CHEMISTRY LETTERS, pp. 1911-1914, 1994. 

# Stereodynamics of *N*-Benzyl-*N*-methyl-9-aminotriptycene

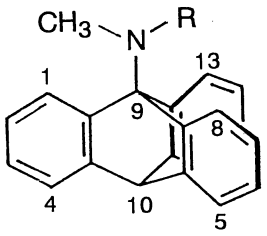
Gaku YAMAMOTO,* Hiroyuki HIGUCHI,† Masami YONEBAYASHI,† and Jūro OJIMA†,*
Department of Chemistry, School of Science, Kitasato University, Kitasato, Sagamihara, Kanagawa 228
†Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930

Stereodynamics of *N*-benzyl-*N*-methyl-9-aminotriptycene is studied by $^{1}H$ and $^{13}C$ dynamic NMR spectroscopy. The energy barriers to internal motion are governed by the eclipsing interaction between an *N*-alkyl group and an *o*-benzeno bridge of the triptycene moiety together with the intrinsic barrier to nitrogen inversion.

Pyramidality of nitrogen atoms in amines and facile inversion of the configuration have been well recognized and the stereodynamics of relatively simple trialkylamines has been studied predominantly by dynamic NMR spectroscopy.[1] It has been shown that interconversion among stable conformers involves inversion at nitrogen and rotation about C-N and C-C bonds, which takes place either simultaneously or successively depending on the degree of congestion in the molecules.

9-Substituted triptycene derivatives have served as a unique and excellent model system for the stereodynamic studies because of the skeletal rigidity and high rotational barrier of the bridgehead-to-substituent bond.[2] Stereodynamic studies of 9-alkyl and 9-oxy substituted triptycene derivatives have been extensively done but those on 9-aminotriptycene derivatives have been rather scarce.[3]

We have studied the stereodynamic behavior of *N*-benzyl-*N*-methyl-9-aminotriptycene (**1**) and *N,N*-dimethyl-9-aminotriptycene (**2**) using the temperature dependent $^{1}H$ and $^{13}C$ NMR spectra in order to elucidate the inversion-rotation interplay in the triptycene system. The preliminary results are reported in this article.




**1**: R=$CH_2C_6H_5$

**2**: R=$CH_3$

Compound **1** was synthesized from 9-aminotriptycene[4] by condensation with benzaldehyde (82%), reduction of the *N*-benzylidene derivative with $LiAlH_4$ (73%), and *N*-methylation of the resulting *N*-benzyl-9-aminotriptycene with MeI/BuLi (31%).[5,6] Compound **2** was obtained by reductive methylation of 9-aminotriptycene with $CH_2O/HCO_2H$ (70%).[7]

The $^{1}H$ NMR spectrum of **1** in $CDCl_3$ at 25 °C indicates that the internal motion is fast although the signals due to the aromatic protons of the triptycene (Tp) skeleton are somewhat broadened. Therefore the temperature dependence of the $^{1}H$ and $^{13}C$ spectra was studied in detail. The lineshape of the signals due to the protons and carbons 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 △)

sharpen while either of the larger signals (● and ▲) further 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, 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 1. 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, when the methyl group is still rapidly moving between the remaining two notches. In this situation, the Tp carbons appear as sets of two peaks with a 2:1 ratio and the methylene protons appear as a singlet. At lower temperatures, the methyl group becomes frozen into one of the notches. Here the Tp carbons appear as sets of three peaks with a 1:1:1 ratio and the methylene protons as an AB-quartet. The rate constant $k_{Bn}$

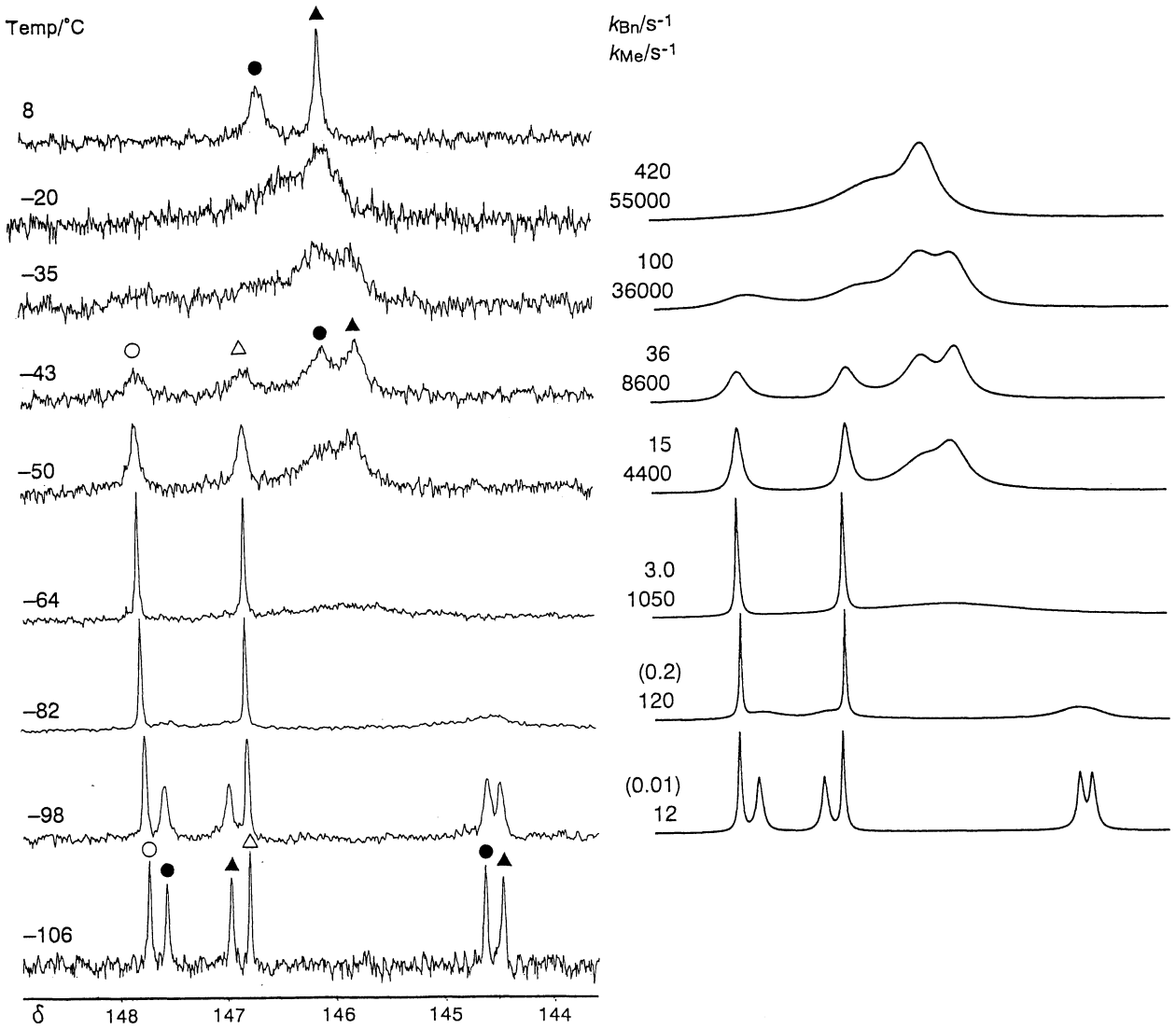



Fig. 1. The quaternary carbon signals of the triptycene moiety of compound **1** in acetone-$d_6$ at 125 MHz at various temperatures (left) and the calculated spectra (right).

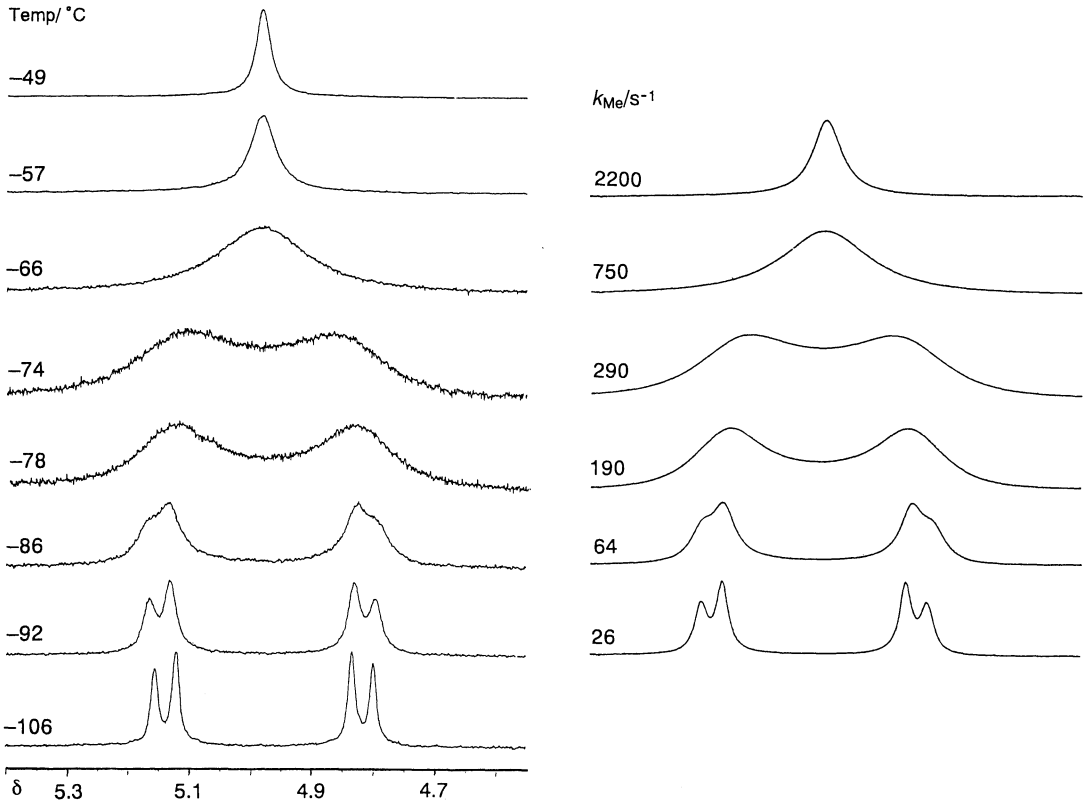
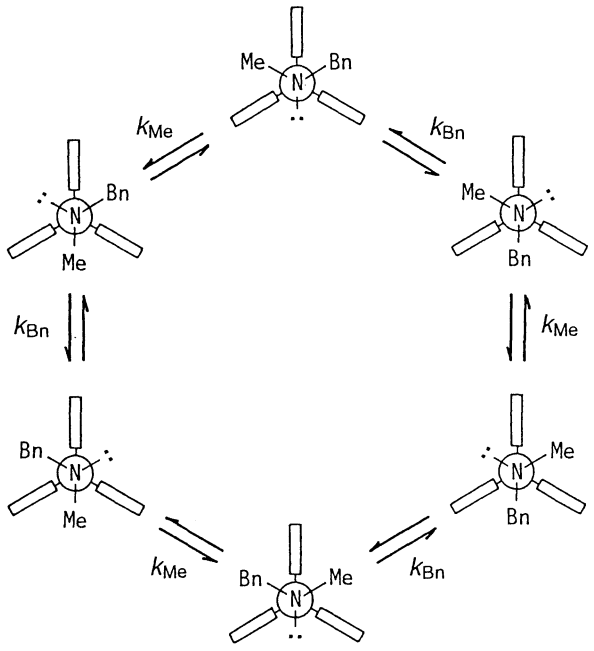



Fig. 2. The observed (left) and the calculated (right) spectra of the methylene protons of **1** in acetone-$d_6$ at 500 MHz




Scheme 1.

corresponds to the process in which the benzyl group passes over one of the *o*-benzeno bridge of the Tp moiety with concomitant inversion of the nitrogen configuration, while $k_{Me}$ corresponds to the process in which the methyl group passes over an *o*-benzeno bridge, which also is accompanied by nitrogen inversion. The $k_{Me}$ process takes place faster and thus has a lower energy barrier than the $k_{Bn}$ one. The $k_{Bn}$ process may therefore be regarded as "Tp–N rotation" since the nitrogen is considered planar on the NMR time scale during this process because of the fast $k_{Me}$ process and the benzyl group rotates about the Tp–N bond, while the $k_{Me}$ process is regarded as "nitrogen inversion" in the sense that the configurational identity of the nitrogen atom is lost in this process. Rotation of the Tp–N bond without nitrogen inversion is incompatible with the observed lineshape change and thus would have a far higher barrier.

The total lineshape analysis[8] of the methylene proton signal at six temperatures between –57 and –92 °C afforded $k_{Me}$ at each temperature (Fig. 2, right) and the following kinetic parameters were obtained by least-squares analysis: $\Delta H^{\ddagger}$=9.2±0.2 kcal mol$^{-1}$, $\Delta S^{\ddagger}$=–0.3±1.2 cal mol$^{-1}$ K$^{-1}$, $\Delta G^{\ddagger}$(200K)=9.24 kcal mol$^{-1}$. The lineshapes of the quaternary Tp carbon signals, which are governed by both $k_{Bn}$ and $k_{Me}$, were simulated at several temperatures between –20 and –98 °C.[8] At each temperature, a fixed $k_{Me}$ value was used which was obtained by extrapolation of the $k_{Me}$ data 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, the following kinetic parameters were obtained: $\Delta H^{\ddagger}$=11.5±0.9 kcal mol$^{-1}$, $\Delta S^{\ddagger}$=–0.8±3.9 cal mol$^{-1}$ K$^{-1}$, $\Delta G^{\ddagger}$(200K)=11.66 kcal mol$^{-1}$. In both processes the energy barrier is 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 *N*-alkyl group and an *o*-benzeno bridge. The intrinsic barrier to rehybridization is estimated to be ca. 5 kcal mol$^{-1}$ judging from the data reported for ammonia[9] and methylamine.[10] In 9-aminotriptycene, the barriers to Tp–N rotation and nitrogen inversion have been estimated to be 2.6 and 5.4 kcal mol$^{-1}$, respectively.[3a] In the present compound **1** carrying alkyl groups on nitrogen, the steric effect significantly contributes to the barrier. It is interesting that the passing of the benzyl group over an *o*-benzeno bridge has a higher energy barrier by ca. 2.4 kcal mol$^{-1}$ than that of the methyl group. This large difference may be rationalized by the gearing of the methyl group, though the detail should await further study including molecular mechanics calculations.

Compound **2** showed no lineshape change down to –95 °C in the $^1$H NMR spectrum. This suggests either that the internal motion is fast on the NMR time scale even at the lowest temperature or that the chemical shift difference between the diastereotopic protons is accidentally very small. Further study is in progress to clarify this point.

References

1) See for example: C. H. Bushweller, "Acyclic Organonitrogen Stereodynamics," ed by J. B. Lambert and Y. Takeuchi, VCH Publishers, New York (1992), pp. 1–55.
2) See for example: M. Ōki, "The Chemistry of Rotational Isomers," Springer-Verlag, Berlin (1993); G. Yamamoto, *Pure Appl. Chem.*, **62**, 569 (1990).
3) a) F. Imashiro, K. Hirayama, T. Terao, and A. Saika, *J. Am. Chem. Soc.*, **109**, 729 (1987); b) Y. Kawada and H. Iwamura, *J. Org. Chem.*, **51**, 1472 (1986); c) N. Nakamura, *Chem. Lett.*, **1982**, 1611.
4) W. Theilacker and K.-H. Beyer, *Chem. Ber.*, **94**, 2968 (1961).
5) All new compounds gave satisfactory elemental analysis and spectroscopic data.
6) Compound **1:** 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=3.35 (3H, s), 4.96 (2H, s), 5.27 (1H, s), 6.96-7.02 (6H, m), 7.33-7.40 (4H, m), 7.49 (2H, t, *J*=7.7 Hz), 7.61 (3H, br), 7.77 (2H, d, *J*=7.7 Hz).
7) Compound **2**: 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=3.41 (6H, s), 5.23 (1H, s), 6.96 (3H, td, *J*=7.3 and 1.2 Hz), 7.00 (3H, td, *J*=7.5 and 1.4 Hz), 7.34 (3H, dd, *J*=7.2 and 1.3 Hz), 7.61 (3H, dd, *J*=7.5 and 0.9 Hz).
8) The DNMR3 program was used: D. A. Kleier and G. Binsch, QCPE Program No. 165.
9) J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **36**, 1914 (1962).
10) M. Tsuboi, A. Y. Hirakawa, and K. Tamagake, *J. Mol. Spectrosc.*, **22**, 272 (1967).

(Received June 24, 1994)