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OBSERVATION OF RESTRICTED ROTATION ABOUT C-O BONDS BY NMR SPECTROSCOPY IN 9-(2-ALKYLPHENOXY)TRIPTYCENES, A GEAR ROTATION SYSTEM [1]

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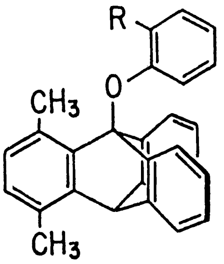
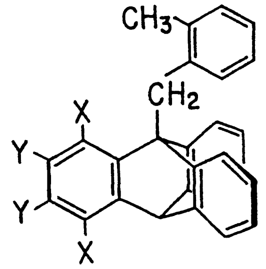
Dynamic NMR study on 9-(2-alkylphenoxy)-1,4-dimethyltriptycenes revealed that, when the *o*-alkyl group is methyl or isopropyl, two conformers, *ap* and ±*sc*, are separately observed at room temperature and that the interconversion between them occurs by gear rotation with an energy barrier of *ca*. 18 kcal mol^{-1}

Abundant examples of restricted rotation about $C(sp^3)-C(sp^3)$ bonds studied by NMR spectroscopy have appeared in the literature,[2] but no study has hitherto been reported on restricted rotation about $C(sp^3)-O$ bonds.[3] We report in this letter the first example of observation of restricted rotation about $C(sp^3)-O$ bonds by NMR spectroscopy.

Our experience in studies on restricted rotation about C-C bonds in 9-alkyltriptycene derivatives suggested that 9-alkoxy(or aryloxy)triptycenes should be a suitable system for observing the C-O restricted rotation. We chose 9-(2-alkylphenoxy)-1,4-dimethyltriptycene system as the object and studied the dynamic NMR behavior of compounds **1b**-**1d** as well as the *o*-unsubstituted derivative **1a**.



	R	Mp / °C
1a	H	202-203
1b	CH_3	193-194
1c	$CH(CH_3)_2$	161-162
1d	$C(CH_3)_3$	224-225



	X	Y
2a	OCH_3	H
2b	CH_3	H
2c	Cl	Cl

The reason for the choice comes from our previous study on the stereodynamics of *peri*-substituted 9-(2-methylbenzyl)triptycenes (**2**).[5] These compounds are regarded as a gear system with a two-toothed and a three-toothed wheels, and reside in two types of conformation, *ap* and ±*sc*, with the *o*-methyl group pointing outside of the triptycene skeleton (Fig. 1). Interconversion among the stable conformers occurs by correlated rotations of the C_9-CH_2 and the CH_2-Ar bonds by way of the unstable conformers, *ap'* and ±*sc'*. The *ap* $\rightleftharpoons$ ±*sc* process has a higher barrier than the +*sc* $\rightleftharpoons$ -*sc* one because the aryl group must pass over the bulky *peri*-substituent in the former process. Both processes can be observed by dynamic NMR spectroscopy.

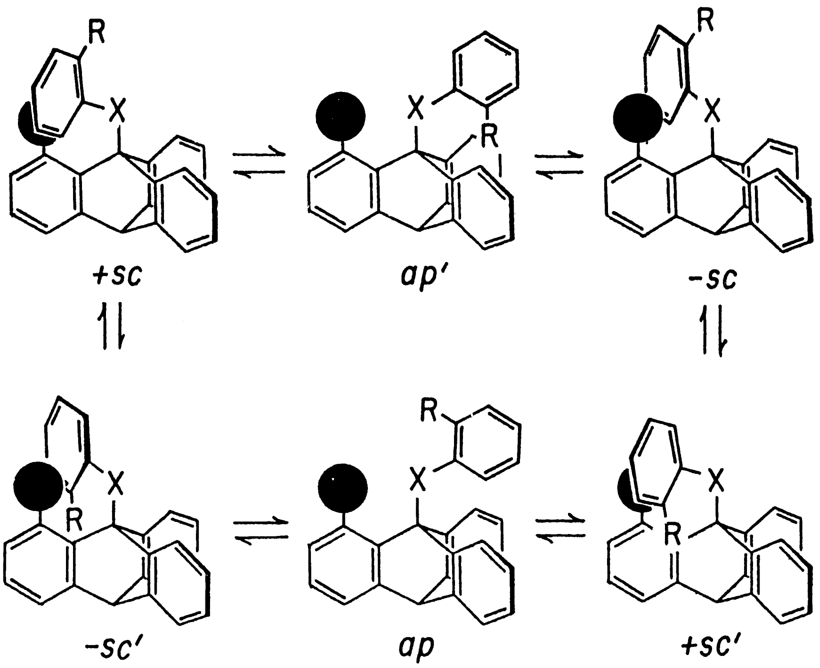
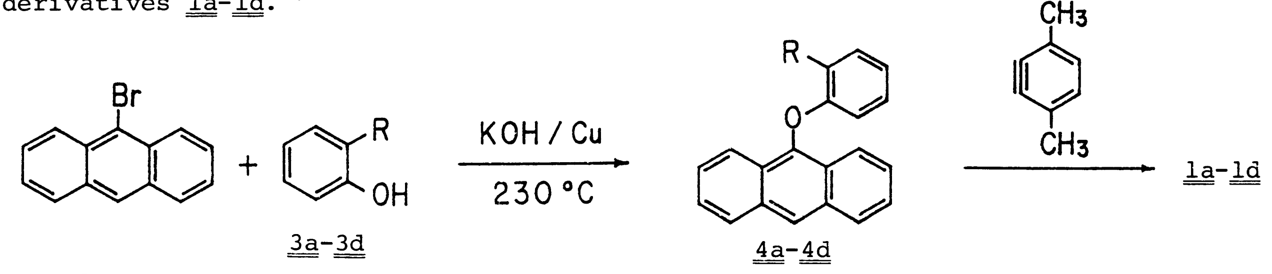


Fig. 1. Gear rotational circuit for 1-substituted 9-(2-alkylbenzyl)-triptycenes ($X=CH_2$) and 9-(2-alkylphenoxy)triptycenes (X=O).

One of the important features in a gear rotation system like this is that a high-barrier process in which the aryl group passes over the bulky *peri*-substituent can be observed in a singly *peri*-substituted compound. This feature prompted us to use a gear rotation system in our present study.

Ullman reactions of 9-bromoanthracene with phenols 3a-3d gave 9-aryloxyanthracenes 4a-4d, which reacted with 3,6-dimethylbenzyne generated *in situ* from 3,6-dimethylanthranilic acid and isopentyl nitrite to afford the desired triptycene derivatives 1a-1d.$^{5)}$



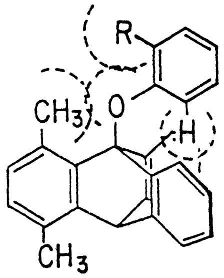
^{1}H NMR data of 1a-1d in $CDCl_3$ at *ca.* 35 °C are given in Table 1. Compound 1a shows only conformer-averaged signals indicating the fast interconversion among the conformers. The spectra of 1b and 1c show that both of the compounds reside as two NMR-distinguishable conformers and the interconversion between them is sufficiently slow at 35 °C. It is reasonable to infer that they are *ap* and ±*sc* conformers shown in Fig. 1. Among the singlets which appear at δ 2.0-3.0 due to the aromatic methyl groups, the highest-field one can be assigned to the 1-methyl group of the ±*sc* conformer, because this methyl group is supposed to suffer the shielding effect of the flanking aryl group. Then from the relative signal intensities and the coalescence pattern on raising the temperature, all the other

Table 1. ^{1}H NMR data of 9-aryloxy-1,4-dimethyltriptycenes[a)]

Compd	Rotamer	Population/%	1-CH_3	4-CH_3	2'-R	10-H
1a			2.77	2.44		5.62
1b	*ap*	55	2.90	2.41	2.69	5.62
	±*sc*	45	2.03	2.54	2.68	5.62
1c	*ap*	33	2.90	2.42	1.46 d, 4.05 sep (J = 6.9 Hz)	5.62
	±*sc*	67	2.09	2.55	1.51 d, 3.93 sep (J = 6.9 Hz)	5.62
1d	±*sc*	>98	2.14	2.55	1.73	5.61

a) The data are obtained in $CDCl_3$ at *ca.* 35 °C. Aromatic protons are omitted. Chemical shifts are given in δ. Signals are singlets unless otherwise noted; d: doublet, sep: septet.

methyl signals are assigned as shown in Table 1 together with the conformer populations. In compound **1d**, the 1- and 4-methyl groups as well as the *t*-butyl group show only one singlet for each. This implies that the compound exists almost exclusively as a single conformer. As the chemical shifts of the signals ascribable to the 1- and 4-methyl groups, δ 2.14 and 2.55, are very similar to those of the corresponding signals of the ±*sc* conformer of **1b** and **1c**, the conformer observed for **1d** should be ±*sc*.



Large dependence of the conformer population on the *o*-alkyl group is intriguing and may be explained as follows. The 6'-hydrogen in the aryl group is located close to the triptycene skeleton. In the *ap* conformer the 1-methyl group buttresses the aryloxy group and forces the 6'-hydrogen even closer to the triptycene skeleton. The presence of the *o*-alkyl group (R) also increases the congestion because of the repulsion between R and the oxygen. Therefore, as the bulkiness of R increases, the *ap* conformer is steeply destabilized while the ±*sc* conformer is not destabilized so much because of the absence of the buttressing *peri*-substituent antiperiplanar to the aryl group.

The methyl protons of the isopropyl group in **1c** are isochronous at 35 °C and this suggests that the interconversion between +*sc* and -*sc* is fast at this temperature. The same should be the case for **1b** and **1d**, although the experimental verification is not easily obtained. Therefore, in **1b**-**1d**, the correlated to-and-fro process, $+sc \rightleftharpoons ap' \rightleftharpoons -sc$ (and probably $+sc' \rightleftharpoons ap \rightleftharpoons -sc'$ as well) is occurring fast at 35 °C but the complete cycle of the gear rotational circuit is not realized because the $\mp sc' \rightleftharpoons \pm sc$ step is still slow.

At higher temperatures, ^{1}H NMR spectra of **1b** and **1c** exhibit coalescence phenomena owing to the acceleration of the $ap \rightleftharpoons \pm sc$ process. The line-shapes of the 1- and 4-methyl signals were simulated at five to six temperatures in the range of

Table 2. Dynamic NMR data in chlorobenzene [a)]

$$ap \underset{k_{-1}}{\overset{2k_1}{\rightleftharpoons}} \pm sc \qquad K = 2k_1 / k_{-1}$$

Compd	Signal Obsd	K	T_c °C	$\Delta G_c^{\ddagger}$ kcal mol^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal $mol^{-1}K^{-1}$
1b	4-CH_3	0.92	57	18.1	18.7 ± 0.5	1.8 ± 1.4
1c	4-CH_3	2.0	59	18.2	17.2 ± 1.5	-3.0 ± 4.3
2b[b)]	CH_2	1.2	98	20.0		

a) The kinetic parameters refer to the *ap*→±*sc* process. b) Ref. 4.

40-90 °C using a modified version of the DNMR 3 program by Binsch,[6)] and the Eyring kinetic parameters were obtained as given in Table 2. Rate constants at the coalescence temperatures (T_c) of the 4-methyl signals were also evaluated by the graphical method according to Jaeschke *et al.*,[7)] which agreed well with the results from the total line-shape analysis. In Table 2 are also included the data for **2b**.[4)]

A feature of interest is that **1b** and **1c** have almost the same barrier heights. It is inferred that the difference in the transition state energies between **1b** and **1c** can be as small as the difference in the ground state energies, if it is taken into account that the isopropyl group in **1c** can adopt a conformation in which the methine hydrogen points toward the triptycene moiety.

^1H NMR spectrum of **1c** in CD_2Cl_2 at -60 °C shows considerable broadening of the isopropyl methyl signal of the ±*sc* conformer, suggesting the slow-down of the +*sc*⇌-*sc* process. However, overlap of the signal with that of the *ap* conformer precludes the elucidation of the detailed kinetic parameters and the energy barrier of 10-12 kcal mol^{-1} is roughly estimated, which is somewhat lower than the barrier of 14.1 kcal mol^{-1} obtained for the similar process in **2b**.[4)]

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