DUAL MECHANISMS OF THE ARYL GROUP ROTATION IN 9-(3,5-DIMETHYLBENZYL)TRIPTYCENE DERIVATIVES[1]
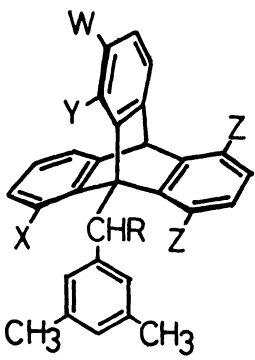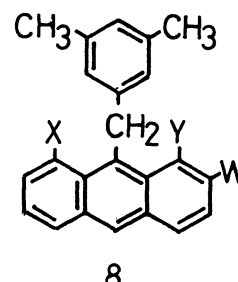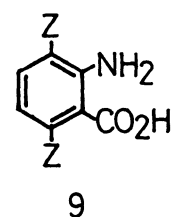
Gaku YAMAMOTO and Michinori ŌKI
Department of Chemistry, Faculty of Science,
The University of Tokyo, Bunkyo-ku, Tokyo 113

9-(3,5-Dimethylbenzyl)triptycene derivatives exchange their two m-methyl groups by two mechanisms: rotation about the CH_2-Ar bond and synchronous rotation about the CH_2-Ar and the CH_2-C_9 bonds. The relative contribution of the processes is dependent on the peri-substituents.

During the course of our study on the restricted rotation about the bridgehead-to-substituent bond in 9-substituted triptycene derivatives[2], 9-benzyltriptycenes exhibited interesting properties in conformational behaviors.[3,4,5] In order to obtain a deeper insight into the dynamic conformational behavior of the benzylic aryl group, we planned to introduce nmr probe groups into the benzene ring, i.e. two m-methyl groups which do not give significant alteration to the system. 9-(3,5-Di-methylbenzyl)triptycene derivatives with a variety of substituents in the peri-positions (1, 8, and 13 positions) were thus sythesized. Their dnmr spectra indicate that the rotation about the methylene-to-aryl bond is frozen on the nmr time scale at low temperatures and that two different mechanisms of the rotation are operating depending on the substitution in the peri-positions.
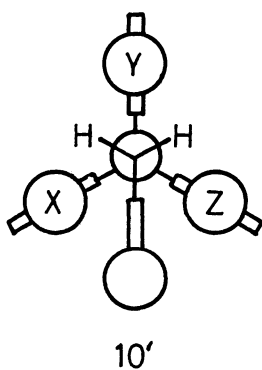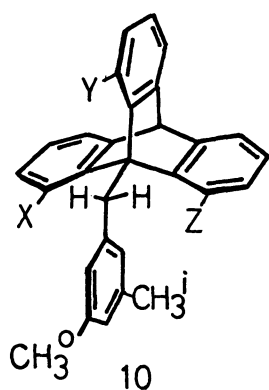
The compounds examined (1 ~ 7) were synthesized by the reaction of anthracenes 8 with benzynes generated in situ from anthranilic acids 9 and isopentyl nitrite, and gave satisfactory elemental analyses.

	R	W	X	Y	Z	Mp (°C)
ap-1[4]	H	H	Cl	Cl	CH_3	>300
sc-1[4]	H	H	Cl	Cl	CH_3	>300
2[4]	H	H	Cl	Cl	OCH_3	277-278
3	H	H	Cl	Cl	H	272-274
4	H	H	OCH_3	H	H	239-240
5	H	H	H	H	H	216-217
6	H	OCH_3	H	H	H	196-197
7	CH_3	H	H	H	H	179-180

Compound 1 exists as two stable rotameric forms, ap and sc, at room temperature, as reported previously.[4] The presence of ap and sc isomers were detected at low temperatures for compounds 4 and 6, whereas only sc isomers were detected for compounds 2 and 3, due to the steric effects of the peri-substituents.

In all compounds but one, m-methyl groups in the aryl moiety gave two equally intense singlets for the respective rotamer in low temperature ^{1}H-nmr spectra. Compound 6 exibited only a pair of singlets in spite of the fact that it existed as an ap-sc mixture, because of the small chemical shift difference between the rotamers in the solvent examined.

The stable conformation with respect to the aryl group should be the one in which the aryl ring is coplanar with the bridgehead-to-methylene bond as shown by 10 or by the Newman projection 10'. This notion which is most compatible with the dnmr behavior described below is supported not only by molecular model considerations,

but also by large coupling constants (ca. 18 Hz) of the benzylic methylene protons.[3] Then, of the two methyl signals, the higher-field one can be assigned to the inner methyl group (CH$_3^i$) and the lower-field one to the outer methyl (CH$_3^o$)(Table I), if one considers the ring current effects of the triptycyl benzene rings.

The two peaks due to the m-methyl groups coalesced into a singlet on raising the temperature. Free energies of activation at the coalescence temperatures T_c were calculated according to the conventional approximation method[6] and are shown in Table I together with the relevant nmr data. Compound 4 gave two sets of doublets due to two rotamers with respect to the bridgehead-to-methylene bond, but the coalescence phenomena could not be observed separately, and only a rough estimate of the barrier was obtained for this compound.

Two processes may be considered by which two methyl groups exchange their magnetic environments with each other. (i) Rotation about the methylene-to-aryl bond by 180° takes place without rotation about the bridgehead-to-methylene bond. We call this process as "isolated rotation (IR)". The transition state for the IR process should be shown by 11. (ii) Rotation about the methylene-to-aryl bond by 180° takes place synchronously with rotation about the bridgehead-to-methylene bond by 120°. We call this process as "gear motion (GM)". The transition state for the GM process should be represented by 12. Rigorously speaking, exchange of the methyl groups by this process occurs only when the conformations before and after the process are homomeric or enantiomeric to each other. But approximate methyl exchange rates could be estimated for other cases as well.

The actually observed exchange of the methyl groups may occur by either or both of these mechanisms depending on the substitution patterns in the peri-positions which would directly affect the relative stability of the transition states 11 and 12.

It is reasonable to assume that rotation about the bridgehead-to-methylene bond is always accompanied by rotation about the methylene-to-aryl bond.

Table I.   Dnmr Data for the Methyl Exchange (at 60 MHz)

Compound	peri-Groups Flanking the Aryl Group		Solvent	$\delta_{CH_3}i$	$\delta_{CH_3}o$	$\Delta\delta$ b) (Hz)	T_c (°C)	$\Delta G_{EX}^{\ddagger}$ c) (kcal/mol)
sc-1	Cl	CH$_3$	CDCl$_3$	1.84	2.39	33	58 e)	16.6
ap-1	Cl	Cl	CDCl$_3$	1.87	2.38	31	35	15.5
2	Cl	OCH$_3$	CDCl$_3$	1.88	2.39	31	38	15.6
3	Cl	H	CDCl$_3$	1.89	2.41	31	30	15.2
4 ap	H	H	CS$_2$	1.80	2.37	34	-20 d)	~12.6 d)
sc	H	OCH$_3$		1.91	2.37	28		
5	H	H	CS$_2$	1.93	2.40	28	-67	10.2
6	H	H	CS$_2$	1.93 a)	2.41 a)	29	-71	10.0
7	H	H	CDCl$_3$	1.98	2.49	29	-8	13.3

a) Coincident between the ap and sc rotamers. b) Independent of the temperature within the experimental errors. c) With errors of ±0.1 kcal/mol due mainly to the errors in T_c of ±2°. d) See text. e) Obtained from the sample containing the equilibrium mixture of ap- and sc-1.

Comparison of the activation parameters concerned with the IR and the GM processes will reveal the mechanism which are truly occurring, if the parameters can be obtained separately. Fortunately the GM process can be independently observed by other means, e.g. dnmr of the benzylic methylene protons of 2 and 3 or of the methoxyl protons of 4 and 6, and such data are shown in Table II.

11

12

The data in Tables I and II indicate that in compounds 1 and 2 with three peri-substituents, energy barriers to the GM process are so high that the methyl exchange occurs mainly by the IR process.

Compound 7 showed broadening of the signals in the aromatic region at 80-100°C reflecting the high barrier (ca. 18-20 kcal/mol) to the GM process, and this indicates that the 13.3 kcal/mol barrier to the methyl exchange corresponds to that to the IR process. If one can assume that the presence of a methyl group in the methylene position does not significantly affect the IR barrier and therefore compounds 5 and 6 which do not carry peri-substituents have the IR barrier of about the same height, then the methyl exchange barrier of 10 kcal/mol for 5 and 6 represents the GM barrier for these compounds. The GM barrier for 6 obtained independently (Table II) agrees well with this value if the probable large error is taken into account.

The methyl-exchange and gear-motion barriers for compound 3 have the similar values of 15.2 and 15.7 kcal/mol, respectively. Since the IR barrier for this compound in the conformation with the peri-substituents of Cl and H flanking the aryl group should not exceed 15.6 kcal/mol, which is the IR barrier for compound 2 in the
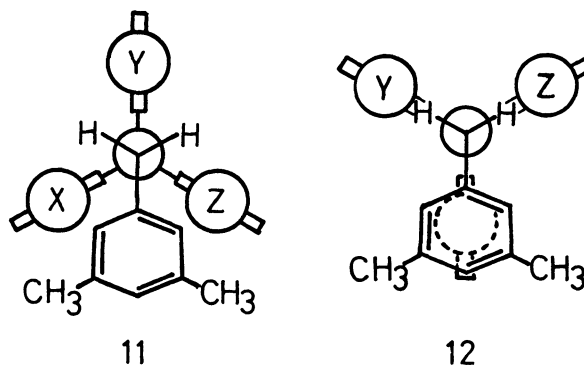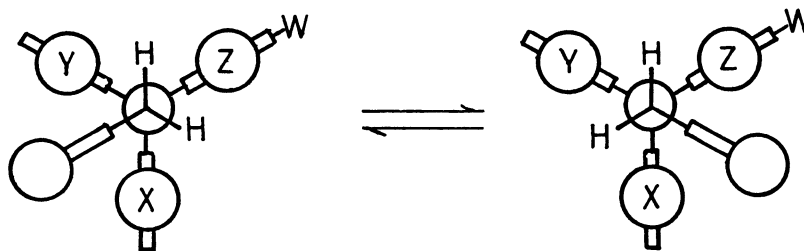
Table II.   Energy Barriers to the Gear Motion Processes[a]

Compound	X	Y	Z (W)	Observed Process	Observed Protons	$\Delta G^{\ddagger}_{GM}$ (kcal/mol)	(T) (°C)	sc/ap
1[b]	Cl	Cl	CH_3	ap ⇌ sc	—	24.8	(61)[c]	2.0
2	OCH_3	Cl	Cl	+sc ⇌ -sc	$C\underline{H}_2$	22.1	(167)	∞
3	H	Cl	Cl	+sc ⇌ -sc	$C\underline{H}_2$	15.7	(51)	∞
4	H	H	OCH_3	ap ⇌ sc	$OC\underline{H}_3$	12.4	(-28)[c,d]	3.3
6	H	H	H (OCH_3)	ap ⇌ sc	$OC\underline{H}_3$	11.0	(-64)[c,d]	1.3

a) Obtained by dnmr unless otherwise noted. b) Obtained by Classical kinetics.[4]
c) ap→sc Barriers are shown. d) Obtained with the approximation method
according to Shanan-Atidi and Bar-Eli[7].

conformation with Cl and OCH_3 as the flanking peri-groups, both of the IR and GM processes may comparably contribute to the methyl exchange in compound 3.

Comparable contribution of both processes may also be inferred for compound 4 with one peri-substituent.

In conclusion, interchange of the main contributor in the exchange process occurs on successive substitution in the peri-positions, from the GM process in peri-unsubstituted compounds to the IR process in triply peri-substituted ones. This is because the sharp increase in the GM barrier occurs on substitution in the peri-positions, whereas the increase is rather small in the IR barriers.

References.
1) Restricted rotation involving the tetrahedral carbon. XXIX.   Part XXVIII:
   S. Otsuka, H. Kihara, T. Mitsuhashi, and M. Ōki,   Bull. Chem. Soc. Jpn.,
   in press.
2) M. Ōki, Angew. Chem., Int. Ed. Engl., 15, 87 (1976).
3) F. Suzuki and M. Ōki,   Bull. Chem. Soc. Jpn., 48, 596 (1975).
4) G. Yamamoto and M. Ōki,   Angew. Chem., Int. Ed. Engl., 17, 518 (1978).
5) M. Kono, H. Kihara, N. Nakamura, F. Suzuki, and M. Ōki,   Bull. Chem. Soc. Jpn.,
   52, 1682 (1979).
6) D. Kost, E. H. Carlson, and M. Raban,   Chem. Commun., 656 (1971).
7) H. Shanan-Atidi and K. H. Bar-Eli, J. Phys. Chem., 74, 961 (1970).