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9-DIMETHYLAMINO-9,10-DIHYDRO-9,10-ETHENOANTHRACENE N-OXIDE: AN EXAMPLE WHICH SHOWS SLOW INTERNAL ROTATION ABOUT A N_{sp3}-C_{sp3} BOND[1)]

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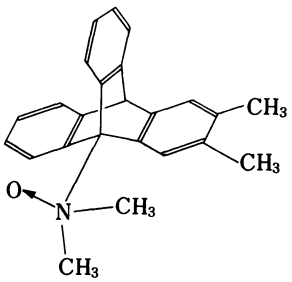
9-Dimethylamino-9,10-dihydro-9,10-ethenoanthracene was prepared by reductive dechlorination of its tetrachloro derivative and was oxidized to produce the title compound. The compound crystallized as an ap conformer. On dissolution, it isomerized to its ±sc conformer with a rate constant 2.52×10^{-5} s^{-1} at 30 °C until the equilibrium (±sc/ap = 0.16) was reached. The following activation parameters were obtained: $\Delta H^{\ddagger}$ 23.1 ± 4.4 kcal mol^{-1}, $\Delta S^{\ddagger}$ -3.9 ±14.1 e. u.

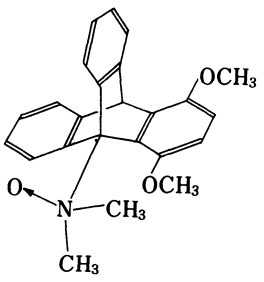
Although various types of atropisomerism about a single bond involving at least one tetrahedral carbon in the bond in question have been manifested,[2)] a number of atropisomers about a hetero atom-to-tetrahedral carbon bond is limited. One of the factors, which we have to consider in discussing barriers to rotation about a C_{sp3}-X bond where X is a hetero atom, is that the C-X bond length is affected by the nature of the hetero atom. The force constant for the angle deformation varies as well to affect the height of the barrier.[3)]

As for a nitrogen-to-carbon bond, the bond distance is much shorter than that of a corresponding carbon-to-carbon bond. This will make the energy of the ground state high as well as that of the transition state for rotation. Nakamura was able to isolate atropisomers of 2,3-dimethyl-9-dimethylaminotriptycene N-oxide (1) but attempts to measure the barrier to rotation failed because they decomposed on being heated.[4)] Attempts to obtain 1,4-dimethoxy-9-dimethylaminotriptycene N-oxide (2) by oxidation of the parent amine failed because an elimination reaction took place with great ease owing to the instability of the oxide 2.[4)]



(1)

(±*sc* forms were isolated as well.)

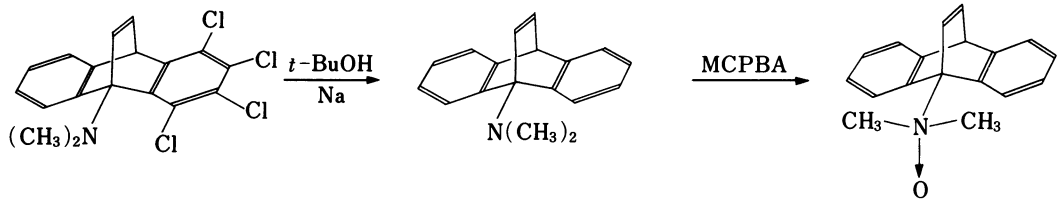


(2)

(This and its ±*sc* isomers were too unstable to be isolated.)

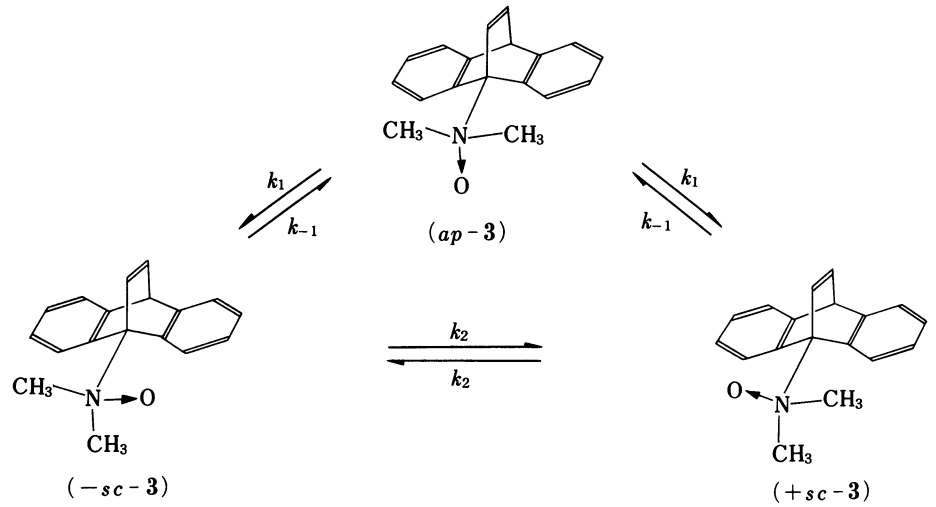
Although switching one of the benzeno bridges in 9-substituted triptycenes to an etheno bridge would reduce the barrier to rotation to a great extent, it would lower the ground state energy as well.[2] To explore the possibility of obtaining stable rotamers of this sort, we have undertaken the synthesis of 9-dimethylamino-9,10-dihydro-9,10-ethenoanthracene N-oxide (3). This paper is to report the synthesis of and the barrier to rotation in 3. The latter proved to be the first example of determining the rates of rotation about a N_{sp^3}-C_{sp^3} bond by a classical method at room temperature and above, to the best of our knowledge.

The synthesis of the compound was accomplished in the following way. 1,2,3,4-Tetrachloro-9-dimethylamino-9,10-dihydro-9,10-ethenoanthracene (4), which was prepared by addition of tetrachlorobenzyne to 1-dimethylaminonaphthalene,[5] was treated with sodium and t-butyl alchohol to produce 9-dimethylamino-9,10-dihydro-9,10-ethenoanthracene (5), the manipulation being essentially the same with that developed for the preparation of benzobarrelene.[6] Compound 5 was oxidized with m-chloroperoxybenzoic acid to produce the desired compound 3, which melted at 205 - 206 °C.



(4) (5) (3)

^{1}H NMR spectra[7] of 3 in chloroform-d suggested that the crystals were made of ap conformers only. The chloroform-d solution of 3 exhibited a growing signal due to a methyl group at δ 4.35 at 60 MHz on standing. This is an indication that isomerization takes place. In principle, the ±sc form should exhibit two methyl signals as is clear from the Newman projections of 3. A ^{1}H NMR spectrum at 400 MHz showed really two peaks at δ 3.91 and 4.35, the former peak apparently overlapping in the 60 MHz spectra with that at δ 3.93 due to the ap form. Recovering the



(ap-3)

(−sc-3) (+sc-3)

material out of the solution produced crystals which contain the ap form only. The results suggest that the crystal lattice of the ap form is so stable relative to that of the ±sc that the compound crystallized into one form, i.e. ap. The results also imply that the process observed in the present work is the diastereomerization by rotation, although the ±sc isomer has not been isolated.

The equilibrium constants, which indicate that the ap form is favored, are reasonable because a methyl group is larger than an oxygen group and the larger groups are better accommodated in the notch made by the etheno and the benzeno bridges than that made by two benzeno bridges. The populations of the rotamers in triptycene systems are known to be sensitive to the steric requirements.[8)]

The rates of isomerization and the equilibrium constants were obtained by ^{1}H NMR spectroscopy. The data were treated by assuming a first order reversible reaction. The results are shown in Table 1. Putting these data into the Eyring equation, we obtained $\Delta H^{\ddagger} = 23.1 \pm 4.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -3.9 \pm 14.1$ e. u. Thus $\Delta G^{\ddagger}_{298}$ is 24.3 kcal mol^{-1}. From the temperature dependence of the equilibrium constants, $\Delta H°$ and $\Delta S°$ were obtained as 3.1 ± 0.3 kcal mol^{-1} and 6.5 ± 0.9 e. u., respectively.

A work to compare the barrier heights for rotation about a C-C and a C-N bond in similar situations is under way.

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Table 1 Kinetic Data for Diastereomerization (ap ⇄ ±sc) of 9-Dimethylamino-9,10-dihydro-9,10-etheno-anthracene N-Oxide in Chloroform-d

Temp/°C	k_1/s^{-1}	K (±sc/ap)
30.0	2.52×10^{-5}	0.16
36.0	3.68×10^{-5}	0.18
39.5	4.71×10^{-5}	0.20
60.0	7.50×10^{-4}	0.26
64.0[a)]	———	0.27

a) The equilibrium constant only was determined.

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1) Restricted Rotation Involving the Tetrahedral Carbon. Part XLVIII. For Part XLVII, see G. Yamamoto, M. Suzuki, and M. Ōki, Bull. Chem. Soc. Jpn., in press.
2) M. Ōki, Angew. Chem. Int. Ed. Engl., 15, 87, (1976): Top. Stereochem., 14, in press.
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6) N. J. Hales, H. Heaney, and J. H. Hollinshead, Org. Synth., 59, 71 (1980).
7) The following ^{1}H NMR data were obtained at 400 MHz and at 60 °C ($CDCl_3$ δ). ap: 3.93 (6H, s), 4.96 (1H, dd, J=6.0 and 1.0 Hz), 6.67 (1H, dd, J=7.5 and 1.0 Hz), 6.9 - 7.6 (7H, m), 8.68 (2H, m). sc: 3.91 (3H, s), 4.35 (3H, s), 5.04 (1H, dd, J=6.0 and 1.0 Hz), 7.55 (1H, dd, J=7.5 and 1.0 Hz), 6.9 - 7.6 (7H, m), 8.41 (1H, m). A signal due to the peri-proton flanked by the N-O and the C-CH_3 groups in the ±sc form seems to be buried in the ap signal at δ 8.68.
8) If a group, which is one of the three subsituents of a tertiary group in the 9-position of the triptycene system, is smaller than a methyl, ±sc forms are favored over the ap form to a degree which is determined by the size of the group and the peri-substituent. See S. Otsuka, T. Mitsuhashi, and M. Ōki, Bull. Chem. Soc. Jpn., 52, 3663 (1979): M. Ōki, Y. Tanaka, G. Yamamoto, and N. Nakamura, Bull. Chem. Soc. Jpn., 56, in press. If a 9-substituent is a secondary group, it constitutes an extreme case and we hardly observe the existence of a conformer in which the hydrogen, the smallest substituent, in the 9-substituent takes the ap position to a peri-substituent. See F. Suzuki, M. Ōki, and H. Nakanishi, Bull. Chem. Soc. Jpn., 47, 3114 (1974): M. Suzuki, G. Yamamoto, H. Kikuchi, and M. Ōki, Bull. Chem. Soc. Jpn., 54, 2383 (1981): H. Kikuchi, S. Hatakeyama, G. Yamamoto, and M. Ōki, ibid., 3832.

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