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TWO CONSECUTIVE GEAR MOTIONS IN CONFORMATIONAL INTERCONVERSION IN 9-(2-METHYLBENZYL)TRIPTYCENE DERIVATIVES[1)]

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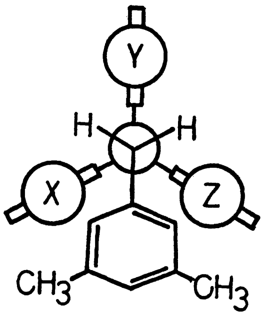
The conformational interconversion among ±sc and ap forms of 9-(2-methylbenzyl)triptycenes is found to occur by two consecutive gear motions: methyl-inside conformers formed by the synchronous rotation about the CH_2-Ar and CH_2-C_9 bonds of the methyl-outside conformers are so unstable that another synchronous rotation takes place in succession to afford methyl-outside conformers. The change in ^{1}H-nmr line shapes and the barriers to rotation are discussed.

9-(3,5-Dimethylbenzyl)triptycene derivatives were shown to undergo conformational changes through two types of processes: "isolated rotation" about the CH_2-Ar bond without rotation about the CH_2-C_9 bond and synchronous rotation ("gear motion") about the CH_2-Ar and CH_2-C_9 bonds, transition states of which are shown by Newman projections along the CH_2-C_9 bond axis, 1 and 2, respectively. Here we report observations which are best interpreted on the basis of two consecutive gear motions in 9-(2-methylbenzyl)triptycene derivatives.



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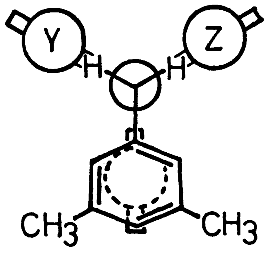

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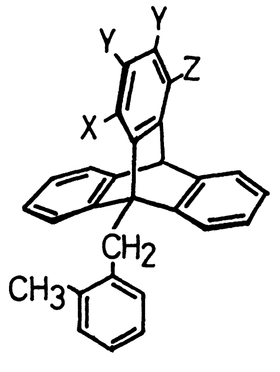
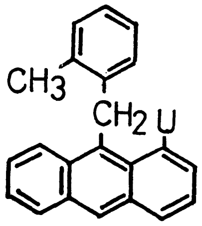
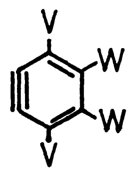
The compounds examined (3~6) were synthesized by the reaction of anthracenes 7a-c with benzynes 8a-c generated in situ from the corresponding anthranilic acids and isopentyl nitrite (7a+8a, 7b+8b, 7c+8a, and 7b+8c, respectively). The anthracene 7a was synthesized by dehydration,



	X	Y	Z	Mp (°C)
3	OCH_3	H	H	258-259
4	CH_3	H	CH_3	208-209
5	Cl	H	H	265-266
6	Cl	Cl	Cl	286-288



7a: U = OCH_3
b: U = H
c: U = Cl



8a: V = W = H
b: V = CH_3, W = H
c: V = W = Cl

with thionyl chloride-pyridine, of 4-methoxy-10-(2-methylbenzyl)-9,10-dihydroanthracen-9-ol, which was prepared by the reaction of 4-methoxyanthrone with 2-methylbenzyl chloride in the presence of potassium hydroxide in methanol followed by reduction with sodium borohydride. The anthracenes 7b and 7c were synthesized by addition of 2-methylbenzylmagnesium chloride to anthrone and 1-chloroanthrone, respectively, followed by dehydration with thionyl chloride-pyridine. All the new compounds were satisfactorily analyzed.

All four compounds showed a similar dnmr behavior. At low temperatures (ca. -30°C) ^{1}H-nmr spectra showed the presence of two kinds of rotamers with respect to the CH_2-C_9 bond, ap and ±sc, in the ratio shown in Table I. Benzylic methylene protons of the ap isomer gave a singlet, while those of the ±sc isomer gave an AB-quartet. 1-Methoxyl protons of compound 3 gave rise to two peaks as well as both of 1- and 4-methyl protons of compound 4. o-Methyl signals in the benzyl group also appeared as two singlets except for compound 3 in $CDCl_3$ where accidental coincidence of the chemical shifts occurred.

In these stable conformers, the o-methyl group in the benzyl moiety is assumed to point toward the outside of the triptycyl skeleton (ap and ±sc in Scheme). Molecular model considerations easily reject the possibility of a methyl-inside conformation as a stable entity(ap' and ±sc' in Scheme).

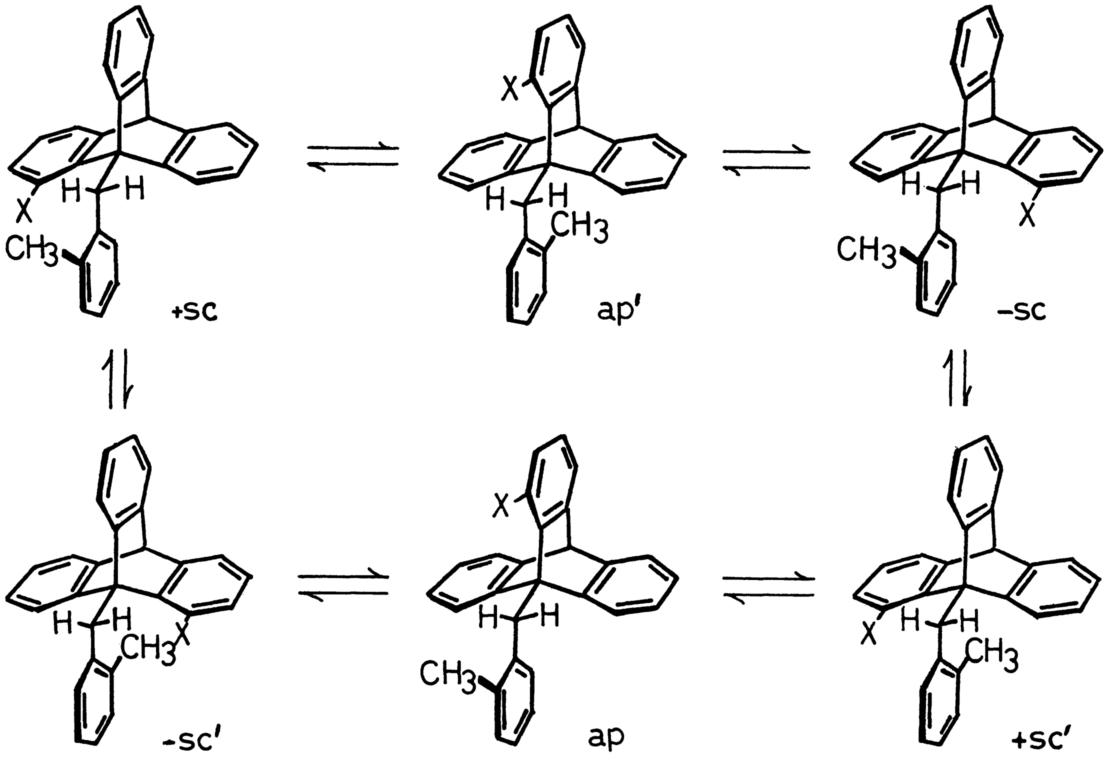
Upon raising the temperature, the AB-quartet signal due to the sc-methylene protons coalesced into a singlet at the temperature range of +3∼+13°C, while the other part of the spectrum except for the aromatic region showed no appreciable change. At 34°C signals due to the methylene protons appeared as two singlets. Further elevation of the temperature caused the coalescence of both sets of two singlets due to methylene and o-methyl protons. The peaks due to 1-methoxyl of 3 and 1- and 4-methyls of 4 coalesced as well.

These dnmr behaviors indicate that the interconversion between the +sc and -sc conformers occurs without intervention of the ap conformer and that the interconversion between the ap and ±sc conformers has a higher barrier.

Table I. Low Temperature ^{1}H-nmr Data (δ in $CDCl_3$)

Compound	±sc/ap	Methylene		o-Methyl		1-Substituent		Bridgehead		Temp. (°C)
		ap	±sc a)	ap	±sc	ap	±sc	ap	±sc	
3	2.9	4.73	4.00 4.65	2.66 (2.51	2.66 2.31)b)	3.82	2.92	5.50	5.50	-32
4	1.0	4.57	4.14 4.54	c)		2.81	1.93	5.76	5.76	-33
5	0.7	4.79	4.08 4.85	2.68	2.62			5.48	5.48	-30
6	0.7	4.79	4.08 4.91	2.70	2.64			6.18	6.13	-35

a) Appeared as an AB-quartet with J_{AB} of 18 Hz. b) In toluene-d_8 at - 32°C.
c) While 1-methyl signals were assigned from the coalescence behavior, those due to o-methyls and 4-methyls at δ 2.47, 2.58, 2.63, and 2.67 could not be assigned.



Scheme

Rate constants at the coalescence temperatures and free energies of activation therefrom were calculated using the approximate equation by Ōki, Iwamura, and Hayakawa[3] for the +sc⇌-sc process and the graphical method by Shanan-Atidi and Bar-Eli[4] for the ap⇌±sc process. The results are shown in Table II.

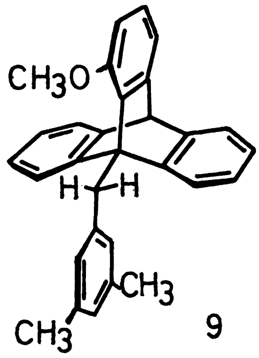
Interconversion between the +sc and -sc conformers can be best explained in terms of two consecutive gear motions by way of the unstable ap' conformer with o-methyl group pointing toward the inside (Scheme). In the enantiomeric transition states the aryl group passes over a peri-hydrogen. Support for this notion may be obtained from the similarity of the barrier for compound 3 (13.5 kcal/mol) and the ap⇌ ±sc barrier

Table II. Dnmr Data

Compound	Solvent	±sc/ap	+sc⇌-sc Process			ap⇌±sc Process a)		
			T_c (°C)	k_c (sec^{-1})	$\Delta G_c^{\ddagger}$ (kcal/mol)	Tc (°C)	k_c (sec^{-1})	$\Delta G_c^{\ddagger}$ (kcal/mol)
3	$CDCl_3$	2.9	3	128	13.5	65 75 b)	25 55 b)	17.7 17.7 b)
4	$C_6D_5CD_3$	1.0	14	114	14.1	98	14	19.9
5	C_6H_5Cl	0.7	9	150	13.7	98	14	19.9
6	C_6H_5Cl	0.7	13	151	13.9	112	14	20.7

a) Obtained from the methylene signals unless otherwise stated. k_c's and $\Delta G_c^{\ddagger}$'s denote the conversion from ap to either of ±sc isomers. b) Obtained from 1-methoxyl signals.

for compound 9 (12.4 kcal/mol),[2] if one takes it into account that the presence of the o-methyl group may raise the transition state to some extent.



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Two types of pathways are possible for the ap ⇌ ±sc interconversion. One is a pathway consisting of two consecutive gear motions (ap ⇌ ∓sc' ⇌ ±sc), and the other is the one involving an isolated rotation (IR) step (ap ⇌ ap' ⇌ ±sc or ap ⇌ ±sc' ⇌ ±sc). The rate determining transition state in the former pathway should be the one where the aryl group passes over the peri-substituent (∓sc' ⇌ ±sc), while in the latter the IR step should be rate determining for the following reasons. Since the barriers to the +sc ⇌ -sc interconversion are approximately 14 kcal/mol and those to the ap ⇌ ±sc over 17.7 kcal/mol, the rate determining step in the latter process must be the ap ⇌ ap' step, if the exchange occurs by the ap ⇌ ap' ⇌ ±sc pathway: barriers are common for both the +sc ⇌ -sc and the ap ⇌ ±sc processes except that for the ap ⇌ ap'. Similarly the rate determining step in the ap ⇌ ±sc' ⇌ ±sc pathway should be the ±sc' ⇌ ±sc. The ±sc ⇌ ±sc' IR step should have higher barrier than the ap ⇌ ap' IR step because the bulky peri-substituent X flanks the aryl group in the former while two peri-hydrogens flank it in the latter. The bulkier flanking groups have been shown to raise the IR barrier in 9-(3,5-dimethylbenzyl)triptycenes and the present system with an o-methyl group would suffer even larger effects of the peri-substituents.

Looking at the conformations of ap and ap', one notes that the barrier to the ap ⇌ ap' process must practically be invariant irrespective of the peri-substituents, because the latter is remote from the rotation site. The effects of perisubstituents on the barrier (Table II) are contradictory to this expectation and thus the ap ⇌ ap' ⇌ ±sc pathway is ruled out. And hence the ap ⇌ ±sc' ⇌ ±sc pathway is also ruled out on the basis of the discussion above.

The increase in the barrier by 2kcal/mol on the change in the peri-substituent, from methoxyl to methyl or chloro, is reasonable with the ap ⇌ ∓sc' ⇌ ±sc pathway because the aryl group must pass over a bulkier peri-substituent.

Thus we conclude that the ap ⇌ ±sc interconversion occurs by the ap ⇌ ∓sc' ⇌ ±sc pathway, which consists of two consecutive gear motions, the ∓sc' ⇌ ±sc step being rate determining.

References.

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