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# RESTRICTED INTERNAL ROTATION OF A *t*-BUTYL GROUP BONDED TO AN AROMATIC RING[1)]

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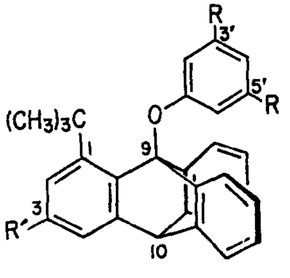
Summary: Low temperature $^1$H NMR study of 1,3-di-*t*-butyl-9-(3,5-dimethylphenoxy)triptycene revealed restricted rotation of the 1-*t*-butyl group with an energy barrier of 9.2 kcal mol$^{-1}$, which is the highest ever reported for internal rotation of an aromatic *t*-butyl group.

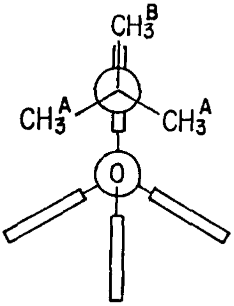
In contrast with the abundant examples of restricted rotation of a primary or a secondary alkyl group attached to an sp$^2$-hybridized atom, dynamic NMR studies on the counterparts with a tertiary alkyl group, especially when three groups of similar bulkiness are bonded to the central carbon of the *t*-alkyl group, have rarely been reported because of generally very low rotational barriers.[2)]

Several attempts at observing restricted rotation of a *t*-butyl group bonded to an aromatic ring by NMR spectroscopy have failed to produce an unambiguous result.[3,4)] An apparent exception may be 1,8-di-*t*-butylnaphthalene derivatives, where an energy barrier of 6.5 kcal mol$^{-1}$ was reported for the internal rotation of the *t*-butyl groups,[5a)] although the geometry around the 1- and 8-carbons is far from what is expected for the normal sp$^2$-hybridization.[5b)] We report here an unprecedentedly high rotational barrier of an aromatic *t*-butyl group in a 1-*t*-butyltriptycene derivative where the 9-substituent serves as an effective obstacle to rotation.

During the course of our investigations on the stereodynamics of 9-aryloxytriptycene derivatives,[6)] we had a chance to synthesize 1,3-di-*t*-butyl-9-(3,5-dimethylphenoxy)triptycene (**1**)[7)] and to study its dynamic NMR. Lineshape change of the 3'- and 5'-methyl proton signals resulting from the C-O restricted rotation occurs above room temperature with an energy barrier of 17.6 kcal mol$^{-1}$.[6)] Of two singlets assignable to two *t*-butyl groups in the $^1$H NMR spectrum ($CD_2Cl_2$, 400 MHz) of **1** at 24 °C, the singlet at δ 1.715 appears considerably broader than the other at δ 1.247. On lowering the temperature, the low-field signal further broadens and below -75 °C it splits into two peaks. At -96.2 °C, they appear as a three-proton singlet at δ 1.489 and a six-proton singlet at δ 1.815, while the high-field signal remains a sharp nine-proton singlet at δ 1.264. This feature would reasonably be interpreted that internal rotation of the 1-*t*-butyl group is restricted at low temperatures while that of the 3-*t*-butyl group is fast throughout the temperature range examined. Lineshape analysis of the spectra at -83 to -56 °C[8)] using the DNMR3



**1**: $R=CH_3$, $R'=C(CH_3)_3$
**2**: R = R' = H



program9a) gave the following activation parameters: $\Delta H^{\ddagger} = 9.2 \pm 0.6$ kcal mol$^{-1}$, $\Delta S^{\ddagger} = -1.7 \pm 2.9$ cal mol$^{-1}$K$^{-1}$, $\Delta G^{\ddagger}_{200} = 9.5$ kcal mol$^{-1}$.

Molecular mechanics calculations (MM29b)) on 1-*t*-butyl-9-phenoxytriptycene (**2**) indicates that the most stable conformation is the one shown by the Newman projection. The molecule has a plane of symmetry: it resides in the *ap* conformation with respect to the $C_9$-O bond, the ±*sc* rotamer being 7.8 kcal mol$^{-1}$ less stable than *ap*; the plane of the phenoxy moiety is coplanar with the $C_9$-O bond, constituting a static meshed bevel gear;6) neither the 1-*t*-butyl group nor the benzene ring bearing it shows out-of-plane deformation; two enantiotopic methyl groups ($CH_3^A$) face the oxygen atom and the other methyl ($CH_3^B$) eclipses C-2. Compound **1** should reasonably adopt a similar conformation as **2**. The low-field singlet is assigned to $CH_3^A$ and the high-field one to $CH_3^B$.

The origin of the high energy barrier to rotation of the 1-*t*-butyl group in **1** may reside in the rigidity of the triptycene skeleton and the rather small oxygen atom as the obstacle to rotation: the transition state for rotation is effectively raised while the ground state is not raised too much. Further studies on this point are in progress.

References and Notes

1) Restricted rotation involving the tetrahedral carbon. 58. Part 57: G. Yamamoto and M. Ōki, *Bull. Chem. Soc. Jpn.*, 58, 1953 (1985).
2) S. Sternhell, in "Dynamic Nuclear Magnetic Resonance Spectroscopy," ed by L. M. Jackman and F. A. Cotton, Academic Press, New York (1975), p. 163; M. Ōki, "Applications of Dynamic NMR Spectroscopy to Organic Chemistry," VCH Publishers, Inc., Florida (1985), p. 194.
3) For example: B. Miller and K.-H. Lai, *Tetrahedron Lett.*, 1971, 2957; M. Ōki and N. Nakamura, *Bull. Chem. Soc. Jpn.*, 44, 1880 (1971).
4) The 4-*t*-butyl proton signal of 2,4-di-*t*-butylphenanthrene does not split down to -90 °C and the X-ray crystal structure of this compound shows considerable distortion from planarity: H. J. Lindner, H. Scherübl, and A. Mannschreck, unpublished results. We are grateful to Professor Mannschreck for informing us the results.
5) a) J. E. Anderson, R. W. Franck, and W. L. Mandella, *J. Am. Chem. Soc.*, 94, 4608 (1972). b) J. Handal, J. G. White, R. W. Franck, Y. H. Yuh, and N. L. Allinger, *ibid.*, 99, 3345 (1977); 101, 5456 (1979).
6) The details will be published elsewhere.
7) **1**: mp 203-205 °C; $^1$H NMR data ($CDCl_3$, 24 °C): $\delta$ 1.227 (9H, s, 3-*t*-Bu), 1.722 (9H, s, 1-*t*-Bu), 1.905 (3H, s, 5'-Me), 2.429 (3H, s, 3'-Me), 5.322 (1H, s, 10-H), 5.720 (1H, s, 6'-H), 6.601 (1H, s, 4'-H), 6.8-7.5 (11H, m).
8) Below -90 °C, the three-proton singlet shows extra broadening due probably to restricted rotation of the methyl group, although no further splitting is observed down to -111 °C.
9) a) D. A. Kleier and G. Binsch, *QCPE*, No. 165. b) N. L. Allinger and Y. H. Yuh, *QCPE*, No. 395. A modified version of the program by Professor E. Ōsawa of Hokkaido University has been used.

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