged since they deviated by less than ±0.15 kcal mol^{-1} which is the estimated experimental error.[9]

Compound **2c** displayed, in any solvent suitable for high temperature measurements, a very small chemical shift difference for the NCH_2 anisochronous hydrogens, the largest separation being that observed in toluene-d_8. Even in this case, however, the shift difference is much smaller than the geminal J_{HH} coupling (12.7 Hz) so that only the two central lines of the AB pattern were clearly visible. The separation of these lines is obviously much smaller than the shift difference and, furthermore, it decreases rapidly on raising the temperature. Thus at 25 °C the central lines are separated by 1.7 Hz but at 60 °C the separation becomes 0.8 Hz (the corresponding shift differences being, respectively, 6.7 and 4.5 Hz at 200 MHz). Accordingly, at even higher temperatures it was impossible to unambiguously distinguish between a coalescence phenomenon and a line overlap without exchange. In the case of **2b** the situation, although quite similar, is more favorable as the chemical shift difference is much less temperature dependent (for instance the central lines are separated by 1.5 Hz at 25 °C and by 1.3 Hz at 50 °C, with a shift difference which is, respectively, 6.5 and 6.0 Hz at 200 MHz, the geminal J_{HH} being 12.7 Hz). Determination of the chemical shift difference in a large temperature range (between −10 °C and 50 °C) yielded a sufficiently large extrapolated value (5.2 Hz at 200 MHz) in the exchange region (80–85 °C) as to allow one to obtain a meaningful spectral simulation.

The NOE measurements were obtained by preirradiating the signal for 10 s and acquiring the spectrum with the decoupler turned off. The decoupler power was kept at a value giving a complete saturation of the irradiated signals in the case of **2a–d** and **6** (Table II) and at a lower value (to avoid irradiation of unwanted nearby signals) in the cases of **1a**, **2a**, **4a**, and **5** (Table IV). A control experiment, where irradiation was kept away from any spectral line, was also acquired. After one dummy scan four accumulations were collected for the irradiated signals and the control as well. The cycle was repeated from a minimum of 8 to a maximum of 500 times, depending on the signal to noise ratio. The FID's, acquired with 16K for 3-KHz sweep, were subtracted

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and transformed with 32K (zero filling) and with a 4–6-Hz line broadening. The samples ($CDCl_3$ as solvent) were carefully degassed with nitrogen, and the level of the liquid in the tube was kept at the minimum (0.4 mL) compatible with a reasonable resolution. The temperature was maintained constant (within ±0.1 °C) throughout the whole experiment.

Acknowledgment. One of the authors (L.L.) gratefully thanks Dr. J. K. M. Sanders, Cambridge, U.K., for reading the manuscript prior to publication and for helpful comments on the NOE experiments. Financial support from the Ministry of Scientific Research (MURST) and from the National Research Council, Rome, is also acknowledged.

Registry No. **1a**, 130523-07-8; **1b**, 130523-10-3; **1c**, 130523-14-7; **1d**, 130523-18-1; **2a**, 21614-05-1; **2b**, 130523-11-4; **2c**, 130523-15-8; **2d**, 130523-19-2; **3a**, 130523-08-9; **3b**, 130523-12-5; **3c**, 130523-16-9; **3d**, 130523-20-5; **4a**, 130523-09-0; **4b**, 130523-13-6; **4c**, 130523-17-0; **4d**, 130523-21-6; **5**, 130523-24-9; **6**, 130523-22-7; *N*-isopropyl(2-isopropyl-1-naphthyl)amine, 130523-23-8; 2-methyl-1-nitronaphthalene, 881-03-8; 2-ethyl-1-nitronaphthalene, 130523-25-0; 2-isopropyl-1-nitronaphthalene, 98515-20-9; 2-methyl-1-naphthylamine, 36357-84-3; 2-ethyl-1-naphthylamine, 36357-84-3; *N*-ethyl(2-methyl-1-naphthyl)amine, 60632-35-1; *N*-isopropyl(2-methyl-1-naphthyl)amine, 130523-26-1; *N*-ethyl(2-ethyl-1-naphthyl)amine, 130551-55-2; *N*-isopropyl(2-ethyl-1-naphthyl)-amine, 130523-27-2; *N*-ethyl(2-isopropyl-1-naphthyl)amine, 130523-28-3; *N*-ethyl(2-*tert*-butyl-1-naphthyl)amine, 110014-57-8; *N*-isopropyl(2-*tert*-butyl-1-naphthyl)amine, 130523-29-4; *tert*-butyl alcohol, 75-65-0; 2-*tert*-butyl-1-naphthylamine, 110014-56-7; 1-naphthylamine, 134-32-7; 8-methyl-1-naphthylamine, 130523-30-7; *N*-ethyl(8-methyl-1-naphthyl)amine, 130523-31-8; 1-methyl-8-nitronaphthalene, 90745-27-0; 1-methylnaphthalene, 90-12-0; 1-methyl-4-nitronaphthalene, 880-93-3; 2-isopropyl-1-naphthylamine, 106213-85-8.

Rearrangement of 1,3-Diradicals. Arylcyclopropane Photochemistry†,[1,2]

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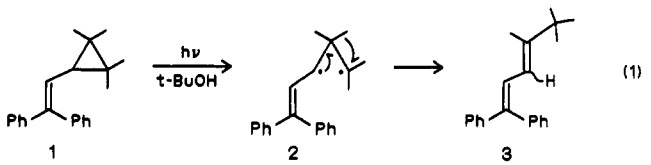
Received May 21, 1990

The photochemistry of a series of aryl-substituted cyclopropanes was investigated as part of our continuing investigations of these systems. The literature held a puzzling discrepancy in which several similar reactants exhibited differing photochemistry. A series of 3-aryl-1,1,2,2-tetramethylcyclopropanes was found to rearrange photochemically to give primarily two types of products, the anticipated 4-aryl-2,3,3-trimethyl-1-butenes and, additionally, 1-aryl-2,3,3-trimethyl-1-butenes. The latter arise from regioselective methyl migration of intermediate singlet 1,3-diradicals. Also, the usual Griffin carbene fragmentation was encountered as a minor pathway. Biphenylyl-, *p*-cyanophenyl-, and *p*-anisyl-substituted cyclopropanes were studied. Also, the photochemistry of 3-phenyl-1,1,2,2-tetramethylcyclopropane was reinvestigated and found to conform to the general pattern of reactivity. Throughout, it was the singlet excited states responsible for the observed reactivity, and the triplet counterparts were found to be unreactive. In addition, the photochemistry of 3-biphenylyl-2,2-dimethyl-1,1-diphenylcyclopropane was studied. Again, the triplet was unreactive. The singlet gave rise to 4-biphenylyl-2-methyl-3,3-diphenyl-1-butene exclusively. The differing behavior of the various arylcyclopropanes is discussed from a mechanistic viewpoint. In the case of the 3-aryl-1,1,2,2-tetramethylcyclopropanes, the regioselectivity of the 1,3-diradical intermediate favors migration toward the less delocalized odd-electron center. This selectivity is understood on a quantum mechanical basis. Finally, quantum yields are reported.

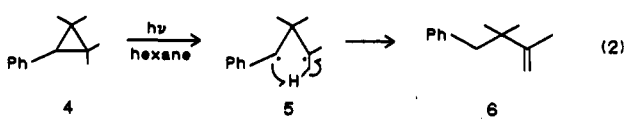
Introduction

The photochemistry of π-substituted cyclopropanes is extensive.[3] Our own research has focussed on unusual rearrangements,[4] and one aspect of interest has been the behavior of 1,3-diradicals.[4a,b,e] Particularly fascinating have been rearrangements in which substituents on C-2 of the 1,3-diradical migrate to one of the odd-electron centers. One example is shown in eq 1, involving a rearrangement



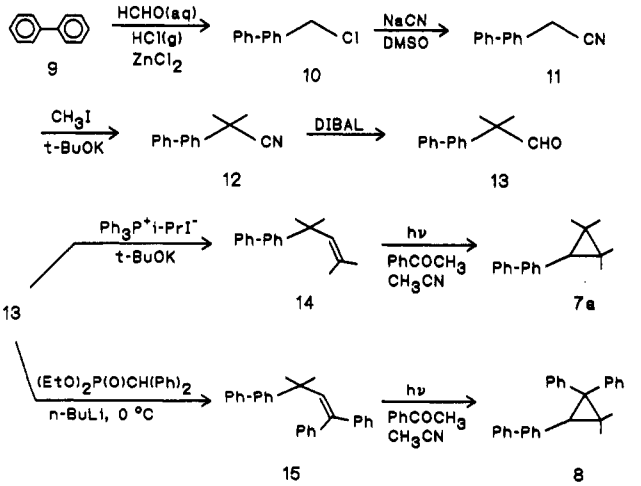
(1)

of a singlet 1,3-diradical.[5] In contrast, the most common behavior of such 1,3-diradicals has been intramolecular hydrogen transfer as depicted in eq 2.[3]



(2)

Scheme I. Syntheses of Biphenylyl-Containing Cyclopropanes 7a and 8



In view of the wide variation in behavior in cyclopropane photochemistry, we decided to investigate in detail 3-

† Dedicated to the 60th birthdays of Horst Prinzbach and Kurt Schaffner.

(1) This is paper 161 of our photochemical series and 222 of the general papers.

0022-3263/91/1956-1747$02.50/0