Restricted Rotation Involving the Tetrahedral Carbon. IL. Singly *peri*-Substituted 9-Isopropyltriptycenes Revisited[1)]

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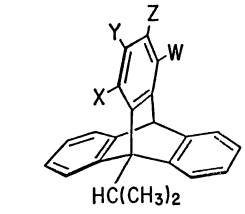
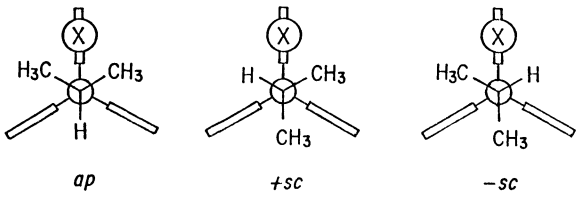
9-Isopropyltriptycene derivatives carrying a fluoro, chloro, bromo, or *t*-butyl substituent in a *peri*-position were synthesized and their dynamic NMR behavior was studied to see the dependence of the barrier to rotation of the bridgehead substituent upon the bulkiness of the *peri*-substituent. The data obtained in this work together with those reported earlier disclose that, among the derivatives in which the *peri*-substituent is not buttressed by the 2-substituent, the *peri*-methoxy compound has the highest barrier and the barrier decreases as the bulkiness of the *peri*-substituent increases. 1,2,3,4-Tetrachloro and tetrabromo derivatives show the slightly positive buttressing effect.

In 1974, we reported the rotational barriers in a *peri*-unsubstituted 9-isopropyltriptycene (**1**) and several singly *peri*-substituted derivatives (**2**—**5**).[2)] The data are included in Table 2 and Fig. 1. One of the interesting features is that the barrier heights have no apparent correlation with the bulkiness of the *peri*-substituent as judged from the van der Waals radii of the groups. The low barrier of **3** was ascribed to the gearing of the *peri*-methyl group[2)] but the explanation was criticized that the results could be interpreted on the basis of the buttressing effect.[4)]



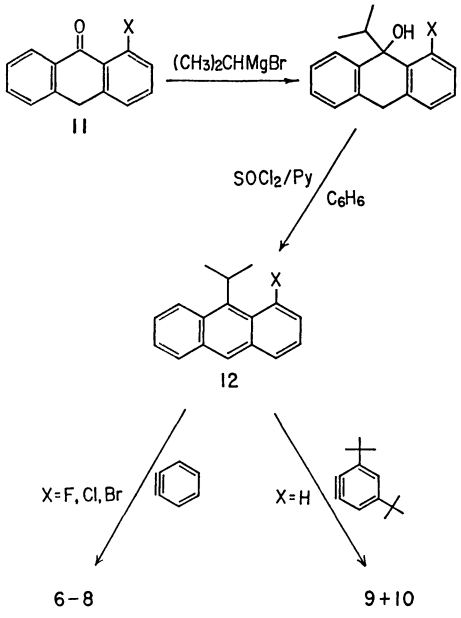
	X	Y	Z	W
1	H	CH_3	H	CH_3
2	OCH_3	H	H	OCH_3
3	CH_3	H	H	CH_3
4	Cl	Cl	Cl	Cl
5	Br	Br	Br	Br
6	F	H	H	H
7	Cl	H	H	H
8	Br	H	H	H
9	t-Bu	H	t-Bu	H
10	H	t-Bu	H	t-Bu



In view of the intriguing dependence of the rotational barriers in singly *peri*-substituted 9-(1,1-dimethyl-2-phenylethyl)triptycenes upon the *peri*-substituents, in which the *peri*-fluoro derivative has the highest barrier in the series,[5,6)] a reexamination of the rotational barriers in 9-*s*-alkyltriptycenes will be of value. 9-Isopropyltriptycenes exhibited a plateau in the diagram of the rotational barrier *vs.* the bulkiness of the *peri*-substituent.[2)] Other 9-*s*-alkyltriptycenes hitherto studied appear to give the maximal barriers in the 1,2,3,4-tetrachloro or tetrabromo derivatives.[7)] However it is desirable to erase the buttressing effect if we wish to discuss the relationship between the rotational barrier and the bulkiness of the *peri*-substituent in any detail. Such a work will also constitute a partial answer to the criticism for neglecting the buttressing effect.[4)] We therefore prepared 1-halo-9-isopropyltriptycenes (**6**—**8**) and determined the barriers to rotation in these compounds to compare with those in the tetrahalo counterparts **4** and **5**. In order to see the effect of an extremely bulky *peri*-substituent, the 1-*t*-butyl derivative (**9**) was also prepared.

Results and Discussion

1-Halo-9-isopropyltriptycenes (**6**—**8**) were synthesized by reactions of benzyne with 1-halo-9-isopropylanthracenes (**12**: X=F, Cl, and Br), which were prepared by Grignard reactions of isopropylmagnesium bromide with 1-haloanthrones (**11**) followed by dehydration. The reaction of 3,5-di-*t*-butylbenzyne[8)] with **12** (X=H) afforded two isomeric 9,10-adducts, **9** and **10**, in a ratio of *ca.* 1:2, which were separated by liquid chromatography.



NMR Spectra and Rotamer Distributions. ^1H NMR spectral data of compounds **6**—**10** taken in chloroform-*d* at *ca.* 35 °C are given in Table 1. Rotation about the bridgehead-to-substituent bond in these compounds is sufficiently slow on the NMR time scale under these conditions to observe the signals due to the diastereotopic methyl groups separately.

Compound **6** carrying a fluoro substituent in a *peri*-position is shown by NMR spectroscopy to exist in

Table 1. ^{1}H NMR data in $CDCl_3$ at *ca.* 35 °C[a]

Compound	Rotamer	$(C\underline{H}_3)_2CH$	$(CH_3)_2C\underline{H}$	10-H	$(C\underline{H}_3)_3C$
6	$\pm sc$	1.80 dd (6.8, *0.9*) 1.85 dd (6.7, *5.8*)	3.82 d sep (6.8, *2.0*)	5.26 d (*1.6*)	
	ap	1.81 dd (6.7, *5.8*)	3.58 d sep (6.7, *2.0*)	5.28[b]	
7	$\pm sc$	1.76 d (6.7) 1.92 d (6.8)	4.29 sep (6.8)	5.20	
8	$\pm sc$	1.76 d (6.8) 1.93 d (7.0)	4.43 sep (6.9)	5.19	
9	$\pm sc$	1.73 d (7.1) 1.78 d (6.8)	4.26 sep (7.0)	5.10	1.22, 1.35
10	$\pm sc$	1.88 d (6.8) 1.90 d (6.8)	3.60 sep (6.8)	6.08	1.24, 1.53
	ap	1.90 d (6.8)	3.62 sep (6.8)	6.06	1.27, 1.61

a) Chemical shifts are given in δ. Signals are singlets unless otherwise noted; d: doublet, dd: double doublet, sep: septet, d sep: double septet. In parentheses are coupling constants in Hz. Those in italics are couplings with ^{19}F. b) Presumably a doublet. Obscured by overlap with the signal due to $\pm sc$.

two rotameric states, *ap* and $\pm sc$. ^{19}F NMR spectrum of **6** exhibits a small peak at 58.9 ppm downfield from internal hexafluorobenzene together with a large peak at 49.7 ppm with an intensity ratio of 1:9. The ^{1}H NMR spectrum of **6** is complex not only because of the existence of two rotamers but also due to the presence of long-range ^{1}H-^{19}F spin-spin couplings. The methyl protons of the isopropyl group of the major rotamer appear as two sets of double doublets suggesting the diastereotopicity of the two methyl groups, while those of the minor rotamer as a double doublet reflecting the enantiotopicity of the methyl groups. These features clearly show that the major isomer is the $\pm sc$ rotamer and the minor *ap*. The existence of the *ap* rotamer in **6** should be a reflection of the small bulkiness of the *peri*-fluoro group, because the *ap* rotamer is not detected if the *peri*-substituent is bulkier than fluorine: Methyl protons of the isopropyl group in compounds **7**—**9** appear as a pair of equally intense doublets, indicating that these compounds reside solely in the $\pm sc$ rotamer.

Compound **10** lacking a *peri*-substituent shows two singlets with an intensity ratio of 2.1:1 for each of the *t*-butyl groups indicating the existence of the $\pm sc$ and *ap* rotamers in almost a statistical ratio. The slight preference for the $\pm sc$ rotamer may be due to the larger effective bulkiness of the 1-hydrogen than the other *peri*-hydrogens because of the buttressing effect of the 2-*t*-butyl group.

Dynamic NMR Studies. The double doublet signal for the isopropyl methyl groups of compounds **7**—**9** broadened and coalesced into a doublet upon raising the temperature. Rate constants (k_c) for the $+sc \rightleftarrows -sc$ interconversion at the coalescence temperatures (T_c) were obtained graphically according to Jaeschke *et al.*,[9] regarding the signal as two overlapping sets of mutually coalescing singlets. The coalescence phenomenon of the *t*-butyl signals in compound **10** gave the rate constants for the $ap \rightleftarrows \pm sc$ interconversion at two temperatures. The kinetic data obtained are compiled in Table 2 together with those obtained before, some of which are recalculated to express in terms of the free energies of activation at the coalescence temperatures.

As for the methyl signals in **6**, three overlapping sets of double doublets coalesce into a double doublet on elevation of the temperature by two processes of $+sc \rightleftarrows -sc$ and $ap \rightleftarrows \pm sc$. The change should therefore be analyzed as a three-site exchange problem of an eight-spin system ($A_3B_3MX \rightleftarrows B_3A_3MX \rightleftarrows C_6KY$). Such an analysis was beyond the capacity of the computer simulation program available[10] and was abandoned. Neglecting the presence of a small amount of the *ap* rotamer and simulating the spectra as a mutually exchanging four spin system (ABMX$\rightleftarrows$BAMX) gave a rough estimate of the barrier to the $+sc \rightleftarrows -sc$ interconversion as 22—23 kcal mol^{-1} (1 cal=4.184 J) at the temperature range of 110—150 °C.

The dependence of the barrier in **1**—**10** on the bulkiness of the *peri*-substituent as represented by the van der Waals radii is shown in Fig. 1. Although the data for **1** were obtained by observing the $ap \rightleftarrows \pm sc$ process, the barrier height should not differ significantly from that for the $+sc \rightleftarrows -sc$ process, because the two processes should have the identical barrier height in the absence of the buttressing effect by the 2-substituent; the buttressing effect of the 2-methyl group is negligible. Points for the unbuttressed compounds form a flat curve with a maximum at the *peri*-methoxy compound (**2**) and those for the tetrahalo compounds (**4** and **5**) deviate upward from the curve manifesting the positive buttressing effect.

Appearance of a maximum at a rather small *peri*-substituent is a similar trend as was found in 9-(1,1-dimethyl-2-phenylethyl)triptycene derivatives,[5] although the variation of the barrier heights is far smaller. It can therefore be inferred that the lowering of the barrier height with a bulky *peri*-substituent is not a special phenomenon exhibited only by 9-*t*-alkyl derivatives but is also observable in 9-*s*-alkyltriptycenes.

As discussed in some detail in the previous paper,[5]

TABLE 2. DYNAMIC NMR DATA[a)]

Compound	van der Waals radius of X[b)]/Å	T_c / °C	$\Delta\nu_c$ / Hz	k_c / s^{-1}	ΔG_c^{*} [c)] / kcal mol^{-1}	Solvent[d)]
1	1.20	100			20.6[e)]	TCE
10[f)]		99	2.3	2.1	21.4	TCE
		106	4.4	4.4	21.3	
2	1.52	140			23.2[e)]	HCB
7	1.75	158	10.6	23	22.9	HCB
3		164			23.3[e)]	HCB
8	1.85	153	11.0	23	22.6	HCB
4[g)]		175	9.4	19	24.0	HCB
5	1.97[h)]	128			22.0[e)]	HCB
9	2.79[h)]	89	1.6	2.2	20.8	TCE

a) Data for **1** and **10** refer to the $ap \rightarrow \pm sc$ process, and those for the others to the $+sc \rightleftarrows -sc$ process. b) According to Charton: M. Charton, *J. Am. Chem. Soc.*, **91**, 615 (1969). c) Reliable to ± 0.1 kcal mol^{-1}, which comes from the uncertainty of ± 2 °C for determination of T_c. d) TCE: Tetrachloroethylene. HCB: Hexachloro-1,3-butadiene. e) Calculated using ΔH^{*} and ΔS^{*} values reported in Ref. 2. f) Values in the upper row are obtained from the higher field pair of the *t*-butyl signals due presumably to the one at 2-position. g) Re-evaluated. *cf.* Ref. 7a. h) $(r_{v,min}+r_{v,max})/2$.

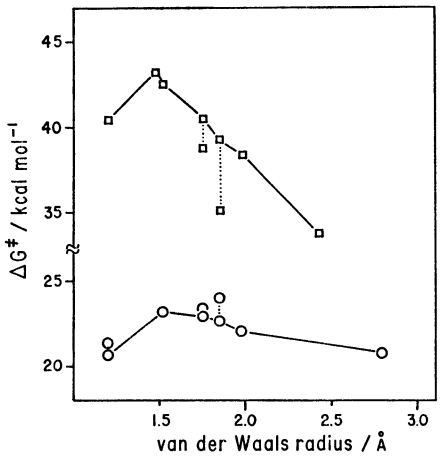


Fig. 1. Dependence of the rotational barriers on the bulkiness of the *peri*-substituent. ○: ΔG_c^{*} for 1-substituted 9-isopropyltriptycenes. □: ΔG_{500}^{*} for 1-substituted 9-(1,1-dimethyl-2-phenylethyl)triptycenes. Points for the unbuttressed compounds are connected by a solid line. Points deviated from the lines are those for the buttressed derivatives.

the phenomenon seems to be partly explained in terms of the molecular deformation in highly congested systems which causes the lesser stabilization of the transition state for rotation than the ground state upon introduction of a bulky *peri*-substituent. Because the congestion in the 9-*s*-alkyl series is considerably smaller than that in the 9-*t*-alkyl one, even such a bulky *peri*-substituent as a *t*-butyl group destabilizes the ground and the transition states rather similarly, resulting in only a small decrease in the barrier.

The small positive buttressing effect found in **4** and **5** is in sharp contrast with the large negative effect found in 1,2,3,4-tetrachloro- and tetrabromo-9-(1,1-dimethyl-2-phenylethyl)triptycenes.[6)] In the less congested system, the transition state may be destabilized to a greater extent than the ground state upon introduction of the buttressing substituent reflecting the increased rigidity of the 1-halogen substituent.

The barrier to the $ap \rightleftarrows \pm sc$ process in the 2,4-di-*t*-butyl derivative (**10**) is somewhat higher than that in the 2,4-dimethyl one (**1**). This may be ascribed to the positive buttressing effect on the 1-hydrogen exerted by the 2-*t*-butyl group. The $+sc \rightleftarrows -sc$ barrier in **10** may be slightly lower than the $ap \rightleftarrows \pm sc$ barrier because the 1-hydrogen eclipses the methyl group in the latter process while it eclipses the methine hydrogen in the former.

We have made it clear through our investigation on the dependence of the rotational barrier of the 9-substituent of triptycene systems upon the *peri*-substitution that the barrier height does not always increase with the bulkiness of the *peri*-substituent and shows a rather complex behavior. This comes from the fact that *peri*-substituents affect not only the transition state for rotation but also the ground state in congested sp^3–sp^3 systems. This is quite different from the cases in sp^2–sp^2 systems in which substituents close to the rotating bond does not significantly affect the ground state energy of the system and even a quantitative correlation between the barrier heights and the bulkiness of the substituents can be made.[11)]

From the data presented above, the low barrier to rotation in the 1,4-dimethyl compound (**3**) can be attributed to the raise of the ground state energy, although the possibility of gearing is not completely erased.

Experimental

Melting points are not corrected. The routine ^1H and ^{19}F NMR spectra were recorded on a Varian EM-390 spectrometer at 90.0 and 84.67 MHz, respectively, at *ca.* 35 °C. ^{19}F chemical shifts are shown in ppm downfield from internal hexafluorobenzene. Variable temperature ^1H NMR spectra were obtained on a Hitachi R-20B spectrometer operating at 60.0 MHz. Temperatures were calibrated by using an ethylene glycol sample.[12)] High performance liquid chromatography was carried out on a Waters M6000A system using a Microporasil semipreparative column with

hexane as an eluent.

*1-Bromoanthrone (**11**: X=Br).* To a magnetically stirred solution of 2.87 g (10.0 mmol) of 1-bromoanthraquinone in 50 mL of concentrated sulfuric acid was added portionwise 1.0 g of aluminium powder. The mixture was stirred at room temperature for 20 h and poured onto ice. The solid formed was collected by filtration, washed with water and dried in air. Recrystallization from benzene-hexane gave 1.71 g (63%) of **11** (X=Br) as yellow crystals, mp 129—130 °C. Found: C, 61.35; H, 3.18; Br, 29.72%. Calcd for $C_{14}H_9BrO$: C, 61.56; H, 3.32; Br, 29.26%. ^{1}H NMR ($CDCl_3$, δ): 4.31 (2H, s), 7.2—7.7 (6H, m), 8.24 (1H, s).

*General Procedure for Preparation of 1-Halo-9-isopropylanthracenes (**12**).* To an ethereal solution of the Grignard reagent prepared from 1.0 g (8.1 mmol) of isopropyl bromide was added portionwise 3.0 mmol of 1-haloanthrone. The mixture was stirred under reflux for 1 h and decomposed with aqueous ammonium chloride to afford 1-halo-9,10-dihydro-9-isopropyl-9-anthrol. The alcohol was, without further purification, heated with 1.5 mL of thionyl chloride and 3 mL of pyridine in 50 mL of benzene for 15 min. The reaction mixture was washed with water and dried over magnesium sulfate. Column chromatography on alumina with hexane as an eluent gave the desired anthracene as a yellow oil, which was used in the subsequent reaction.

*1-Fluoro-9-isopropylanthracene (**12**: X=F)* was obtained from 1-fluoroanthrone[5] in 38% yield by way of 1-fluoro-9,10-dihydro-9-isopropyl-9-anthrol [^{1}H NMR ($CDCl_3$, δ): 0.65 (3H, dd, J=6.8 and 0.6 Hz), 0.92 (3H, dd, J=6.8 and 1.2 Hz), 2.14 (1H, m), 3.21 (1H, br s), 3.90 (2H, s), 6.7—8.1 7H, m)]. ^{1}H NMR ($CDCl_3$, δ): 1.67 (6H, dd, J=7.3 and 2.4 Hz), 4.71 (1H, d sept, J=7.3 and 5.0 Hz), 6.8—8.7 (8H, m).

*1-Chloro-9-isopropylanthracene (**12**: X=Cl)* was obtained from 1-chloroanthrone[13] in 33% yield by way of 1-chloro-9,10-dihydro-9-isopropyl-9-anthrol [^{1}H NMR ($CDCl_3$, δ): 0.54 (2H, d, J=6.7 Hz), 1.03 (3H, d, J=6.9 Hz), 2.50 (1H, sept, J=6.8 Hz), 3.73 (1H, br s), 3.95 (2H, s), 6.8—8.0 (7H, m)]. ^{1}H NMR ($CDCl_3$, δ): 1.70 (6H, d, J=7.0 Hz), 5.07 (1H, sept, J=7.0 Hz), 7.0—8.0 (6H, m), 8.17 (1H, s), 8.4—8.6 (1H, m).

*1-Bromo-9-isopropylanthracene (**12**: X=Br)* was obtained from 1-bromoanthrone in 35% yield by way of 1-bromo-9,10-dihydro-9-isopropyl-9-anthrol [^{1}H NMR ($CDCl_3$, δ): 0.49 (3H, d, J=7.0 Hz), 1.01 (3H, d, J=7.0 Hz), 2.54 (1H, sept, J=7.0 Hz), 3.10 (1H, br s), 3.83 and 4.00 (2H, AB-q, J=19.5 Hz), 6.8—8.3 (7H, m)]. ^{1}H NMR ($CDCl_3$, δ): 1.70 (6H, d, J=7.2 Hz), 5.13 (1H, sept, J=7.2 Hz), 6.9—8.0 (6H, m), 8.15 (1H, s), 8.4—8.6 (1H, m).

*General Procedure for Preparation of 1-Halo-9-isopropyltriptycenes (**6**—**8**).* To a boiling solution of 3.0 mmol of 1-halo-9-isopropylanthracene (**12**) and 1.5 mL of isopentyl nitrite in 30 mL of 1,2-dimethoxyethane (DME) was added a solution of 1.0 g (7.3 mmol) of anthranilic acid in 15 mL of DME during the course of 1 h and the mixture was heated under reflux for 1 h. Column chromatography on alumina with hexane as an eluent followed by recrystallization from tetrahydrofuran-hexane gave the desired triptycene as colorless crystals.

*1-Fluoro-9-isopropyltriptycene (**6**)* was obtained from **12** (X=F) in 74% yield, mp 202—203 °C. Found: C, 87.89; H, 5.80%. Calcd for $C_{23}H_{19}F$: C, 87.87; H, 6.09%. ^{19}F NMR ($CDCl_3$): 49.65 (m, $\pm sc$), 58.86 (m, *ap*).

*1-Chloro-9-isopropyltriptycene (**7**)* was obtained from **12** (X=Cl) in 32% yield, mp 178—180 °C. Found: C, 83.33; H, 5.49; Cl, 10.83%. Calcd for $C_{23}H_{19}Cl$:C, 83.50; H, 5.79; Cl, 10.71%.

*1-Bromo-9-isopropyltriptycene (**8**)* was obtained from **12** (X=Br) in 60% yield, mp 211—213 °C. Found: C, 73.87; H, 5.25; Br, 21.17%. Calcd for $C_{23}H_{19}Br$: C, 73.60; H, 5.10; Br, 21.30%.

*1,3-Di-t-butyl-9-isopropyltriptycene (**9**) and 2,4-Di-t-butyl-9-isopropyltriptycene (**10**).* To a boiling solution of 683 mg (3.1 mmol) of 9-isopropylanthracene (**12**: X=H)[14] and 1 mL of isopentyl nitrite in 20 mL of DME was added dropwise a solution of 1.10 g (4.4 mmol) of 3,5-di-*t*-butylanthranilic acid[8] in 20 mL of DME during the course of 1.5 h and the mixture was heated under reflux for 1 h. ^{1}H NMR spectrum of the crude reaction mixture indicated the presence of **9** and **10** in a ratio of *ca.* 1:2. Separation of the isomers was affected by liquid chromatography. The 2,4-di-*t*-butyl derivative (**10**) eluted faster than the other isomer and was recrystallized from tetrahydrofuran-ethanol, mp 170—172 °C. Found: C, 90.95, H, 8.94%. Calcd for $C_{31}H_{36}$: C, 91.12; H, 8.88%. The 1,3-di-*t*-butyl derivative (**9**) was recrystallized from dichloromethane-hexane, mp 202—204 °C. Found: 91.34; H, 9.04%. Calcd for $C_{31}H_{36}$: C, 91.12; H, 8.88%.

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