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Hindered Internal Rotation of N,N-Dimethylamino Group in Peri-substituted Naphthalenes

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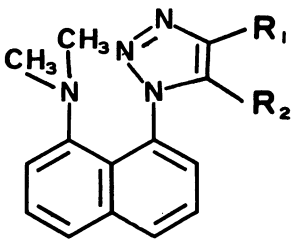
The rotation around the C-N bond between the dimethylamino group and the naphthalene ring in 1-(8-dimethylamino-1-naphthyl)-1H-1,2,3-triazoles is strongly restricted and the rotational barrier is enhanced by the substituent at 5-position of the triazole ring.

Owing to the weak conjugation between the amino group and the aromatic ring, the C-N bond about the two moieties in aminoaromatics exhibits partial double bond character, and the rotational barrier of the bond has been measured by dynamic NMR methods in several dimethylamino compounds.[1] The activation energies for the restricted rotation, however, are so small that the NMR measurements required very deep temperatures.

On the other hand, 1,8-disubstituted naphthalenes are known to show several unique properties due to the steric overcrowding at the peri-position.[2] We recently reported the syntheses of novel 1,1'-(1,8-naphthylene)di-1H-1,2,3-triazoles[3] and their very distorted structure because of the repulsion between the two triazole rings.[4] In connection with the study, we have synthesized 1-(8-dimethylamino-1-naphthyl)-1H-1,2,3-triazoles, (**1** - **4**), which are new peri-substituted naphthalenes with a dimethylamino group.[5] In this paper, we report that the rotation around the C-N bond between the dimethylamino group and the naphthalene ring in these compounds is strongly



1 : $R_1 = R_2 = CO_2Et$
2 : $R_1 = H$, $R_2 = CO_2Et$
3 : $R_1 = CO_2Et$, $R_2 = H$
4 : $R_1 = R_2 = H$

restricted and that the rotation of the C-N bond between the triazole and naphthalene rings is frozen even at high temperatures.

The ^{1}H NMR spectrum of 1 at room temperature showed two sharp signals for the N-methyl protons (δ=1.956 and 2.434 ppm from TMS, in DMSO-d_6, 399.65MHz with a JEOL GX-400 spectrometer). This indicates the nonequivalence of the two N-methyl groups in 1. As the temperature was increased, the line broadening of the N-methyl signals occurred and the two signals coalesced at ca. 371 K. At 393 K, the N-methyl signal became one considerably sharp peak as shown in Fig. 1. The line-shape changes can be explained in terms of the existence of very slow rotation in the NMR time scale. Concerning this point, we must consider two possibilities for the restricted rotation around the following two bonds:

(1) the C-N bond between the triazole and naphthalene rings

(2) the C-N bond between the dimethylamino group and the naphthalene ring.

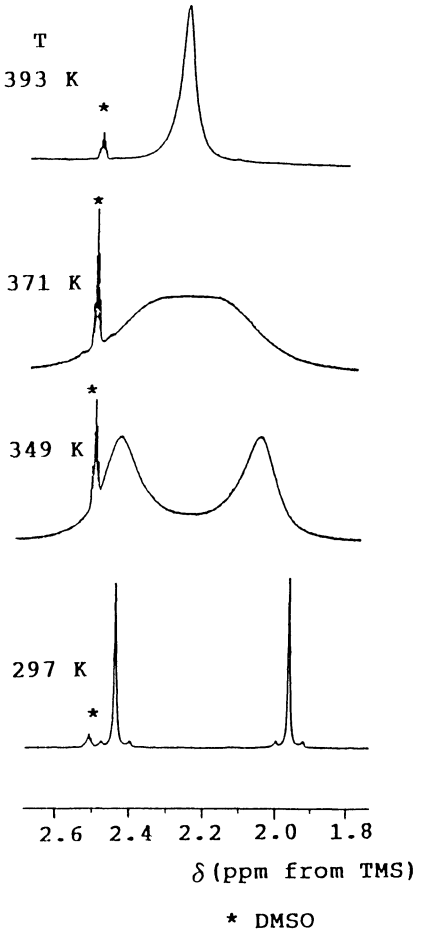


Fig. 1. ^{1}H NMR spectra of the N-methyl group in 1 at several temperatures.

If the rotation around the C-N bond between the triazole ring and the naphthalene ring in 1 is frozen or sufficiently slow in the NMR time scale, it is expected that the two methylene protons in the each ethoxycarbonyl group are magnetically non-equivalent due to a molecular asymmetry in 1. Then, the signals of the each ethyl group in 1 ought to show AA'X_3 coupling pattern arising from non-equivalency and the pattern should change to A_2X_3 as the rotation becomes faster. In fact, the signals of the two methylene protons of the ethoxycarbonyl group at the 5-position were found to be AA'X_3 coupling pattern even at the high temperature as 393 K (see Fig. 2). The methylene protons of the 4-ethoxycarbonyl group appearing at 4.40 ppm showed similar phenomena. These findings indicate that the rotation of the triazole ring is strongly frozen. Thus, it is concluded that the ^{1}H NMR line shape

change described above resulted from the slow rotation of the dimethylamino group. Similar NMR spectral behavior was observed in 2. In the case of 3 and 4, the proton signal of the dimethylamino group is one sharp peak at room temperature. But it becomes broad with decrease of the temperature and finally splits into two sharp peaks at the lower temperatures. The activation parameters for the rotations of the dimethylamino groups are shown in Table 1. These parameters are determined by the complete line-shape analyses of the NMR signals using the computer program EXNMR0[6]. The rotational barriers in 1 - 4 are much higher than those previously reported in N,N-dimethylaniline[7] ($\Delta G^{\ddagger}$= 21.3 kJ mol^{-1} at 133 K) and 2-chloro-4-dimethylamino quinazoline[8] ($\Delta G^{\ddagger}$= 34.7 kJ mol^{-1} at 173 K). Moreover, 1-dimethylaminonaphthalene did not show such a line broadening and splitting even at 183 K. Obviously, the triazole ring located at close proximity strongly affects the rotation of the dimetylamino group. It is interesting that the free energies of activation in 1 and 2 are almost the same, but much larger than the energies in 3 and 4 which are also approximately equal each other. This indicates that the presence of the ethoxycarbonyl group at 4-position of the triazole ring does not influence the rotational barrier of the dimethylamino group, but the ester group substituted at 5-position in the triazole ring extremely enhances the rotational barrier.

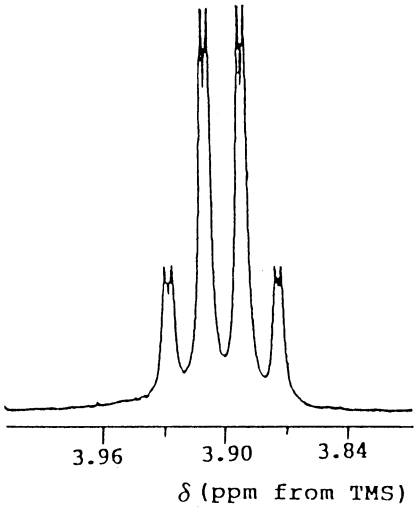


Fig. 2. ^{1}H NMR spectrum of the 5-methylene group in 1 at 393 K.

Table 1. Activation parameters for internal rotation of the dimethylamino group

Compound	Tc / K	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{Tc}$ / kJ mol^{-1}	Solvent
1	371	63.7 ± 1.7	-26 ± 4	73.2 ± 2.0	DMSO-d_6
2	369	64.5 ± 1.6	-32 ± 4	73.9 ± 1.9	DMSO-d_6
3	233	36.9 ± 1.6	-38 ± 5	46.2 ± 2.1	acetone-d_6
4	241	37.0 ± 1.9	-30 ± 6	44.2 ± 2.3	acetone-d_6

There are large differences in the chemical shifts of the splitted two methyl signals of the dimethylamino group in 1 as described before. This suggests that the two methyl groups exist in magnetically very different environment. If the conformation of the two methyl groups is such as shown in Fig. 3, a ring current effect of the triazole ring is fairly different toward the two methyl protons. In this conformation, the lone pair of the nitrogen atom of the dimethylamino group exists in sterically overcrowding circumstances. These considerations are supported by the following experiment; when quarternization of the dimethylamino group was attempted by large excess of methyl tosylate, it did not occur in 1 whereas easily occurred in 1-dimethylaminonaphthalene. These results suggest the conformation in Fig. 3 is probably true.

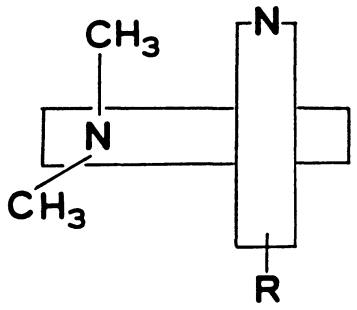


Fig. 3. Conformation of the dimethylamino group and the triazole ring.

In conclusion, the strongly restricted rotation of dimethylamino group due to the steric hindrance of the substituent at the peri-position of the naphthalene ring is clearly observed by the ^{1}H NMR at room temperature.

References

1) M.Ōki, "Applications of Dynamic NMR Spectroscopy to Organic Chemistry," Methods in Stereochemical Analysis, Vol.4, VCH, Florida, (1985), p.86.
2) V.Balasubramaniyan, Chem. Rev., 1966, 567.
3) K.Honda, H.Nakanishi, Y.Nagawa, and A.Yabe, Chem. Commun., 1984, 450; Y.Nagawa, K.Honda, and H.Nakanishi, Bull. Chem. Soc. Jpn., 60, 2931(1987).
4) Y.Nagawa, M.Goto, K.Honda, and H.Nakanishi, Acta Crystallogr., Sect. C, 42, 478(1986); Y.Nagawa, M.Goto, K.Honda, and H.Nakanishi, Bull. Chem. Soc. Jpn., 61, 3553(1988).
5) Y.Nagawa, K.Honda, and H.Nakanishi, Synthesis, 1987, 905.
6) O.Yamamoto, K.Hayamizu, H.Nakanishi, and M.Yanagisawa, J. Nat. Chem. Lab. Ind. (Tokyo), 69, 14(1974).
7) R.F.Mackenzie and D.D.Macnicol, Chem. Commun., 1970, 1299.
8) J.Almong, A.Y.Meyer, and H.S.Atidi, J. Chem. Soc., Perkin Trans. 2, 1972, 453.

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