Restricted Rotation Involving the Tetrahedral Carbon. L. Rotamer Distributions and Rotational Barriers in Some 9-(1-Methoxyethyl)triptycene Derivatives[1]

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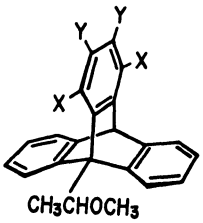
(Received April 22, 1983)

1,4-Dimethyl- and 1,2,3,4-tetrahalo-9-(1-methoxyethyl)triptycenes (halogen=F, Cl, and Br) were synthesized by reactions of 9-(1-methoxyethyl)anthracene with appropriate benzynes. Rotamer distributions and rotational barriers about the bridgehead-to-substituent bond were studied by NMR spectroscopy. Rotamer distributions are governed mainly by the steric effect; the major rotamer is assigned to *sc**(*S**), the minor one to *ap*, and the third one found only in the tetrafluoro derivative to *sc**(*R**). Rotational barriers are 21—23 kcal mol^{-1} which are slightly lower than those for the corresponding 9-isopropyltriptycenes.

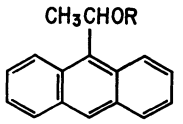
We have reported on the energy barriers to rotation about the bridgehead-to-substituent bond in triptycene derivatives carrying several types of secondary alkyl groups at the bridgehead position and on the dependence of the barriers upon *peri*-substituents. Among the compounds investigated are 9-isopropyl-,[2] 9-(2-methoxy-1-methylethyl)-,[3] and 9-(1-methyl-2-propenyl)triptycenes.[4] These compounds have rather similar barrier heights irrespective of the type of 9-alkyl groups. These findings allured us to study the rotational barriers in 9-(1-methoxyethyl)triptycenes which carry an oxygen function in the α-position of the 9-substituent and to compare the behavior with that exhibited by the 9-*s*-alkyltriptycenes mentioned above. We also found that singly *peri*-substituted 9-(1-hydroxy or methoxy-1-methylethyl)triptycenes have strong preference for the $\pm sc$ rotamers over the *ap* because of the smaller bulkiness of an oxy group than a methyl.[5] Therefore, the rotamer distributions in 9-(1-methoxyethyl)triptycenes are of interest because they are determined by the differential steric interactions of the methoxyl and methyl groups with the *peri*-substituent. Furthermore, the populations of rotamers may be affected by other factors than the steric because of the polar nature of a methoxyl group.

In this paper we report the syntheses of 9-(1-methoxyethyl)triptycenes **1**—**4** and the studies of the rotational equilibria and the rotational barriers measured by means of NMR spectroscopy.



1: X = Y = F
2: X = Y = Cl
3: X = Y = Br
4: X = CH_3, Y = H

The compounds studied were prepared as follows. 9-(1-Hydroxyethyl)anthracene (**5**) obtained by reduction of 9-acetylanthracene was methylated to give 9-(1-methoxyethyl)anthracene (**6**). Reactions of **6** with appropriate benzynes afforded the desired triptycene derivatives **1**—**4**. Tetrafluorobenzyne was generated by lithiation of bromopentafluorobenzene followed by *in situ* elimination of lithium fluoride. The other benzynes were generated by aprotic diazotization of the corresponding anthranilic acids followed by *in situ* pyrolysis of the resulting 2-diazoniobenzoates.



5: R = H
6: R = CH_3

Experimental

Melting points are not corrected. ^{1}H and ^{19}F NMR spectra at ambient temperature (*ca.* 35 °C) were obtained on a Varian EM 390 spectrometer at 90.0 and 84.67 MHz, respectively. ^{1}H NMR spectra were obtained also on a Hitachi R-20B spectrometer at 60.0 MHz. ^{1}H NMR data for **1**—**4** are compiled in Table 1. ^{19}F chemical shifts are shown in ppm downfield from internal hexafluorobenzene.

9-(1-Hydroxyethyl)anthracene (5). To a solution of 5.0 g (23 mmol) of 9-acetylanthracene[6] in 250 mL of diethyl ether was added 500 mg (13 mmol) of lithium tetrahydridoaluminate and the mixture was heated under reflux for 4 h with stirring. The reaction mixture was treated with 10 mL of ethyl acetate and then with 50 mL of water. The ether layer was washed with water and dried over magnesium sulfate. After the solvent was evaporated, the residue was recrystallized from dichloromethane-hexane to afford 4.3 g (85%) of the desired compound, mp 122—123 °C (lit,[7]: 125—126 °C). ^{1}H NMR ($CDCl_3$, δ): 1.85 (3H, d, J=6.3 Hz), 2.1 (1H, br s), 6.35 (1H, q, J=6.3 Hz), 7.3—7.6 (4H, m), 7.8—8.1 (2H, m), 8.30 (1H, s), 8.5—8.7 (2H, m).

9-(1-Methoxyethyl)anthracene (6). To a solution of 2.2 g (10 mmol) of **5** in 70 mL of tetrahydrofuran was added 10 mL of 1.5 mol L^{-1} solution of butyllithium in hexane and the mixture was stirred for 1 h at room temperature. To this solution was added dropwise 10 mL of methyl iodide and the mixture was stirred for 2 h. After evaporation of the volatile part of the reaction mixture, the residue was taken up in ether. The ether layer was washed with water and dried over magnesium sulfate. Evaporation of the solvent followed by recrystallization from dichloromethane-pentane gave 1.85 g (78%) of **6** as yellow crystals, mp 94—95 °C. Found: C, 86.41; H, 6.82%. Calcd for $C_{17}H_{16}O$: C, 86.48; H, 6.81%. ^{1}H NMR ($CDCl_3$, δ): 1.84 (3H, d, J=6.3 Hz), 3.19 (3H, s), 5.89 (1H, q, J=6.3 Hz), 7.3—7.6 (4H, m), 7.8—8.1 (2H, m), 8.37 (1H, s), 8.5—8.8 (2H, m).

1,2,3,4-Tetrafluoro-9-(1-methoxyethyl)triptycene (1). To a solution of 908 mg (3.8 mmol) of **6** and 1.1 g (4.5 mmol) of bromopentafluorobenzene in 100 mL of diethyl ether was

TABLE 1. ^{1}H NMR DATA AND POPULATION OF THE ROTAMERS IN $CDCl_3$ AT *ca.* 35°C[a)]

Compd	Rotamer[b)]	Population/%	9-Substituent			10-H	Other signals
			CH_3	OCH_3	CH		
1	*ap*	39	2.05 dd (5.9, *7.1*)	3.73	5.19 dq (5.9, *2.9*)	5.69 d (*1.5*)	6.9—7.6 m, 7.9—8.2 m
	sc(S*)*	55	2.00 dd (6.0, *1.0*)	3.69 d (*0.9*)	5.16 dq (6.0, *1.6*)	5.71 d (*1.5*)	
	sc(R*)*	6	1.99 dd (5.9, *7.4*)	3.71	5.01 dq (5.9, *2.7*)	5.71[c)]	
2	*ap*	24	2.13 d (5.8)	3.71	5.77 q (5.8)	5.94	6.8—7.6 m, 7.9—8.2 m
	sc(S*)*	76	1.90 d (6.0)	3.65	5.75 q (6.0)	5.96	
3	*ap*	22	2.13 d (5.9)	3.71	6.00 q (5.9)	6.01	6.8—7.6 m, 7.9—8.2 m
	sc(S*)*	78	1.88 d (6.0)	3.67	5.97 q (6.0)	6.05	
4	*ap*	22	2.12 d (6.0)	3.71	5.44 q (6.0)	5.54	2.47[d)]; 6.62 d, 6.70 d (7.8) (7.8) 6.8—7.4 m, 7.9—8.2 m
	sc(S*)*	78	1.92 d (6.0)	3.65	5.40 q (6.0)	5.54	2.40, 2.55; 6.59

a) Chemical shifts are given in δ. Signals are singlets unless otherwise noted; d: doublet, dd: double doublet, q: quartet, dq: double quartet, m: multiplet. In parentheses are coupling constants in Hz. Those in italics are couplings with 1-F. b) For the rotamer assignments, see text. c) Not definitely identified. d) Two methyl signals coincide.

TABLE 2. DYNAMIC NMR DATA

Compd	Obsd protons	T_c / °C	$\Delta\nu_c$ / Hz	k_c[a)] / s^{-1}	$\Delta G_c^{\ddagger}$[a)] / kcal mol^{-1}	K_c[b)]	ΔH°[a)] / kcal mol^{-1}	ΔS°[a)] / eu	Solvent
2	CH_3	145.5[c)]	15.4	8.0 (20.0)	23.1±0.1 (22.3±0.1)	0.40	1.6	1.9	C_6H_5Cl
3	OCH_3	109.5	1.8	0.53 (1.6)	23.2±0.1 (22.2±0.1)	0.33	2.1	3.4	1-$ClC_{10}H_7$
4	CH_3	114[c)]	11.8	4.3 (13.0)	21.7±0.1 (20.9±0.1)	0.33	1.3	1.0	C_6H_5Cl
	OCH_3	106	4.7	2.7 (8.7)	21.6±0.1 (20.7±0.1)	0.31			

a) Refers to the *sc*(S*)*→*ap* process. In parentheses are the data for the *ap*→*sc*(S*)* process. b) $K=[ap]/[sc^*(S^*)]$. c) The temperature at which the rate constant was obtained by simulation.

added 3.0 mL of 1.5 mol L^{-1} solution of butyllithium in hexane at −78 °C.[8)] The mixture was stirred at this temperature for 1 h, allowed to warm up to room temperature and then heated under reflux for 40 h. The reaction mixture was treated with dilute hydrochloric acid. The organic layer was washed with water and dried over magnesium sulfate. Column chromatography of the product on silica gel with hexane–dichloromethane as the eluent followed by recrystallization from dichloromethane–hexane gave 180 mg (12%) of **1** as colorless crystals, mp 193—195 °C. Found: C, 71.84; H, 4.19%. Calcd for $C_{23}H_{16}F_4O$: C, 71.87; H, 4.20%. ^{19}F NMR ($CDCl_3$): 2.0—4.0 (m, 2- and 3-F of the three rotamers), 12.0—14.0 (m, 4-F of the three rotamers), 19.6 (apparent quintet, 1-F of *sc*(S*)*), 25.3 (br, 1-F of *ap*) 33.5 (br, 1-F *sc*(R*)*).

1,2,3,4-Tetrachloro-9-(1-methoxyethyl)triptycene (2). To a boiling solution of 498 mg (2.1 mmol) of **6** and 1 mL of isopently nitrite in 40 mL of 1,2-dimethoxyethane (DME) was added a solution of 1.1 g (4.1 mmol) of tetrachloroanthranilic acid[9)] in 50 mL of DMF during the course of 3 h. The mixture was heated under reflux for 1 h. Evaporation of the solvent followed by column chromatography of the residue on silica gel with hexane–dichloromethane as the eluent and recrystallization from dichloromethane–hexane gave 84 mg (9%) of **2**, mp 264.5—266 °C. Found: C, 61.22; H, 3.50; Cl, 31.63%. Calcd for $C_{23}H_{16}Cl_4O$: C, 61.36; H, 3.58; Cl, 31.50%.

1,2,3,4-Tetrabromo-9-(1-methoxyethyl)triptycene (3), mp 288—289 °C, was synthesized similarly as **2** from **6** and tetrabromoanthranilic acid[10)] in 8% yield. Found: C, 44.13; H, 2.64; Br, 50.75%. Calcd for $C_{23}H_{16}Br_4O$: C, 43.99; H, 2.57; Br, 50.89%.

9-(1-Methoxyethyl)-1,4-dimethyltriptycene (4), mp 219—220 °C, was synthesized similarly as **2** from **6** and 3,6-dimethylanthranilic acid[11)] in 25% yield. Found: C, 88.18; H, 7.00%. Calcd for $C_{25}H_{24}O$: C, 88.20; H, 7.10%.

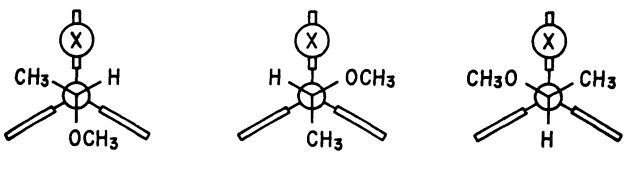
Dynamic NMR Studies. Variable temperature NMR spectra were recorded on a Hitachi R-20B spectrometer at 60.0 MHz as solutions in chlorobenzene or 1-chloronaphthalene. Temperatures were calibrated using an ethylene glycol sample.[12)] Chemical shift differences ($\Delta\nu_c$) at the coalescence temperatures (T_c) were obtained by linearly extrapolating the chemical shift differences at low tempera-

tures. Equilibrium constants (K_c) at T_c were calculated using the van't Hoff parameters shown in Table 2 which were obtained from the equilibrium constants at low temperatures. Rate constants (k_c) at T_c of the methoxyl signals were obtained by two methods: graphically following Jaeschke *et al.*[13] and by computer simulation of the spectra. Values obtained by the two methods agreed quite well. As for the coalescence of the methyl doublets, it was difficult to define T_c and the rate constants were obtained by simulating the spectra at a temperature which was estimated to be close to T_c.

Computer Simulation of the NMR Spectra. The calculations of the theoretical spectra were carried out on a Hitachi M280H computer at the Computer Center of the University of Tokyo, using a modified version of the DNMR 3 program by Binsch.[14] Spectra of **2**—**4** at or near T_c were simulated using the parameters obtained as described in the preceding section and modifying them if necessary to give the rate constants shown in Table 2. The methyl proton signal of **1** at ambient temperature was also simulated putting the exchange rates as zero. As our version of the program can not accommodate a three-site exchange problem of a five-spin system (AM_3X with a methine and methyl protons and a fluorine nucleus), we treated the system as a three-spin system regarding the methyl group as a single nucleus. The fluorine chemical shifts were assumed to be 9000 Hz upfield of the methyl protons, because the computation failed if the actual chemical shift differences between the proton and fluorine were used. Attempt at rigorous simulation of the variable temperature spectra of **1** was abandoned because of too many variable parameters: three independent rate constants, and temperature dependent chemical shifts and rotamer populations. Instead, the theoretical spectra were calculated using the parameters at ambient temperatures and assuming $k_{ap\rightarrow sc^*(S^*)} = 10\ k_{ap\rightarrow sc^*(R^*)} = 10\ k_{sc^*(S^*)\rightarrow sc^*(R^*)}$. Those with $k_{ap\rightarrow sc^*(S^*)}$ of 10—20 s^{-1} gave the best resemblance with the experimental spectrum at 122 °C, which gives a rough estimate of ΔG^* of 20.5—21.5 kcal mol^{-1} for the $ap\rightarrow sc^*(S^*)$ process.

Results and Discussion

Rotamer Assignments and Equilibria. The compounds examined have high rotational barriers on the NMR time scale and the rotamers about the bridgehead-to-substituent bond are separately observed at room temperature by NMR spectroscopy. Three racemic rotamers, *ap*, *sc*(S*)*, and *sc*(R*)*,[15] are possible and the Newman projections along the bond in question for those with *R*-configuration are shown in Scheme 1.



ap *sc*(S*)* *sc*(R*)*

Scheme 1.

It is shown that all the three rotamers are present in chloroform-*d* solution of the tetrafluoro derivative (**1**). In the ^{19}F NMR spectrum, three separate signals due to 1-F are observed at 19.6, 25.3, and 33.5 ppm downfield from internal hexafluorobenzene with an intensity ratio of 55 : 39 : 6, besides the signals due to 2-, 3-, and 4-F. The least abundant rotamer with the lowest-field 1-F signal can be assigned to *sc*(R*)* because the *sc*(R*)* rotamer should be least stable on the steric ground and the 1-F in this rotamer should be most deshielded: a downfield shift known as the van der Waals (steric compression) shift. Similarly from the standpoint of steric compression, the most abundant rotamer with the highest-field 1-F signal can be assigned to *sc*(S*)* and thus the remainder to *ap*.

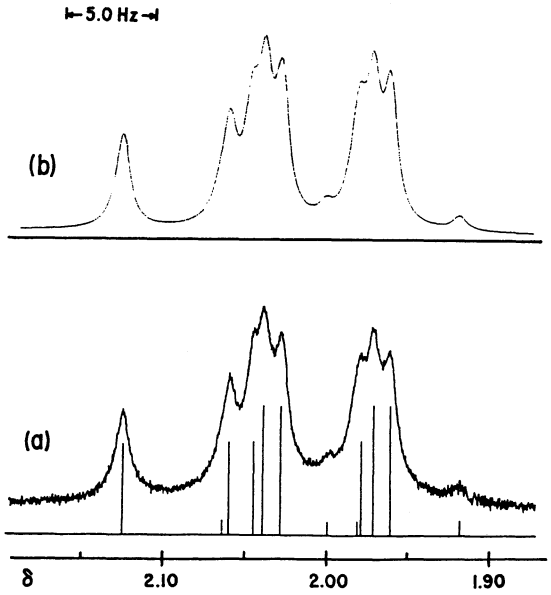


Fig. 1. (a) Observed 90 MHz ^1H NMR spectrum of the methyl region of compound **1** in chloroform-*d* at *ca.* 35 °C. (b) Calculated spectrum using the parameter values given in Table 1.

These assignments are supported by the analysis of the ^1H NMR spectrum of **1**. As found in our previous studies on 1-fluoro-9-(1,1-dimethyl-2-phenylethyl)triptycene atropisomers[16] and on 1-fluoro-9-isopropyltriptycene,[2] the methyl group in a $\pm sc$ site to the *peri*-fluoro substituent shows a large long-range spin-spin coupling with 1-F with a magnitude of 6—9 Hz, while the methyl in an *ap* site which is remote from the *peri*-fluoro group shows only a small coupling, if any, reflecting the through-space nature of the coupling.[17]

The methyl proton signal of **1** looks very complex consisting of three overlapping sets of double doublets due to the coupling with the methine proton and with the 1-F nucleus. The spectrum at 90.0 MHz is shown in Fig. 1. The analysis of the signals is almost unambiguously made by comparing the spectra obtained at 60 and 90 MHz. Furthere, the calculated spectrum (Fig. 1b) using the chemical shifts, the coupling constants and the rotamer populations, given in Table 1, properly reproduces the experimental spectrum.

The methyl signal due to the most abundant rotamer shows a small coupling with 1-F (1.0 Hz) indicating that the methyl group is in the *ap* site and therefore the rotamer is *sc*(S*)*. The second abundant rotamer has a large ^1H–^{19}F coupling of 7.1 Hz which is consistent with the *ap* rotamer. The least abundant rotamer also gives a large coupling of 7.4 Hz.

The chemical shifts of the methyl protons in **1** fall in a

narrow range of δ 1.99—2.05 and are not helpful in rotamer assignments but those of the methine proton are shown to be clearly site dependent: the protons in the *ap* and *sc**(*S**) rotamers have nearly identical chemical shifts and the proton in the *sc**(*R**) rotamer appears at a higher field by more than 0.15 ppm than the others. A methine proton synclinal to the *peri*-fluorine is deshielded due probably to the steric compression and/or anisotropy effect exerted by the *peri*-substituent.[18]

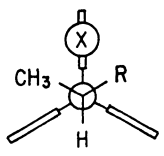
The tetrachloro compound **2** shows the presence of only two rotamers in equilibrium in a ratio of 76 : 24. It is reasonable to deduce that the absent rotamer is *sc**(*R**), because the population of the *sc**(*R**) rotamer of **1** is only 6% and the *peri*-chloro substituent in **2** is bulkier than the *peri*-fluoro one in **1**. The methine proton signals of the two rotamers have nearly the same chemical shifts of δ 5.77 and 5.75 and this supports that the two rotamers have their methine protons in similar environments, *i.e.* $\pm sc$ sites to the *peri*-substituent and that they are the *ap* and *sc**(*S**) rotamers.

Differentiation between the *ap* and *sc**(*S**) rotamers is made by consideration of the chemical shifts of the methyl proton signals. As was shown in our previous studies on 9-*t*-alkyl-[16] and 9-*s*-alkyltriptycenes[2-4] carrying a single *peri*-substituent, a methyl group located synclinal to the *peri*-substituent gives its signal at a considerably lower field than the one antiperiplanar to the *peri*-group probably because of the steric compression effect of the flanking *peri*-substituent. *peri*-Fluoro compounds behave exceptionally as mentioned above. Assuming that this generalization applies to compound **2**, we can assign *sc**(*S**) to the major rotamer because the methyl doublet at a higher field is more intense than that at a lower field (Table 1).

The same arguments apply to compounds **3** and **4**, both of which reside as two rotamers in a ratio of 78 : 22 in chloroform-*d*. In either of the compounds the more intense doublet for the methyl group appears at a higher field, and thus the *sc**(*S**) conformation is assigned to the major rotamer.

It becomes clear from the discussion above that the rotamer distribution in **1**—**4** is principally governed by the steric factor, the electrostatic effect being insignificant. A methoxyl group is less bulky than a methyl and is more confortably accommodated in a $\pm sc$ site, resulting in the predominance of the *sc**(*S**) rotamers. Operation of other factors than the steric one, *i.e.* electrostatic and hydrogen bonding effects, was observed in several 1-oxy-substituted 9-(1-methoxyethyl)triptycenes, which will be discussed in the following paper.[19]

The absence of the *sc**(*R**) rotamer in **2**—**4** may be in accordance with the absence of the corresponding rotamers **7** in 9-*s*-alkyltriptycenes hitherto examined.[2-4] The



R = CH_3, CH_2OCH_3, $CH{=}CH_2$

7

presence of a small amount of the *sc**(*R**) rotamer in **1** corresponds to the existence of the *ap* rotamer (**7**: R=CH_3, X=F) in 1-fluoro-9-isopropyltriptycene.[2b]

Rotational Barriers. Dynamic NMR behavior of **2**—**4** were studied in solutions of chlorobenzene or 1-chloronaphthalene by observing the methyl and/or methoxyl proton signals. These compounds reside as two rotamers, *ap* and *sc**(*S**), in these solvents as well as in chloroform-*d*, although the rotamer ratios are slightly different from those shown in Table 1. Rate constants for the $ap \rightleftharpoons sc^*(S^*)$ interconversion at or near the coalescence temperatures were evaluated by a graphical method or by computer simulation. These data and the free energies of activation therefrom are given in Table 2. The barriers for **2**—**4** are lower than those for the corresponding 9-isopropyltriptycenes[2] by 0.2—0.8 kcal mol^{-1} (1 cal=4.184 J). This may be due to the smaller bulkiness of a methoxyl than a methyl group. The higher barriers for **2** and **3** than for **4** may be ascribed to the operation of the positive buttressing effect in **2** and **3**[2,20] and also to the effective raise of the ground state in **4** due to the bulkiness of the *peri*-substituent as found in 9-isopropyltriptycenes.[2] The barrier for **1** is roughly estimated to be 20.5—21.5 kcal mol^{-1} as described in the Experimental section and this is evidently lower than the barriers for **2** and **3**.

Conformation in Crystalline States. Many compounds reside as only one of the possible rotamers in the crystalline states and this fact constituted a basis for the assignment of rotational isomers in the pioneering spectroscopic studies.[21] There are however some examples in which a crystal contains more than one rotamer.[22] Therefore it is interesting to see whether the crystals obtained here contain one or more rotamers. Although the rotational barriers found in **2**—**4** are too low for the rotamers to be separately isolated at room temperature, they are high enough for the rotamer composition in the crystalline state to be retained on dissolution in a solvent at low temperatures.

Crystals of compound **4** were dissolved in chloroform-*d* at *ca.* −50 °C and the ^1H NMR spectrum of the solution was taken at −40 °C. The sample was shown to be rotamerically homogeneous under these conditions and the rotamer was the one to which we have assigned *sc**(*S**) in the discussion above. The ^1H NMR spectra of **2** and **3** taken at −10——40 °C after dissolving the crystalline compounds at *ca.* −50 °C showed the presence of a small amount of the *ap* rotamer in addition to the *sc**(*S**). This may have been caused by the elevation of the sample temperature in the dissolution process. The crystals of **2**—**4** are therefore inferred to consist solely of the *sc**(*S**) rotameric state which is the major rotamer in solution. X-ray crystallographic studies on these compounds will afford an unambiguous evidence for the rotamer assignments in solution and are now in progress.

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