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Stereodynamics of *N,N*-Dialkyl-9-triptycylamines

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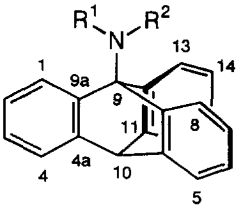
Abstract: Stereodynamics of a series of *N,N*-dialkyl-9-triptycylamines is studied by ^{1}H and ^{13}C dynamic NMR spectroscopy. The energy barriers to the observed internal motions are governed by the eclipsing interaction between an *N*-alkyl group and a benzene ring of the triptycene moiety together with the intrinsic barrier to nitrogen inversion. Copyright © 1996 Elsevier Science Ltd

Stereodynamic studies of amines have long been an active area of investigation.[1] Configurational inversion of pyramidal nitrogen atoms and internal rotation of C-N bonds are the main factors determining the stereodynamic behavior of alkylamines.

Stereodynamics of ammonia and simple alkylamines has been studied by microwave and infrared spectroscopy as well as molecular orbital calculations.[2] The energy barrier to inversion of 5.8 kcal mol^{-1} (1 cal = 4.184 J) was experimentally assigned for ammonia and similar values have been obtained for other simple amines; *e.g.*, 4.8, 4.4, and 7.5 kcal mol^{-1} for methylamine, dimethylamine, and trimethylamine, respectively. The energy barriers to C-N bond rotation have been shown to be 2.0 and 4.4 kcal mol^{-1} for methylamine and trimethylamine, respectively and thus nitrogen inversion has a higher barrier than C-N bond rotation.

For more complex amines, dynamic NMR spectroscopy has been a powerful means of investigation, which is often complemented by molecular mechanics calculations.[3] In some cases nitrogen inversion and C-N bond rotation are separately observed, and in other cases they are suggested to take place by way of a common transition state. For example, diethylmethylamine and triethylamine belong to the first category with the inversion barrier higher than the rotation barrier,[4a] while in 3-(*N,N*-diisobutylamino)-2,4-dimethylpentane rotation about a C-N bond has a higher barrier than nitrogen inversion.[4b] In *N,N*-dialkyl-*t*-butylamines such as *t*-butyldiethylamine and benzyl-*t*-butylmethylamine, nitrogen inversion and *t*-Bu-N rotation are shown to have the same energy barrier suggesting the occurrence via a common transition state.[4c]

Triptycene derivatives carrying a substituent at the bridgehead (9-) position have shown to serve as a unique and excellent model system for stereochemical studies because of the skeletal rigidity and high energy barriers to rotation of the bridgehead-to-substituent bond.[5] Stereodynamics of 9-alkyl and 9-oxy substituted triptycene derivatives has been extensively studied,[5] but those on 9-triptycylamine derivatives have been rather scarce.[6]



1 : $R^1 = R^2 = CH_3$
2 : $R^1 = CH_3$, $R^2 = CH_2C_6H_5$
3 : $R^1 = CH_3$, $R^2 = CH_2CH_3$
4 : $R^1 = R^2 = CH_2CH_3$

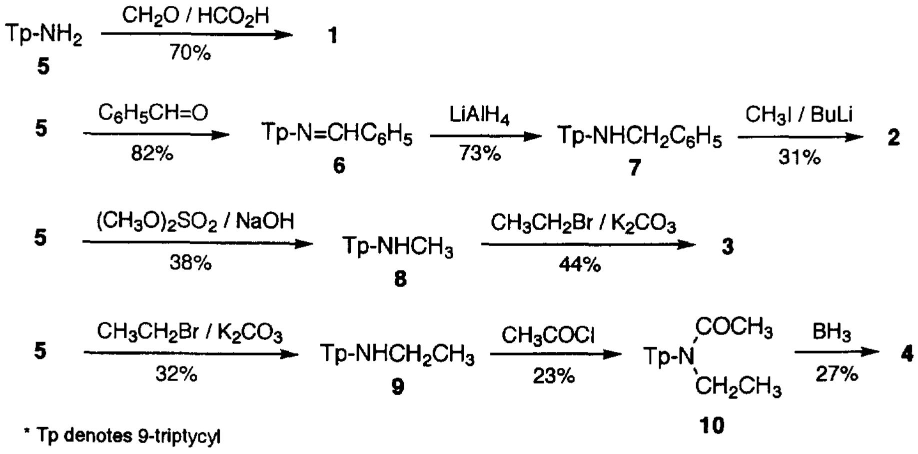
We planned to systematically study stereodynamics of a wide variety of 9-triptycylamine derivatives. In this article we report stereodynamic studies on *N,N*-dialkyl-9-triptycylamines **1–4**.[7]

RESULTS AND DISCUSSION

Synthesis

Triptycene derivatives are generally synthesized by the Diels-Alder reaction of anthracenes with benzynes. However direct preparation of *N*-substituted 9-triptycylamines by reactions of the corresponding *N*-substituted 9-aminoanthracenes with benzynes is not realistic because 9-aminoanthracenes are usually unstable and those having an N-H bond undergo undesirable reactions with benzynes.

The most plausible pathway to *N*-alkyl-substituted 9-triptycylamines seems introduction of alkyl groups to 9-triptycylamine (**5**),[8] either by direct alkylation or by way of *N*-acyl derivatives. Compound **5** is known to be prepared by reduction of either 9-nitrotriptycene[9] or 9-triptycyl azide,[10] of which we adopted the former. 9-Nitrotriptycene was obtained by reaction of 9-nitroanthracene[11] with benzyne in a rather low yield together with a considerable amount of the corresponding 1,4-adduct, 11-nitro-5,12-dihydro-5,12-ethenonaphthacene.[9c] Benzyne is generated in various ways and thermal decomposition of benzenediazonium-2-carboxylate[12] was employed in the present study. 9-Nitrotriptycene was found to be hardly separated from the 1,4-adduct by column chromatography, and was thus purified by first treating the mixture with $KMnO_4$ to convert the 1,4-adduct to the corresponding diol and then subjecting the mixture to column chromatography.



* Tp denotes 9-triptycyl

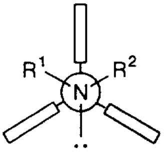
Scheme 1

Synthesis of compounds **1**–**4** from **5** was accomplished as shown in Scheme 1. *N,N*-Dimethyl-9-triptycylamine (**1**) was prepared in 70% yield by reductive methylation of **5** with formaldehyde-formic acid. Reaction of **5** with benzaldehyde-formic acid did not afford the expected reductive benzylation product, *N*-benzyl-9-triptycylamine (**7**), but instead gave the simple condensation product, *N*-benzylidene-9-triptycylamine (**6**) in 82% yield, which was converted to **7** in 73% yield by reduction with $LiAlH_4$. Methylation of **7** with MeI/BuLi afforded *N*-benzyl-*N*-methyl-9-triptycylamine (**2**) in 32% yield. The *N*-ethyl-*N*-methyl compound **3** was obtained by methylation of **5** followed by ethylation of the resulted *N*-methyl compound **8**. Ethylation of **5** with $EtBr/K_2CO_3$ afforded mainly the *N*-monoethyl compound **9**, and the *N,N*-diethyl compound **4** was obtained in a very low yield even with the use of a large excess of EtBr. The *N,N*-diethyl compound **4** was thus synthesized by reduction with borane of *N*-ethyl-*N*-9-triptycylacetamide (**10**) prepared by acetylation of the monoethyl compound **9**. Several lines of attempts at preparing the *N,N*-dibenzyl derivative of **5** have resulted in unsuccess probably because of severe steric hindrance.

Dynamic NMR Studies

In the *N,N*-dialkyl-9-triptycylamines **1**–**4**, the dynamic processes expected to be detected by dynamic NMR spectroscopy are the inversion at the nitrogen atom and the rotation about the triptycene-nitrogen (Tp-N) bond. When both of the processes are fast on the NMR time scale, the three benzene rings of the Tp moiety will be magnetically equivalent and the two methylene protons of the benzyl or ethyl group will also be equivalent. When both of the these processes are frozen on the NMR time scale, one of the Tp-benzene rings will become nonequivalent from the other two in *N,N*-dimethyl-9-triptycylamine (**1**) and *N,N*-diethyl-9-triptycylamine (**4**), while the three benzene rings will be mutually nonequivalent in *N*-benzyl-*N*-methyl-9-triptycylamine (**2**) and *N*-ethyl-*N*-methyl-9-triptycylamine (**3**), as shown by the Newman projection **11** along the Tp-N bond on the assumption of the sp^3-hybridized nitrogen and the staggered Tp-N bond. The methylene protons of the benzyl group in **2** and of the ethyl group in **3** and **4** should be anisochronous under these conditions and give rise to an AB or ABX_3 type signal.

The ^1H NMR spectrum of compound **1** at ambient temperature indicates that any internal motion in **1** is fast on the NMR time scale. The spectrum shows no exchange-broadening at all down to −110 °C, although significant viscosity-broadening is observed at low temperatures. This suggests that the internal motion is fast on the NMR time scale even at the lowest temperature.



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The ^1H NMR spectrum of compound **2** in acetone-d_6 at ambient temperature suggests that the internal motion is fast on the NMR time scale although the signals due to the aromatic protons of the triptycene (Tp) skeleton are somewhat broadened. While the lineshapes of the signals due to the protons and carbons of the benzylic phenyl group show no change at all in the temperature range examined, those of the Tp moiety remarkably changes with temperature as typically illustrated in Fig. 1 (left) for the quaternary carbon signals (● for 8a/9a/12-C and ▲ for 4a/10a/11-C). Upon lowering the temperature, either of the ● and ▲ signals broadens and splits into two peaks. At −43 °C pairs of broad peaks with an intensity ratio of 2:1 are observed (●/○ and ▲/△). With further decrease in the temperature, the smaller signals (○ and △) become sharper while either of the larger signals (● and ▲) further broadens and splits into two peaks with a 1:1 ratio. Thus at −106 °C two sets of three equally intense peaks are observed although the complete sharpening of the ● and ▲ peaks are not yet attained.

The benzylic methylene proton signal appears as a sharp singlet at ambient temperature, decoalesces at ca. −70 °C in concert with the lower-temperature change of the aromatic signals, and appears as an AB-type quartet at −106 °C (Fig. 2, left).

These spectral changes are interpreted as follows on the basis of the interconversion pathways among six staggered conformers as shown in Scheme 2.[13] At ambient temperature all the processes are fast on the NMR time scale. Upon lowering the temperature the benzyl group is first frozen into one of the notches made of two Tp benzene rings, while the methyl group is still rapidly moving between the remaining two notches. Occurrence of this situation will be rationalized if the larger steric requirement of the benzyl group than the methyl group is considered. In this situation, the Tp carbons appear as sets of two peaks with an intensity ratio of 2:1 and the methylene protons appear as a singlet. Upon further lowering of the temperature, the methyl group becomes frozen into one of the notches. Now the three benzene rings of the Tp moiety are mutually non-equivalent and the molecule is chiral. Here the Tp carbons give rise to sets of three peaks with a 1:1:1 ratio and the methylene protons afford an AB-quartet signal.

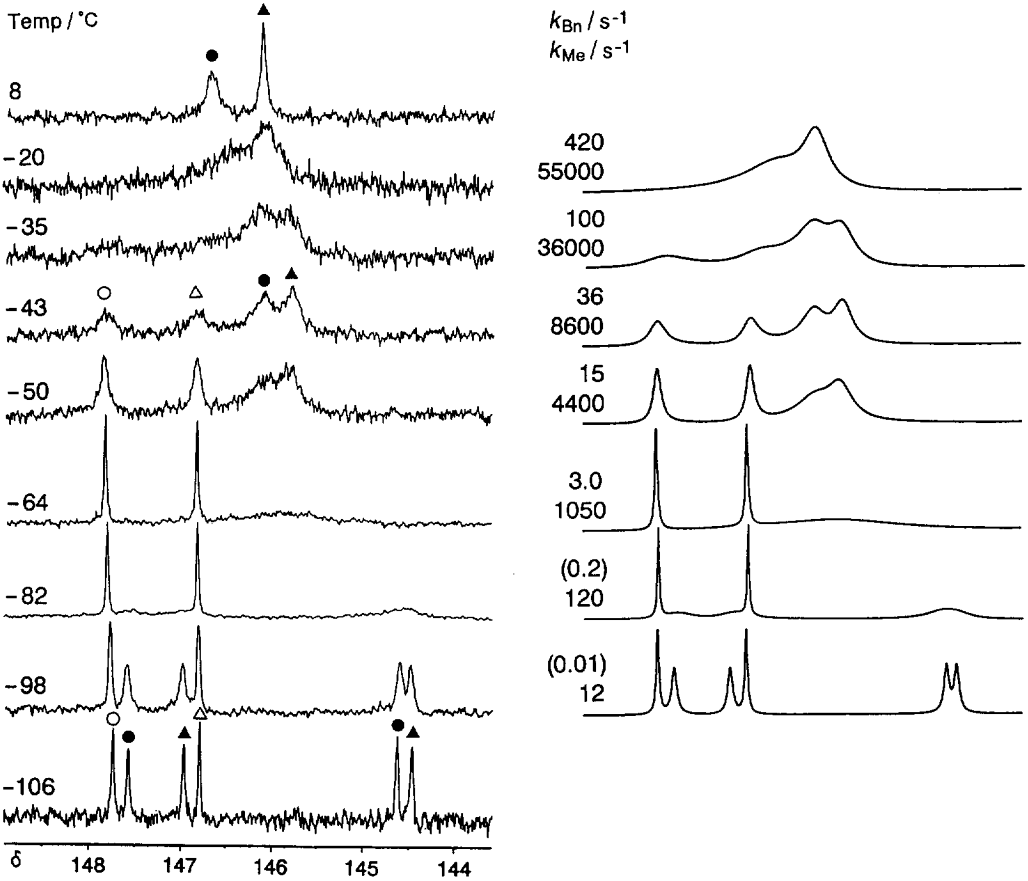


Fig. 1. The quaternary carbon signals of the Tp moiety of compound **2** in acetone-d_6 at 125 MHz at various temperatures (left) and the calculated spectra (right).

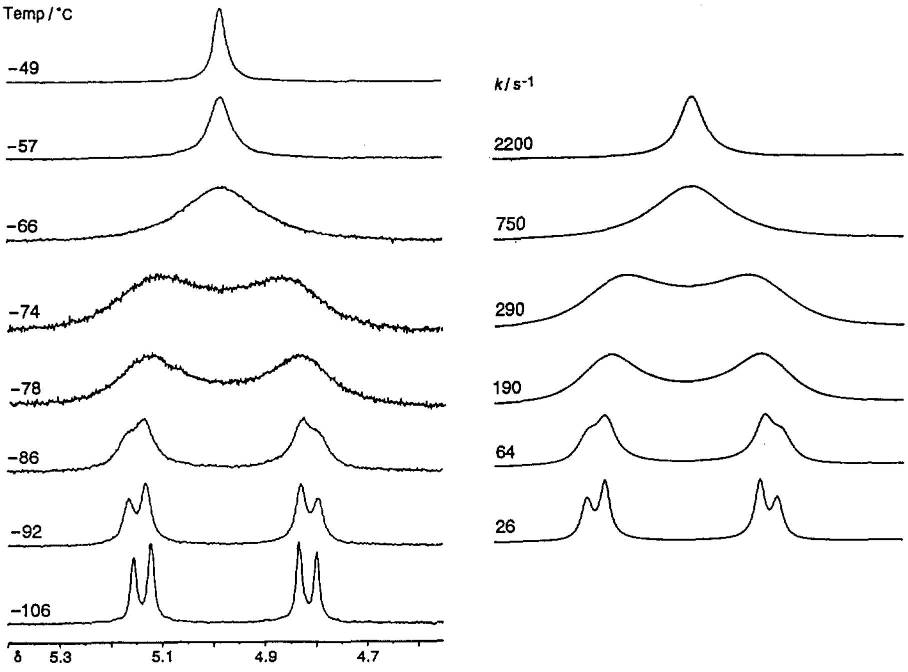
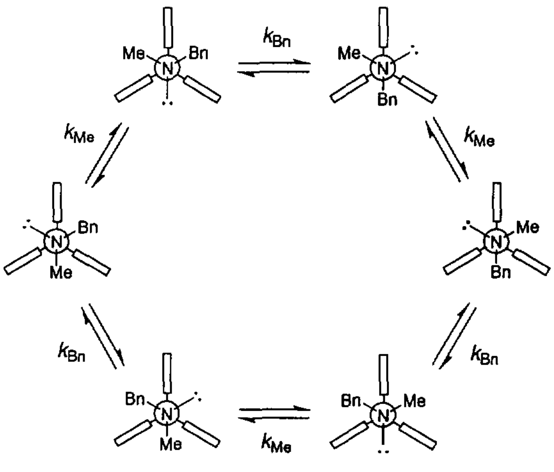


Fig. 2. The observed (left) and the calculated (right) spectra of the methylene protons of **2** in acetone-d_6 at 500 MHz.



Scheme 2

The whole rate processes can therefore be described by two rate constants, k_{Bn} and k_{Me}, in Scheme 2. The rate constant k_{Bn} corresponds to the process in which the benzyl group passes over one of the benzene rings of the Tp moiety with concomitant inversion of the nitrogen configuration, while k_{Me} corresponds to the

Table 1. Kinetic Parameters for Compounds **2**–**4**.

Compd	Solvent	Process[a]	$\Delta H^‡$ kcal mol^{-1}	$\Delta S^‡$ cal mol^{-1} K^{-1}	$\Delta G^‡$ (Temp) kcal mol^{-1} (K)
2[b]	acetone-d_6	Bn	11.5±0.9	−0.8±3.9	11.6$_6$ (200)
		Me	9.2±0.2	−0.3±1.2	9.2$_4$ (200)
3[c]	CD_2Cl_2	Et			~9.6 (195)[d]
		Me			~7.5 (162)[d]
4[c]	CD_2Cl_2	Et			~8.1 (165)[d]

[a] The process in which the indicated group passes over a benzene ring. [b] Measured at 500 MHz/126 MHz. [c] Measured at 300 MHz. [d] Coalescence temperature.

process in which the methyl group passes over a benzene ring, which also is accompanied by nitrogen inversion. Rotation of the Tp-N bond without nitrogen inversion, *i.e.*, a process in which both alkyl groups simultaneously pass over two benzene rings, is incompatible with the observed lineshape change and thus would have a far higher barrier.

The exchange of the anisochronous methylene protons is governed by a single rate constant, *i.e.*, k_{Me}. The total lineshape analysis of the methylene proton signal at six temperatures between −57 and −92 °C afforded the k_{Me} value at each temperature (Fig. 2, right), and the kinetic parameters given in Table 1 were obtained by least-squares analysis.

The lineshape of the quaternary Tp carbon signals is a function of both k_{Bn} and k_{Me}. The total lineshape analysis was performed at several temperatures between −20 and −98 °C. At each temperature, a fixed k_{Me} value was used that was calculated by extrapolation of the k_{Me} data obtained for the methylene proton signal mentioned above, while k_{Bn} was varied until the best-fit spectrum was obtained (Fig. 1, right). Although the k_{Bn} values thus obtained contained rather large errors because of the low quality of the experimental spectra, kinetic parameters given in Table 1 were obtained.

In either process, the transition state will be such that an *N*-alkyl group, methyl or benzyl, eclipses a Tp-benzene ring and the nitrogen is planar. The energy barrier is therefore composed of two terms: the intrinsic barrier to nitrogen inversion, *i.e.*, the energy necessary for rehybridization of the nitrogen atom, and the steric eclipsing interaction energy between an alkyl group and a benzene ring. The intrinsic barrier to rehybridization is estimated to be ca. 5 kcal mol^{-1} judging from the data reported for ammonia and methylamine.[2] In 9-triptycylamine (**5**), the barriers to Tp-N rotation and nitrogen inversion have been estimated to be 2.6 and 5.4 kcal mol^{-1}, respectively.[6a] In compound **2** carrying alkyl groups on nitrogen, the steric effect significantly contributes to the barrier. It is interesting that the passing of the benzyl group over a Tp-benzene ring has a higher energy barrier by ca. 2.4 kcal mol^{-1} than that of the methyl group. This large difference may partly be ascribed to the gearing of the methyl group: Rotation of the N-CH_3 bond in correlation with that of the Tp-N bond can reduce the steric interaction during the itinerary, while the benzyl group can not make correlated rotation due to the bulky phenyl group.

Dynamic NMR studies of *N*-ethyl-*N*-methyl-9-triptycylamine (**3**) and *N*,*N*-diethyl-9-triptycylamine (**4**) were made in CD_2Cl_2 instead of acetone-d_6, because of the too low solubility of the compounds in the latter

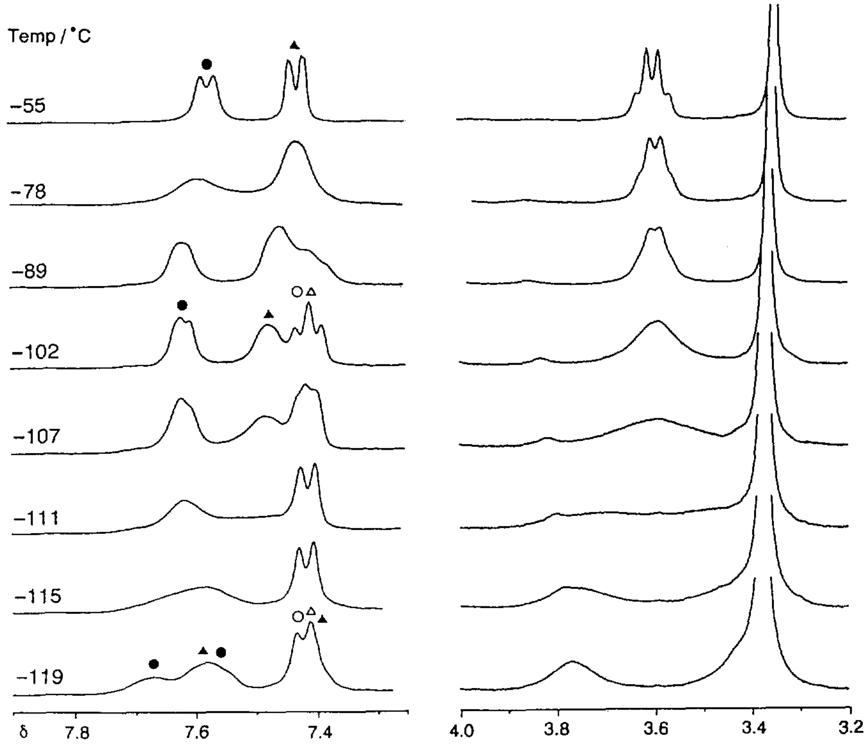


Fig. 3. Temperature dependence of the 1/8/13-H (●), 4/5/16-H (▲), and methylene proton signals of compound 3 in CD_2Cl_2 at 300 MHz. A peak at ca. δ 3.4 is due to the *N*-methyl protons.

solvent at low temperatures. As the effect of aprotic solvents on the barriers to nitrogen inversion and bond rotation is known to be generally small,[1] we assume that the difference in the solvent can be neglected in the present study.

In *N*-ethyl-*N*-methyl-9-triptycylamine (**3**), occurrence of similar rate processes and thus a similar spectral change as in compound **2** are expected. The temperature dependence of the 1/8/13-H and 4/5/16-H signals as well as of the methylene proton signal are shown in Fig. 3. Upon lowering the temperature the aromatic signals broaden and split into two peaks each with a 2:1 ratio. The larger signals further broaden and split into two peaks each with a 1:1 ratio. The spectrum at -119 °C, the lowest temperature in this experiment, indicates the non-equivalence of the three benzene rings, though somewhat ambiguous because of the viscosity-broadening and the residual exchange-broadening. The methylene proton signal which appears as a sharp quartet at ambient temperature broadens with the temperature decrease, decoalesces at ca. –110 °C and appears as two broad signals with the chemical shift difference of ca. 120 Hz at –119 °C.

The rate constant for the passing of the methyl group over a benzene ring, k_{Me}, was roughly estimated from the methylene proton signals as ca. 240 s^{-1} at the assumed coalescence temperature of –110 °C, which gives the free energy of activation of ca. 7.5 kcal mol^{-1} for this process. As the variable-temperature ^{13}C spectra of **3** could not be obtained, quite a rough estimate of the energy barrier to the higher-barrier process in which the ethyl group passes over a benzene ring (hereafter referred to as the k_{Et} process), is made from the change in the 1/8/13-H signal. Judging from the spectra that the signal decoalesces at -78 °C into two signals with an intensity ratio of 2:1 and the chemical shift difference of 60 Hz, the rate constant k_{Et} is estimated as ca. 65 s^{-1} at –78 °C, corresponding to the free energy of activation of ca. 9.6 kcal mol^{-1} at this temperature.

In *N,N*-diethyl-9-triptycylamine (**4**), the process in which an ethyl group passes over a benzene ring is the only one to be observed. Upon decreasing the temperature the methylene proton signal decoalesces at –108 °C to afford two broad peaks with the chemical shift difference of 66 Hz at –117 °C (Fig. 4). The rate constant for the methylene exchange, which corresponds to $2k_{Et}$, is roughly estimated as ca. 140 s^{-1} at –108 °C, affording the free energy of activation of ca. 8.1 kcal mol^{-1} for the k_{Et} process. The aromatic proton signals at –117 °C are still broad and somewhat ambiguous but suggests the presence of two kinds of benzene rings in a ratio of 2:1.

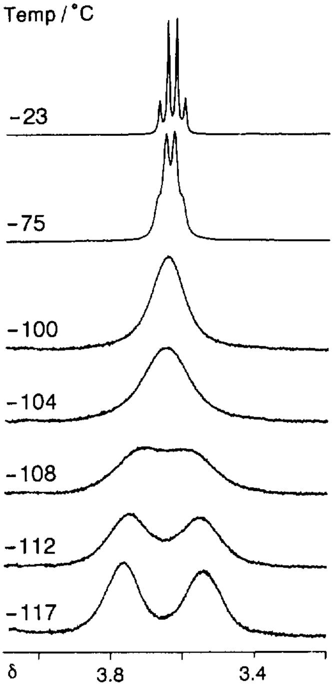


Fig. 4. The methylene proton signal of **4** at several temperatures in CD_2Cl_2.

We have no definite explanation why the barriers for both the k_{Me} and k_{Bn}/k_{Et} processes are lower in **3** than in **2**. The smaller k_{Et} barrier in **4** than in **3** may partly be ascribed to the larger ground-state destabilization in **4**. In *N,N*-dialkyl-*t*-butylamines,[4c] a similar decrease in the rotation/inversion barrier was observed on going from *t*-BuNMeEt to *t*-BuNEt$_2$, $\Delta G^{\ddagger}$ being 7.2 and 6.0 kcal mol^{-1}, respectively, and was ascribed to the greater ground-state destabilization in the latter.

In compounds **2** and **3**, the higher-barrier process may be regarded as "Tp-N rotation" since the nitrogen can be considered planar on the NMR time scale during this process because of the fast k_{Me} process and the benzyl or ethyl group rotates about the Tp-N bond. This corresponds to what Anderson *et al.* named "rotation" in their article.[4b] Meanwhile the k_{Me} process may be regarded as "nitrogen inversion" in the sense that the configurational identity of the nitrogen atom is lost in this process.

EXPERIMENTAL

General. Melting points are not corrected. ^1H and ^{13}C NMR spectra were obtained on a Bruker AM-500 or a Bruker ARX-300 spectrometer operating at 500.1 and 300.1 MHz for ^1H and 125.8 and 75.4 MHz for ^{13}C, respectively. Chemical shifts are referenced with internal tetramethylsilane (δ_H=0) or $CDCl_3$ (δ_C=77.0). ^1H chemical shifts were assigned on the basis of homonuclear double resonance and nuclear Overhauser effect (NOE) experiments. Variable-temperature experiments were made in acetone-d_6 or CD_2Cl_2, and temperatures were calibrated using a methanol or an ethylene glycol sample and are reliable to ±1°C. In the ^{13}C data given below, letters p, s, t, and q denote primary, secondary, tertiary, and quaternary, respectively. ^{13}C chemical shift assignments, when given, were made by ^{13}C-^{1}H COSY experiments.

9-Nitrotriptycene. A chilled suspension in 40 mL of 1,2-dichloroethane of benzenediazonium-2-carboxylate,[12] prepared from 11.0 g (80 mmol) of anthranilic acid, was added in ca. 1 mL portions at an interval of ca. 1 min to a boiling solution of 5.58 g (25 mmol) of 9-nitroanthracene[11] in 60 mL of butanone, and the mixture was heated under reflux for 30 min. After evaporation of the solvent, the residual mass was chromatographed through a short column of alumina with CH_2Cl_2-hexane as the eluent to afford 6.86 g of a mixture of 9-nitrotriptycene and the 1,4-adduct, 11-nitro-5,12-dihydro-5,12-ethenonaphthacene, in a ratio of ca. 3:1, contaminated with a small amount of biphenylene. The 1,4-adduct was typically characterized by double-doublet signals (*J*=5.9 and 1.4 Hz) at δ 5.30 and 5.49 due to 5-H and 12-H.

A solution of this mixture and 0.5 g of benzyltrimethylammonium chloride in 50 mL of dichloromethane was stirred with a solution of 1.45 g (9.2 mmol) of $KMnO_4$ in 50 mL of 1% aq NaOH for 10 h. The mixture was treated with aq. $NaHSO_3$ and the organic layer was washed with water and brine, dried over sodium sulfate, and concentrated. Column chromatography of the residue on alumina with hexane-dichloromethane as the eluent followed by recrystallization from chloroform-hexane afforded 2.51 g (33%) of 9-nitrotriptycene, mp 245–247 °C (lit.[9a] 246–248.5 °C). ^{1}H NMR ($CDCl_3$) δ 5.411 (1H, s, 10-H), 7.07–7.15 (6H, m, 2/7/14-H and 3/6/15-H), 7.436 (3H, m, 4/5/16-H), 7.680 (3H, m, 1/8/13-H). ^{13}C NMR ($CDCl_3$) δ 53.83 (1C, t, 10-C), 96.74 (1C, q, 9-C), 121.94 (3C, t, 1/8/13-C), 123.50 (3C, t, 4/5/16-C), 125.63 (3C, t), 126.72 (3C, t), 140.22 (3C, q), 143.60 (3C, q).

9-Triptycylamine (5). Reduction of 9-nitrotriptycene with Sn/HCl according to the literature procedure[8] afforded 9-triptycylamine (**5**) in 91% yield, mp 225 °C (lit.[8] 213–214 °C; lit.[10] 221–223 °C). ^{1}H NMR ($CDCl_3$) δ 2.607 (2H, br, NH_2), 5.409 (1H, s, 10-H), 7.007 (3H, m, 2/7/14-H), 7.057 (3H, m, 3/6/15-H), 7.383 (3H, m, 4/5/16-H), 7.480 (3H, m, 1/8/13-H). ^{13}C NMR ($CDCl_3$) δ 53.18 (1C, t, 10-C), 64.12 (1C, q, 9-C), 119.35 (3C, t, 1/8/13-C), 123.25 (3C, t, 4/5/16-C), 124.99 (3C, t, 2/7/14-C), 125.24 (3C, t, 3/6/15-C), 144.94 (3C, q), 146.63 (3C, q).

***N*,*N*-Dimethyl-9-triptycylamine (1).** A mixture of 380 mg (1.41 mmol) of 9-triptycylamine (**5**), 0.32 mL (7.5 mmol) of 90% formic acid, and 0.28 mL (3.3 mmol) of 35% formaldehyde was heated under reflux for 6 h. After addition of 0.13 mL of HCl, the mixture was concentrated on an oil bath to remove formic acid and any excess formaldehyde. The residue was dissolved in ca. 50 mL of water, and made alkaline with 12% aq NH_3. The mixture was extracted with dichloromethane (50 mL× 3), and the organic layer was washed with water and brine, and dried over anhydrous sodium sulfate. Column chromatography on alumina with hexane-dichloromethane as the eluent followed by recrystallization from dichloromethane-hexane afforded 296 mg (70%) of **1** as colorless prisms, mp 196–197 °C. Found; C, 89.00; H, 6.53; N, 4.83%. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44, N, 4.71%. ^{1}H NMR ($CDCl_3$) δ 3.412 (6H, s, CH_3), 5.230 (1H, s, 10-H), 6.960 (3H, td, *J*=7.3 and 1.2 Hz, 3/6/15-H), 7.004 (3H, td, *J*=7.5 and 1.4 Hz, 2/7/14-H), 7.342 (3H, dd, *J*=7.2 and 1.3 Hz, 4/5/16-H), 7.609 (3H, dd, *J*=7.5 and 0.9 Hz, 1/8/13-H). ^{13}C NMR ($CDCl_3$) δ 45.23 (2C, p, CH_3), 54.56 (1C, t, 10-C), 77.18 (1C, q, 9-C), 123.45 (3C, t, 4/5/16-C), 124.06 (3C, t, 1/8/13-C), 124.40 (3C, t, 2/7/14-C), 124.80 (3C, t, 3/6/15-C), 145.59 (3C, q), 146.27 (3C, q).

***N*-Benzyl-9-triptycylamine (7).** A mixture of 370 mg (1.38 mmol) of 9-triptycylamine (**5**), 0.154 mL (1.52 mmol) of benzaldehyde in 0.3 mL of 90% formic acid was heated under reflux for 4 h. The formic acid and any residual benzaldehyde was removed by evaporation, and the residue was chromatographed on alumina with hexane-benzene as the eluent to afford 405 mg (82%) of *N*-benzylidene-9-triptycylamine (**6**), mp 276–278 °C (lit.[8] 282–283 °C). ^{1}H NMR ($CDCl_3$) δ 5.481 (1H, s, 10-H), 6.97–7.07 (6H, m, 2/7/14-H and 3/6/15-H), 7.40–7.53 (6H, m, 1/8/13-H and 4/5/16-H), 7.58–7.63 (3H, m, *m*-H and *p*-H), 8.22 (2H, m, *o*-H), 8.946 (1H, s, CH=N). ^{13}C NMR ($CDCl_3$) δ 53.84 (1C, t), 74.17 (1C, q), 121.67 (3C, t), 123.69 (3C, t), 124.76 (3C, t), 125.30 (3C, t), 128.73 (2C, t), 128.89 (2C, t), 131.73 (1C, t), 136.24 (1C, q), 145.08 (3C, q), 145.88 (3C, q), 168.39 (1C, t). To a solution of 55 mg (0.15 mmol) of **6** in 10 mL of dry THF was added 100 mg (2.6 mmol) of $LiAlH_4$ and the mixture was stirred at room temperature for 30 min and then heated under reflux for 40 min. The mixture was cooled, quenched with ethyl acetate, passed through Hyflo Super-Cel, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residual mass was chromatographed on alumina with benzene-hexane (9:1) as the eluent to afford 40 mg (73%) of *N*-benzyl-9-triptycylamine (**7**), mp 180–181 °C. Found: C, 90.48; H, 5.96; N, 3.91%. Calcd for $C_{27}H_{21}N$; C, 90.21; H, 5.89; N, 3.90%. ^{1}H NMR ($CDCl_3$) δ 2.957 (1H, t, *J*=7.4 Hz, NH), 4.826 (2H, d, *J*=7.4 Hz, CH_2), 5.348 (1H, s, 10-H), 6.96–7.07 (6H, m, 2/7/14-H and 3/6/15-H), 7.34–7.40 (4H, m, 4/5/16-H and *p*-H), 7.490 (2H, t, *J*=7.5 Hz, *m*-H), 7.540 (3H, d, *J*=7.6 Hz, 1/8/13-H), 7.784 (2H, d, *J*=7.5 Hz, *o*-H). ^{13}C NMR ($CDCl_3$) δ 48.46 (1C, s, CH_2), 53.90 (1C, t, 10-C), 69.88 (1C, q, 9-C), 121.55 (3C, t), 123.41(3C, t), 124.93 (3C, t), 125.13 (3C, t), 126.98 (1C, t, *p*-C), 127.26 (2C, t), 128.71 (2C, t), 141.85 (1C, q, *i*-C), 145.65 (3C, q), 146.04 (3C, q).

***N*-Benzyl-*N*-methyl-9-triptycylamine (2).** To a solution of 110 mg (0.31 mmol) of *N*-benzyl-9-triptycylamine (**7**) in 5 mL of dry THF was added dropwise 0.21 mL of a 10 w/v% solution of butyllithium in hexane at -50 °C and the mixture was stirred at -48 °C for 30 min under Ar atmosphere. Then a solution of 1 mL (16.1 mmol) of methyl iodide in 3 mL of dry THF was added at -48 °C, and the mixture was allowed to warm up to room temperature. The reaction mixture was poured into water, extracted with dichloromethane (50 mL × 3), washed twice with brine, and dried over anhydrous sodium sulfate. Column chromatography on alumina with hexane-benzene as the eluent followed by recrystallization from benzene-hexane afforded 35 mg (31%) of **2**, as colorless prisms, mp 208–209 °C. Found; C, 90.30; H, 6.37; N, 3.79%. Calcd for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75%. ^{1}H NMR ($CDCl_3$) δ 3.351 (3H, s, CH_3), 4.958 (2H, s, CH_2), 5.268 (1H, s, 10-H), 6.96–7.02 (6H, m, 2/7/14-H and 3/6/15-H), 7.33–7.40 (4H, m, 4/5/16-H and *p*-H), 7.494 (2H, t, *J*=7.7 Hz, *m*-H), 7.610 (3H, br, 1/8/13-H), 7.774 (2H, d, *J*=7.7 Hz, *o*-H). ^{13}C NMR ($CDCl_3$) δ 43.76 (1C, p, CH_3), 54.63 (1C, t, 10-C), 59.82 (1C, s, CH_2), 77.21 (1C, q, 9-C), 123.49 (3C, t, 4/5/16-C), 123.74 (3C, t, br, 1/8/13-C), 124.56 (3C, t, 3/6/15-C), 124.92 (3C, t, 2/7/14-C), 126.66 (1C, t, *p*-C), 127.06 (2C, t, *o*-C), 128.70 (2C, t, *m*-C), 141.07 (1C, *i*-C), 145.89 (3C, q, 4a/10a/11-C), 146.15 (3C, q, br, 8a/9a/12-C).

***N*-Methyl-9-triptycylamine (8).** To a suspension of 37.6 mg (0.82 mmol) of powdered NaOH in 50 mL of dry acetone was added 200 mg (0.74 mmol) of 9-triptycylamine (**5**), and the mixture was stirred for 30 min at room temperature. To the mixture was added 77 mL (0.82 mmol) of dimethyl sulfate and the mixture was stirred for 8 h at room temperature and extracted with dichloromethane. The organic layer was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent the residue was chromatographed on alumina with hexane-dichloromethane as the eluent affording 36 mg (16%) of the *N,N*-dimethyl derivative **1**, 80 mg (38%) of **8**, and 74 mg (36%) of the starting material **5**, in this order. Recrystallization of the second fraction from hexane-dichloromethane gave a pure sample of **8** as colorless needles, mp 199–200 °C. Found: C, 88.83; H, 6.17; N, 4.91%. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94%. ^{1}H NMR ($CDCl_3$) δ 2.68 (1H, br s, NH), 3.273 (3H, s), 5.333 (1H, s), 6.96–7.08 (6H, m), 7.370 (3H, m), 7.499 (3H, m). ^{13}C NMR ($CDCl_3$) δ 33.57 (1C, p), 53.79 (1C, t), 70.41 (1C, q), 121.48 (3C, t), 123.39 (3C, t), 124.87 (3C, t), 125.07 (3C, t), 145.72 (3C, q), 145.78 (3C, q).

***N*-Ethyl-*N*-methyl-9-triptycylamine (3).** To a solution of 50 mg (0.18 mmol) of *N*-methyl-9-triptycylamine (**8**) in a mixture of 3 mL of dry THF and 4 mL of DMSO was added 8.0 mL (0.11 mol) of ethyl bromide and 1.0 g (7.23 mmol) of anhydrous potassium carbonate, and the mixture was heated under reflux for 10 h under Ar atmosphere. The mixture was extracted with dichloromethane, and the organic layer was washed with water and dried over sodium sulfate. After evaporation of the solvent, the residue was chromatographed on alumina with dichloromethane-hexane as the eluent affording 25 mg (44%) of **3** and 24 mg (47%) of the starting material **8** in this order. Recrystallization of the first fraction from hexane-benzene gave pure **3** as colorless crystals, mp 197–198 °C. Found: C, 88.81; H, 7.10; N, 4.42%. Calcd for $C_{23}H_{21}N$: C, 88.71; H, 6.80; N, 4.50%. ^1H NMR ($CDCl_3$) δ 1.536 (3H, br, CH_2CH_3), 3.365 (3H, br s, CH_3), 3.643 (2H, br q, CH_2), 5.230 (1H, s, 10-H), 6.90–7.05 (6H, m), 7.339 (3H, dd, *J*=6.6 and 1.6 Hz), 7.567 (3H, br d, *J*=6.8 Hz). ^{13}C NMR ($CDCl_3$) δ 15.81 (1C, p, br), 42.92 (1C, p), 50.77 (1C, s, br), 54.59 (1C, t), 77.18 (1C, q), 123.40 (3C, t), 123.93 (3C, t), 124.40 (3C, t), 124.75 (3C, t, br), 145.97 (3C, q, br), 146.16 (3C, q).

***N*-Ethyl-9-triptycylamine (9).** To a solution of 200 mg (0.74 mmol) of **5** in 8 mL of a 1:1 mixture of THF and DMSO were added 12 mL (0.17 mol) of ethyl bromide and 2.0 g of powdered anhydrous potassium carbonate at room temperature, and the mixture was heated under reflux for 14 h under Ar atmosphere. The mixture was extracted with dichloromethane and the organic layer was washed with water and dried over sodium sulfate. After evaporation of the solvent, the residue was chromatographed on alumina with dichloromethane-hexane as the eluent affording 6 mg (2%) of the *N,N*-diethyl compound **4**, 70 mg (32%) of **9**, and 99 mg (50%) of the starting material **5**, in this order. Recrystallization of the second fraction from hexane-benzene gave pure **9** as colorless prisms, mp 191–192 °C. Found: C, 88.80; H, 6.40; N, 4.75%. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71%. ^1H NMR ($CDCl_3$) δ 1.596 (3H, t, *J*=7.1 Hz, CH_3), 2.458 (1H, br s, NH), 3.598 (2H, q, *J*=7.1 Hz, CH_2), 5.323 (1H, s, 10-H), 6.95–7.07 (6H, m), 7.363 (3H, m), 7.488 (3H, m). ^{13}C NMR ($CDCl_3$) δ 17.23 (1C, p), 39.41 (1C, s), 53.87 (1C, t), 69.70 (1C, q), 121.45 (3C, t), 123.37 (3C, t), 124.87 (3C, t), 125.04 (3C, t), 145.65 (3C, q), 146.03 (3C, q).

***N*-Ethyl-*N*-9-triptycylacetamide (10).** To a solution of 40 mg (0.13 mmol) of **9** in 2 mL of dichloromethane was added 0.4 mL (4.91 mmol) of acetyl chloride and the mixture was heated under reflux for 5 h and cooled. After neutralization with aqueous ammonia, the mixture was extracted with dichloromethane. The extracts were washed with water and dried over sodium sulfate. After evaporation of the solvent, the residue was chromatographed on alumina with hexane-dichloromethane as the eluent affording 26 mg (67%) of **9** and 10 mg (23%) of **10** in this order. Recrystallization of the first fraction from hexane-benzene gave pure **10** as colorless powder, mp 221–222 °C. Found: C, 84.58; H, 6.30; N, 4.04%. Calcd for $C_{24}H_{21}NO$: C, 84.92; H, 6.24; N, 4.13%. ^1H NMR ($CDCl_3$) δ 1.488 (ca. 2.2H, br), 1.85 (3H, br), 2.60 (ca. 0.8H, br), 4.31 (2H, br), 5.32 (1H, br), 6.8–7.8 (12H, br).

***N,N*-Diethyl-9-triptycylamine (4).** To a solution of 50 mg (0.15 mmol) of **10** in 4 mL of dry THF was added 0.45 mL of a solution of borane (1.0 M in THF, 0.45 mmol) at 0 °C, and the mixture was heated under reflux for 2 h under Ar. The mixture was poured into 5 mL of dil. HCl at room temperature and the whole was heated under reflux for 1 h. The reaction mixture was neutralized with aq NaOH and extracted with dichloromethane, and the extract was washed with water and dried over sodium sulfate. After evaporation of the solvent, the residue was chromatographed on alumina with hexane-dichloromethane as the eluent affording 13 mg (27%) of **4**, 7 mg (15%) of *N*-ethyl-9-triptycylamine (**9**), and 25 mg (49%) of the starting material **10**, in this order. Recrystallization of the first fraction from hexane-benzene gave pure **4** as colorless prisms, mp 209–210 °C. Found: C, 88.33; H, 6.92; N, 4.13%. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30%. ^1H NMR ($CDCl_3$) δ 1.654 (6H, t, *J*=7.1 Hz, CH_3), 3.667 (4H, q, *J*=7.1 Hz, CH_2), 5.213 (1H, s, 10-H), 6.92–7.03 (6H, m, 2/7/14-H and 3/6/15-H), 7.329 (3H, m, 4/5/16-H), 7.604 (3H, m, 1/8/13-H). ^{13}C NMR ($CDCl_3$) δ 19.74 (2C, p), 51.58 (2C, s), 54.73 (1C, t), 79.14 (1C, q), 123.33 (3C, t), 123.88 (3C, t), 124.36 (3C, t), 124.70 (3C, t), 146.17 (3C, q), 146.37 (3C, q).

Lineshape Analysis. Total lineshape analysis of compound **2** was performed by visual matching of the experimental and theoretical spectra computed on a NEC PC9821Xs personal computer equipped with a Mutoh PP-210 plotter using the DNMR3K program, a modified version of the DNMR3 program[14] converted for use on personal computers by Dr. H. Kihara of Hyogo University of Teacher Education. Temperature dependence of chemical shift differences and T_2 values was properly taken into account. Rough estimates of rate constants at coalescence temperatures in **3** and **4** were made using the program by assuming appropriate spin systems, chemical shift differences, coupling constants, T_2 values, and so on.

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