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ISOLATION AND CHARACTERIZATION OF STABLE ROTATIONAL ISOMERS ABOUT A TETRAHEDRAL NITROGEN-TO-TETRAHEDRAL CARBON SINGLE BOND IN 2,3-DIMETHYL-9-(N,N-DIMETHYLAMINO)TRIPTYCENE N-OXIDE1)

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Oxidation of 2,3-dimethyl-9-(N,N-dimethylamino)triptycene with mCPBA followed by chromatography on alumina afforded two stable rotamers about a C-N single bond, whose assignment was consistently carried out on the basis of their ^{1}H- and ^{13}C-NMR, along with those of the model compound, 9-(N,N-dimethylamino)triptycene N-oxide.

Rotational isomerism has long been one of the continueing subjects in stereochemistry since the discovery of biphenyl isomerism,2) and many atropisomers, especially those about carbon-to-carbon single bonds, are known. Triptycene derivatives with a carbon substituent in a bridge-head position are good models for studying rotational isomerism about a single bond connecting the substituent and the tetrahedral bridge-head carbon atom of the triptycene skeleton. Isolation and characterization of such stable rotamers are well documented.3)

Introduction of heteroatom group in a bridge-head position would provide new kinds of atropisomers about heteroatom-to-carbon single bonds. Herein the author wishes to report the first isolation and spectroscopic characterization of the stable rotamers about a tetrahedral nitrogen-to-tetrahedral carbon single bond.4,5)

Amines are undergoing rapid inversion at nitrogen atom, which lowers the barrier to rotation due to possible passage throuth the common transition states for these two dynamic processes.6) The inversion process can be suppressed on oxidation or quaternization of a tertiary amine to the corresponding amine oxide or quaternary ammonium salt, respectively.

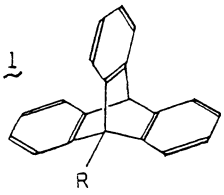
Model experiments on 9-aminotriptycene (1a)7) to prepare the amine oxide 1c are as follows. Methylation of 1a with trimethyloxonium tetrafluoroborate to give 9-(N,N-dimethylamino)triptycene (1b) was followed by its mCPBA oxidation (1.1 equiv) in dichloromethane at 0 °C and by subsequent chromatography on dry alumina (Woelm, neutral) to afford 9-(N,N-dimethylamino)triptycene N-oxide (1c) in 87% yield [mp 159 °C (dec)].8)

The ^{1}H NMR spectrum of 1c indicates that the rotation about the single bond in question is frozen on an nmr time scale, since the peri-protons, i.e., the three protons in the 1-, 8-, and 14-positions of 1c, have split into two portions in a 2 : 1 intensity ratio as expected from the inspection of Newman-type projection along the N-C(9) bond shown. The ^{13}C NMR of 1c also supports the frozen conformation mentioned above, as judged from the number of the aromatic carbon lines and their relative intensities.

Noteworthy also is the large difference between the chemical shift for the protons syn-clinal to the N-O bond and that for the proton anti-periplanar to the same bond. The former resonate at a lower field by ca. 0.6 ppm, while the latter does at a higher field by ca. 0.9 ppm, than the peri-protons of trimethyl(9-triptycyl)ammonium tetrafluoroborate.9) This observation is the first reported example of the anisotropy exhibited distinctly by the N-O bond of amine oxide.

Thermal stability of **1c** up to the boiling point of chloroform for more than 180 min implies the strong possibility for the existence of isolable rotamers about a C-N single bond. Isolation of such conformers was accomplished by introduction of two methyl groups into one of the three aromatic rings of the triptycene, which enabled one to distinguish $\pm$sc and ap conformations from each other.

1



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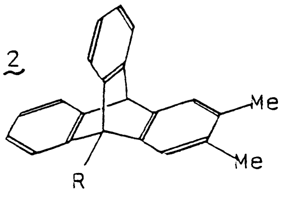
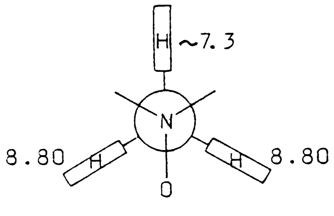
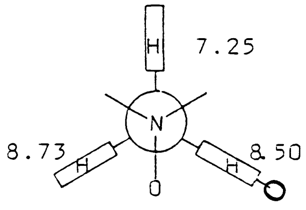


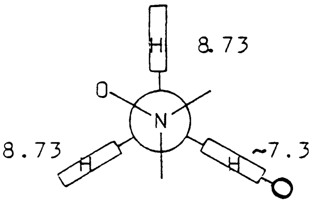
a; R = NH_2
b; R = NMe_2
c; R = $\underset{O}{\overset{}{N}}Me_2$



1c



$\pm$sc-**2c**



ap-**2c**

Starting from 9-nitroanthracene and 4,5-dimethylanthranilic acid, 2,3-dimethyl-9-(N,N-dimethylamino)triptycene (**2b**) was derived in four steps. Oxidation of the amine **2b** under the same conditions as before yielded quantitatively the m-chlorobenzoate of 2,3-dimethyl-9-(N,N-dimethylamino)triptycene N-oxide, whose nmr spectrum revealed a rotamer ratio of about 2 : 1, almost statistical value, as estimated from the intensities of the peri-protons discussed above, with $\pm$sc-isomer being about two thirds of the products.

Chromatography of the m-chlorobenzoate on dry alumina with a 1 : 1 mixture of hexane and dichloromethane gave, as the first eluate, $\pm$sc-2,3-dimethyl-9-(N,N-dimethylamino)triptycene N-oxide ($\pm$sc-**2c**) [mp 162-164 °C (dec)]10), and then, as the second eluate, ap-2,3-dimethyl-9-(N,N-dimethylamino)triptycene N-oxide (ap-**2c**) [mp 173-174 °C (dec)].11) Comparison of the ^{1}H NMR spectra of **2c** with that of the model compound **1c** allows the above assignment, which is completely consistent with the molecular symmetries deduced from the ^{13}C NMR spectra of these two rotameric N-oxides.

Though they are both stable in boiling chloroform, attempts to equilibrate these conformers at higher temperatures have resulted in their quantitative transformation into 2,3-dimethyl-9-(N,N-dimethylamino)triptycene (**2b**) in DMSO-d_6 at 80

°C, or partial conversion into a 1 : 4.5 mixture of **2b** and 2,3-dimethyl-9-(N-methylamino)triptycene, respectively, in acetic acid at 110 °C. Detachment of one methyl group from a tertiary amine has been also observed during the mCPBA oxidation reaction of 1,4-dimethoxy-9-(N,N-dimethylamino)triptycene, where 1,4-dimethoxy-9-(N-methylamino)triptycene was produced quantitatively even at 0 °C.

No detectable change in the ±sc to ap rotameric ratios was observed, during the equilibration at 110 °C, with the remaining starting materials, even if mixtures of both conformers were used. This implies that the barrier to rotation about the C-N single bonds in the present study may be, at least, 30 kcal/mol.

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5) All new compounds in the present communication gave satisfactory elemental analyses. Mp's are not corrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian EM-390 and a Jeol FX 60, respectively, and electron impact mass spectra on a Jeol D 300.

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8) **1c**: Electron impact mass spectrum, found m/e 313.1473, calcd for $C_{22}H_{19}NO$ 313.1467; ^{1}H NMR ($CDCl_3$) δ 4.41 (6H, s, N-CH_3 x2), 5.23 (1H, s, bridge-head), 6.8-7.7 (10H, m, aromatic H's), 8.6-8.9 (2H, m, aromatic H's); ^{13}C NMR ($CDCl_3$)

δ 54.98 (bridge-head C with H), 62.61 (N-CH_3 x2), 89.80 (bridge-head C with N), 123.24, 123.36, 124.21, 124.58, 124.78, 125.31, 126.53, 127.01, 138.86, 140.00, 145.84, 146.17 (aromatic C's).

9) Trimethyl(9-triptycyl)ammonium tetrafluoroborate shows its peri-protons on the same side of the bridge-head substituent at 8.17 ppm, and those on the other side at 7.65 ppm.

10) ±sc-**2c**: Electron impact mass spectrum, found m/e 341.1803, calcd for $C_{24}H_{23}NO$ 341.1778; ^1H NMR ($CDCl_3$) δ 2.13 (3H, s, ArCH_3), 2.18 (3H, s, ArCH_3), 4.43 (6H, s, N-CH_3 x2), 5.16 (1H, s, bridge-head H), 6.8-7.2 (5H, m, aromatic H's), 7.2-7.38 (1H, m, aromatic H), 7.38-7.67 (2H, m, aromatic H's), 8.50 (1H, s, aromatic H), 8.6-8.87 (1H, m, aromatic H); ^{13}C NMR ($CDCl_3$) δ 19.23 (ArCH_3), 20.12 (ArCH_3), 54.70 (bridge-head C with H), 62.65 (N-CH_3), 62.73 (N-CH_3), 89.88 (bridge-head C with N), 123.20, 123.36, 124.21, 124.53, 124.66, 124.82, 125.31, 126.53, 127.05, 128.35, 132.69, 133.71, 137.60, 139.43, 140.45, 143.69, 145.25, 146.69 (aromatic C's).

11) ap-**2c**: Electron impact mass spectrum, found m/e 341.1748, calcd for $C_{24}H_{23}NO$ 341.1778; ^1H NMR ($CDCl_3$) δ 2.21 (3H, s, ArCH_3), 2.23 (3H, s, ArCH_3), 4.50 (6H, s, N-CH_3 x2), 5.16 (1H, s, bridge-head H), 6.76-7.18 (4H, m, aromatic H's), 7.18-7.47 (4H, m, aromatic H's), 8.56-8.8 (2H, m, aromatic H's); ^{13}C NMR ($CDCl_3$) δ 19.19 (ArCH_3), 20.37 (ArCH_3), 54.62 (bridge-head C with H), 62.53 (N-CH_3 x2), 89.84 (bridge-head C with N), 123.24, 124.86, 125.03, 125.43, 125.68, 126.85, 132.53, 135.13, 136.30, 140.16, 143.98, 146.21 (aromatic C's).

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