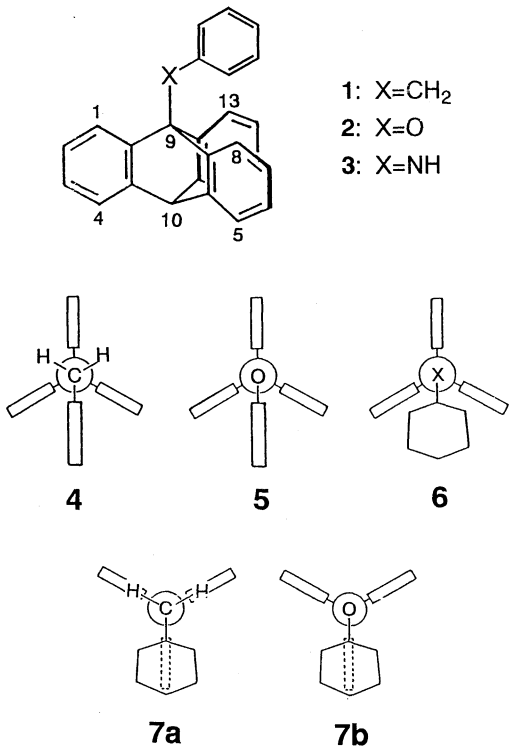
Stereodynamics of *N*-Phenyl-9-triptycylamine as a Gear-rotation System

Gaku Yamamoto,* Hiroyuki Higuchi,† Masami Yonebayashi,† Yuki Nabeta,† 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*

(Received June 19, 1995)

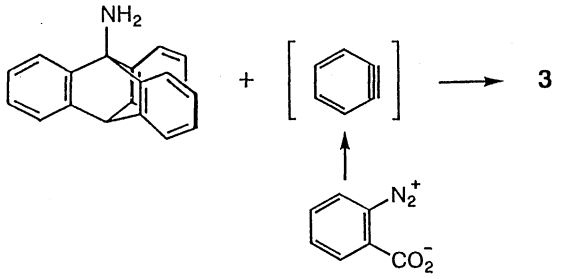
^{13}C Dynamic NMR study of *N*-phenyl-9-triptycylamine (**3**) reveals that "gear rotation" and "isolated rotation" in **3** have almost the same free-energy barriers of ca. 10.8 kcal mol^{-1}.

We have shown that 9-benzyltriptycene (**1**) and 9-phenoxytriptycene (**2**) represented as Tp-X-Ph (X=CH_2 and O) can be regarded as a static bevel gear system composed of a three-toothed wheel (Tp) and a two-toothed wheel (Ph), adopting the conformation approximately represented by the Newman projections **4** and **5**, respectively.[1,2] In compound **1** the lowest-energy process is "isolated rotation" (IR), in which rotation of the Ph-X bond takes place without rotation of the Tp-X bond, the transition state of which is represented by the Newman projection **6**. Meanwhile in compound **2** the lowest-energy process is "gear rotation" (GR), the correlated disrotation of the Tp-X bond and the Ph-X bond, the transition state of which is represented by **7** (**7a** for **1** and **7b** for **2**). The differential behavior between **1** and **2** can be ascribed to two main factors, C-X bond lengths and valency of X: shorter C-O bonds cause the tighter meshing of the wheels and thus raise the IR barrier in **2** while the tetravalency of carbon raises the GR barrier in **1**.[1]



These findings prompted us to study the dynamic behavior of *N*-phenyl-9-triptycylamine (**3**), Tp-NH-Ph. The behavior of **3** is expected to be intermediate between those of **1** and **2**. In addition, another dynamic process, i.e., inversion at the nitrogen atom, may contribute to the total dynamic behavior of the molecule.

Compound **3** was synthesized for the first time by the reaction of 9-triptycylamine[3] with benzyne generated in situ by thermal decomposition of benzenediazonium-2-carboxylate[4] (Scheme 1) in 32% yield.[5]



Scheme 1.

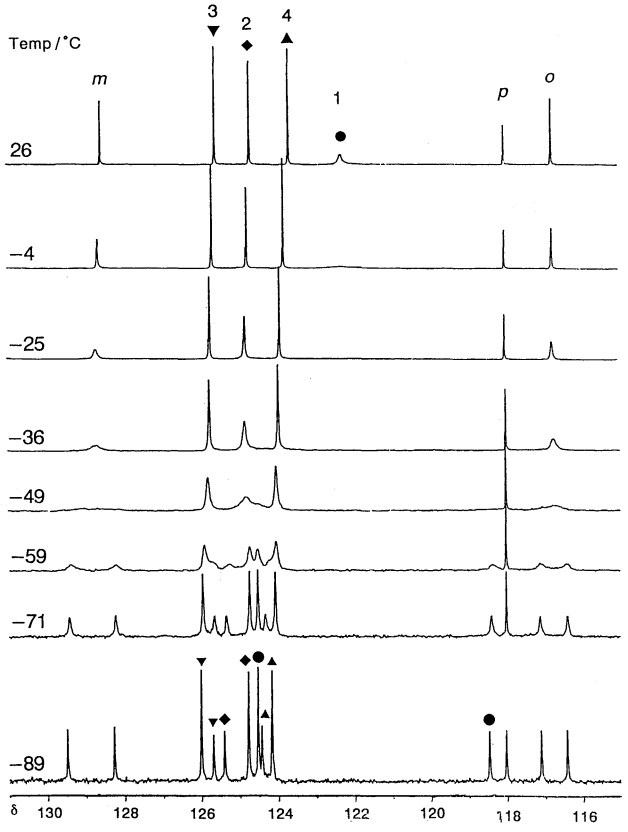
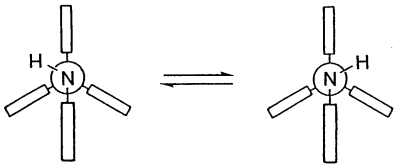


Figure 1. Temperature dependence of the tertiary aromatic carbon signals of compound **3** in CD_2Cl_2 at 125 MHz.

The ^{13}C NMR spectra of **3** in the tertiary aromatic carbon region at various temperatures are shown in Figure 1. At 26 °C the spectrum shows that the molecules are nearly at the fast-exchange limit on the NMR time scale, only the 1/8/13-carbon signal being broadened. Upon lowering the temperature, all the signals except for the one due to the *p*-carbon, broaden, decoalesce, and re-sharpen. At –89 °C, the lowest temperature examined, the signals due to the *o*- and *m*-carbons of the Ph group appear as two peaks of equal intensity, respectively, while the signals due to the tertiary aromatic carbons of the Tp moiety appear as four pairs of peaks with an intensity ratio of 2:1. This means that the rotation of both the Tp-N and Ph-N bonds is slow on the NMR time scale at this temperature but the N-inversion is still fast, and thus the compound is in rapid equilibrium between **8a** and **8b**.[6]



8a **8b**

The lineshape analysis of the *o*- and *m*-carbon signals afforded the free energy of activation of 10.5±0.1 kcal mol^{-1} (1 cal = 4.184 J) for the Ph-N rotation in the temperature range from –36 to –71 °C, while the temperature dependence of the 3/6/15-carbon signals afforded 10.8±0.1 kcal mol^{-1} for the Tp-N rotation in this temperature range. Typically the rate constants at –59 °C are found to be 90 and 36 s^{-1} for the Ph-N and the Tp-N rotation, respectively. As discussed in detail before,[1] the Tp-X rotation takes place only by the GR process, while the Ph-X rotation takes place either by GR or by IR. Thus the rate constants for the GR and IR processes in **3** are 36 and 90–36=54 s^{-1}, respectively, at –59 °C. This means that the two processes have almost the same free energy barriers of ca. 10.8 kcal mol^{-1}. Meanwhile the N-inversion barrier is estimated to be far lower than 9 kcal mol^{-1}.

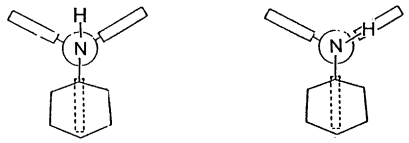
In Table 1 are shown the rate constants and the free energies of activation for the GR and IR processes in compounds **1–3** at –59 °C. The IR rate constant (k_{IR}) monotonously decreases from **1** to **3** to **2** in parallel with the change in the C-X bond length. The shortening of the C-X bonds on going from **1** to **3** to **2** sterically destabilizes both the ground state and the transition state of the IR process and the extent of destabilization would be larger in the latter and thus the IR process takes place slower in this order, i.e., **1**>**3**>**2**.

Table 1. Rate constants and free energies of activation for the GR and IR processes in compounds **1–3** at –59 °C

Compd	X	k_{GR}	$\Delta G^{\ddagger}_{GR}$	k_{IR}	$\Delta G^{\ddagger}_{IR}$
		s^{-1}	kcal mol^{-1}	s^{-1}	kcal mol^{-1}
1[a]	CH_2	52	10.7	2350	9.1
3	NH	36	10.9	54	10.7
2[a]	O	ca. 10^5	ca. 7	ca. 10^{-2} [b]	14.9[b]

[a] Ref. 1. [b] From the molecular mechanics data given in Ref. 1.

On the contrary, the GR rate constant (k_{GR}) is rather similar in **1** and **3** and significantly increases in **2**. The low GR barrier in **2** has been ascribed to the divalency of the oxygen; the eclipsing interaction at the transition state should be considered only between the phenyl group and one of the *o*-benzeno bridges (see **7b**) in contrast with the case of **1** where the eclipsing interaction between the methylene hydrogens and the *o*-benzeno bridges should also be considered (see **7a**).[1] The bond length effect which would more destabilize **7b** than **7a** is completely covered by the valency effect.



9 **10**

In the nitrogen compound **3** the transition state for the GR process would be represented either by **9** or **10**. In **9** the N-inversion takes place simultaneously with the eclipsing of the Ph group with an *o*-benzeno bridge and thus the nitrogen is planar, whereas in **10** the nitrogen retains pyramidality and the N-hydrogen eclipses another *o*-benzeno bridge. Although the determination of the actual geometry of the transition state requires detailed MO calculations, the similar height of the GR barriers in **1** and **3** will be understood in terms of the destabilization of the transition state in **3** either due to the planar nitrogen as shown in **9** or due to the eclipsing effect as in **10**, together with the bond length effect which will more destabilize the GR transition state of **3** than that of **1**.

Further studies on several *N*-alkyl derivatives of **3** are in progress.

References and Notes

1 G. Yamamoto, *Tetrahedron*, **46**, 2761 (1990).
2 G. Yamamoto, *Pure Appl. Chem.*, **62**, 569 (1990).
3 W. Theilacker and K.-H. Beyer, *Chem. Ber.*, **94**, 2968 (1961).
4 F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth., Coll. Vol. V*, 54 (1973).
5 Compound **3**: mp 280–281 °C. Found: C, 90.12; H, 5.74; N, 3.96%. Calcd for $C_{26}H_{19}N$: C, 90.40; H, 5.54; N, 4.06%. ^1H NMR ($CDCl_3$) δ 5.423 (1H, s, 10-H), 5.513 (1H, br s, NH), 6.754 (2H, br d, *J*=7.6 Hz, *o*-H), 6.793 (1H, t, *J*=7.3 Hz, *p*-H), 6.958 (3H, td, *J*=7.5 and 1.0 Hz, 2/7/14-H), 7.011 (3H, td, *J*=7.1 and 1.0 Hz, 3/6/15-H), 7.158 (2H, t, *J*=7.7 Hz, *m*-H), 7.328 (3H, d, *J*=7.4 Hz, 1/8/13-H), 7.418 (3H, d, *J*=7.3 Hz, 4/5/16-H). ^{13}C NMR ($CDCl_3$) δ 53.72 (10-C), 66.69 (9-C), 116.67 (*o*-C), 117.87 (*p*-C), 122.24 (br, 1/8/13-C), 123.50 (4/5/16-C), 124.58 (2/7/14-C), 125.37 (3/6/15-C), 128.49 (*m*-C), 143.58 (8a/9a/12-C), 145.02 (4a/10a/11-C), 145.16 (*i*-C).
6 For the pyramidal structure of the aniline nitrogen, see: J. C. Evans, *Spectrochim. Acta*, **16**, 428 (1960); D. G. Lister and J. K. Tyler, *J. Chem. Soc., Chem. Commun.*, **1966**, 152.