Restricted Rotation Involving the Tetrahedral Carbon. LI. Electrostatic and Hydrogen Bonding Effects on the Rotamer Distribution in 1-Oxy-substituted 9-(1-Methoxyethyl)triptycenes[1)]

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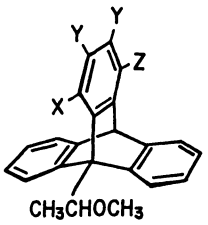
1-Hydroxy-4-methoxy- (**5**) and 1,4-dimethoxy-9-(1-methoxyethyl)triptycenes (**6**) were obtained by the reaction of 9-(1-methoxyethyl)anthracene with *p*-benzoquinone followed by enolization and methylation. Rotamer equilibrium in **6** is principally governed by the electrostatic effects favoring the *ap* rotamer. In weakly proton-accepting chloroform-*d*, **5** exists as *sc**(*R**) and *sc**(*S**) rotamers with the former predominating, both of which contain a strong intramolecular hydrogen bonding between the 1-hydroxyl and the methoxyl group in the 9-substituent. In strongly proton-accepting dimethyl-d_6 sulfoxide, all the three rotamers exist with the *ap* rotamer predominating. It is noteworthy that the *sc**(*R**) rotamer, which is present in 20% ratio in dimethyl sulfoxide, still retains the intramolecular hydrogen bonding in this solvent.

In the preceding paper[1)] we reported that the rotamer equilibrium in 9-(1-methoxyethyl)triptycenes **1**—**4** carrying a halogen or a methyl substitutent in a *peri*-position is principally governed by steric effects, the less crowded *sc**(*S**) rotamer being favored. We report here on the dynamic behavior of 1-oxy-substituted 9-(1-methoxyethyl)triptycenes **5** and **6** in which electrostatic and hydrogen bonding effects are the crucial factors governing the rotamer distribution.



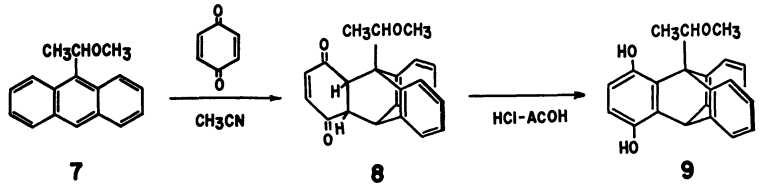
1 : X = Y = Z = F
2 : X = Y = Z = Cl
3 : X = Y = Z = Br
4 : X = Z = CH_3, Y = H
5 : X = OH, Y = H, Z = OCH_3
6 : X = Z = OCH_3, Y = H

Results and Discussion

Syntheses. Reaction of 9-(1-methoxyethyl)anthracene (**7**) with *p*-benzoquinone in acetonitrile gave a 9,10-adduct (**8**) which essentially consists of one diastereomer. In our previous studies on several 9-*s*-alkyl systems,[3)] enolization followed by methylation of a *p*-benzoquinone-anthracene adduct to give a 1,4-dimethoxytriptycene derivative was carried out in one pot under base-catalysis conditions. However, this method was unsatisfactory in the present case and thus the enolization of **8** was effected with acid and the 1,4-dihydroxy compound **9** was once isolated. Action of dimethyl sulfate on **9** in the presence of an aqueous base and a phase-transfer catalyst afforded a monomethylated compound **5**, which was then converted to the dimethylated derivative **6** by action of butyllithium and methyl iodide.

That the monomethylated compound is actually the 1-hydroxy-4-methoxy derivative **5** comes from the following observations. ^{1}H NMR spectrum of the hydroquinone **9** in chloroform-*d* exhibits two types of hydroxyl proton signals. One is a broad signal at δ 5.6 and the other consists of two sharp singlets at δ 9.12 and 9.27 with an intensity ratio of 3 : 1 which is identical with the rotamer ratio of **9** obtained by integration of the methyl and methoxyl signals. The former is assigned to the 4-hydroxyl proton because the chemical shift is in the normal region of phenolic hydroxyl protons.[4)] The latter is ascribed to the 1-hydroxyl group which forms a strong intramolecular hydrogen bonding with the methoxyl group in the bridgehead substituent, as is discussed in detail in the later section. The monomethylated compound **5** in chloroform-*d* shows only the latter type of hydroxyl proton signals, *i.e.* two sharp singlets at δ 9.06 and 9.16 in 3 : 1 ratio, consistent with the presence of the 1-hydroxyl group.

Rotamer Distributions. ^{1}H NMR spectrum of the



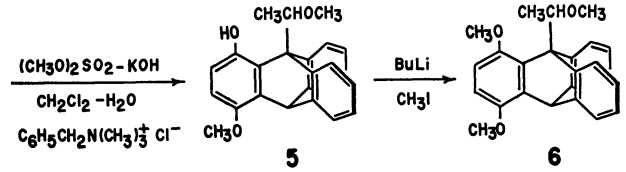


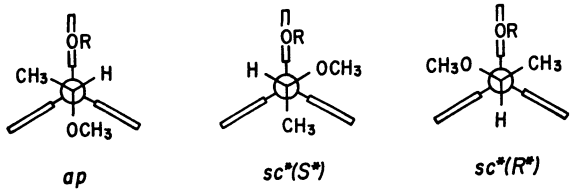
TABLE 1. ^{1}H NMR DATA AND POPULATIONS OF ROTAMERS[a)]

Compd	Solvent	Rotamer[b)]	Population/%	9-Substituent			10-H	2,3-H	Other Aromatic H	1-OR	4-OR
				CH_3	OCH_3	CH					
9	$CDCl_3$	*sc**(*R**)	75	2.09 d (6.0)	3.84	5.11 q (6.0)	5.80	6.48	6.7—7.5 m	9.12	5.6 br
		*sc**(*S**)	25	2.01 d (6.0)	3.79	5.40 q (6.0)	5.78	6.30 d, 6.38 d (8.4) (8.4)	6.7—7.5 m	9.27	
5	$CDCl_3$	*sc**(*R**)	75	2.08 d (5.9)	3.82[c)]	5.10 q (5.9)	5.85	6.61	6.8—7.5 m	9.06	3.81[c)]
		*sc**(*S**)	25	2.00 d (6.1)	3.79[c)]	5.40 q (6.1)	5.83	6.47	6.8—7.5 m 7.8 m	9.16	3.73[c)]
	DMSO-d_6	*sc**(*R**)	20	1.95 d (5.9)	3.82[c)]	5.22 q (5.9)	5.83	6.49 d, 6.71 d (8.9) (8.9)	6.7—7.5 m	9.18	3.77[c)]
		*sc**(*S**)	18	1.86 d (6.0)	3.63[c)]	5.42 q (6.0)	5.77	6.38 d, 6.48 d (8.9) (8.9)	6.7—7.5 m 7.85 m	8.97	3.69[c)]
		ap	62	1.99 d (5.8)	3.59[c)]	5.40 q (5.8)	5.74	6.42 d, 6.55 d (8.9) (8.9)	6.7—7.5 m 7.85 m	9.04	3.73[c)]
6	$CDCl_3$	*ap*	75	2.01 d (5.7)		5.42 q (5.7)	5.79	6.46 d, 6.53 d (8.9) (8.9)	6.7—7.5 m		3.68, 3.70, 3.78[d)]
		*sc**(*S**)	25	1.94 d (6.0)		5.46 q (6.0)	5.79	6.46	7.8—8.2 m		3.66, 3.72, 3.75[d)]
	DMSO-d_6	*ap*	78	1.91 d (5.7)		5.33 q (5.7)	5.79	6.62 d, 6.68 d (9.0) (9.0)	6.7—7.5 m		3.59, 3.67, 3.76[d)]
		*sc**(*S**)	22	1.82 d (6.0)		5.35 q (6.0)	5.79	6.59	7.8—8.2 m		3.55, 3.70, 3.72[d)]

a) Chemical shifts are given in δ. Signals are singlets unless otherwise noted. d: doublet, q: quartet, m: multiplet, br: broad signal. In parentheses are coupling constants in Hz. b) For the rotamer assignments, see text. c) Assignments are unambiguously made by comparing the spectrum of 1-hydroxy-4-trideuteriomethoxy-9-(1-methoxyethyl) triptycene. d) Assignments of the methoxyl signals are not made.

1,4-dimethoxy compound **6** in chloroform-*d* shows that it exists as two rotamers about the bridgehead-to-substituent bond in a ratio of 3 : 1. A criterion for making rotamer assignments is the chemical shifts of the methyl and methine protons in the bridgehead substituent as discussed in the preceding paper.[1)] We rely on the general tendency that either the methyl group or the methine proton gives its signal at a lower field when it is synclinal to the *peri*-substituent than when it is antiperiplanar due mainly to the steric compression effect exerted by the *peri*-substituent.[5)]

From the fact that the methine signals for the two rotamers have very similar chemical shifts (Table 1), it is inferred that the two rotamers are *ap* and *sc**(*S**) because the methine protons in these rotamers are in similar environments, *i.e.* are flanked by the *peri*-methoxyl group. The absence of the *sc**(*R**) rotamer is reasonable because this rotamer should be least stable of the three on both steric and electrostatic grounds.



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

Differentiation between *ap* and *sc**(*S**) comes from the inspection of the methyl signals. The doublet at a low field is more intense than that at a high field, and thus the major rotamer should be *ap* from the criterion. Although similar assignments were made for the rotamers in **2**—**4**,[1)] the one in the present case may be less reliable because the chemical shift difference between the methyl doublets is far smaller in **6** (0.07 ppm) than in **2**—**4** (0.20—0.23 ppm).

In order to confirm the assignment, we studied the effect of solvent polarity on the rotamer ratio. Upon changing the solvent from chloroform-*d* to more polar dimethyl-d_6 sulfoxide (DMSO-d_6), the more abundant rotamer increased its population (75→78%), whereas the less abundant decreased. As is clearly shown by molecular model consideration, *ap*-**6** is more polar than *sc**(*S**)-**6**, and the major rotamer is reasonably assigned to *ap* because a more polar isomer is stabilized in a more polar solvent.

The predominance of the *ap* rotamer in **6** is in sharp contrast with the behavior exhibited by the *peri*-halo compounds **1**—**3** and the *peri*-methyl one **4** where the *sc**(*S**) rotamer is predominant. As shown in the preceding paper, steric effect is the major factor governing the rotamer distribution in **1**—**4**.[1)] The findings here indicate that the electrostatic effect overweighs the steric effect in **6**: the electrostatic repulsion between the oxygen lone pairs in the 1-methoxyl and the 9-(1-methoxyethyl) groups destabilizes the *sc**(*S**) rotamer. An alternative explanation may be possible which includes a hypothetical C–H···O hydrogen bonding.[3,9)] We prefer to attribute the phenomenon to the electrostatic effect until afirm basis of the C–H···O hydrogen bonding is laid.

Compounds **5** and **9**, carrying a hydroxyl group at a *peri*-position, behaved very similarly with each other in ^{1}H NMR spectra, and a detailed study was carried out mainly on **5** because of the low solubility of **9**. ^{1}H NMR spectrum of **5** in chloroform-*d* shows the presence of two rotamers in a ratio of 3 : 1 (Table 1). The most distinguished feature of the spectrum is the appearance of the *peri*-hydroxyl proton signal as two sharp singlets at δ 9.06 and 9.16 in an intensity ratio of 3 : 1. This clearly indicates that the hydroxyl group in each of the rotamers forms a strong intramolecular hydrogen bonding and thus the two are *sc**(*R**) and *sc*(*S**), in both of which the methoxyl group in the 9-substituent flanks the *peri*-hydroxyl. The hydroxyl group in the *ap* rotamer, if present, would appear at a far higher field.[4]

This situation is also evidenced by IR spectroscopy.[10] A dilute solution (*ca.* 2×10^{-3} mol L^{-1}) of **5** in chloroform shows an absorption at 3220 cm^{-1} ($\varepsilon\approx150$) with a half band width of *ca.* 200 cm^{-1} as the only one ascribable to O–H stretching. This frequency is lower by nearly 400 cm^{-1} than the normal one of 3610 cm^{-1} for a phenolic hydroxyl group, suggesting the occurence of an unusually strong intramolecular hydrogen bonding. Such a large shift as found here is unprecedented in an intramolecular hydrogen bonding between a hydroxyl and an alkoxyl group although several examples of large shifts have been reported on *o*-nitrophenol derivatives.[10b]

This spectral feature is retained in a more concentrated solution of **5** (*ca.* 8×10^{-2} mol L^{-1}) in chloroform-*d*, which is the same sample as is used in the ^{1}H NMR measurement.[11] Therefore IR spectroscopy also indicates that **5** in chloroform resides only as the rotamers capable of intramolecular hydrogen bonding: *sc**(*R**) and/or *sc**(*S**).

Conformational assignments of the two rotamers present in chloroform-*d* come again from the chemical shifts of the methyl and methine proton signals. As the lower-field methyl signal and the higher-field methine signal are more intense than their respective counterparts, the major rotamer is deduced to be *sc**(*R**), and thus the minor *sc**(*S**). This assignment looks quite unusual from the standpoint of steric effect because the *sc**(*R**) rotamer is apparently more crowded. The explanation for this still remains unknown.

Although **5** was shown to exist solely as intramolecularly hydrogen-bonded rotamers in chloroform which is very weak as a proton acceptor, the compound was expected to behave differently in a strongly proton-accepting solvent. Actually, ^{1}H NMR spectrum of **5** in DMSO-d_6 disclosed the presence of three rotamers in a ratio of 62 : 20 : 18. As the direct comparison of the spectrum with that in chloroform-*d* did not allow an unambiguous assignment of the rotamers, the change of the rotamer distribution was followed by gradually varying the solvent composition in a mixture of chloroform-*d* and DMSO-d_6. The results, as shown in Fig. 1, clearly reveal that the most abundant rotamer in DMSO is the one which is absent in chloroform, namely *ap*. The major rotamer in chloroform, *sc**(*R**), becomes less and less populous with the increasing content of DMSO, and the minor one in chloroform, *sc**(*S**), does not significantly change its population by the solvent composition.

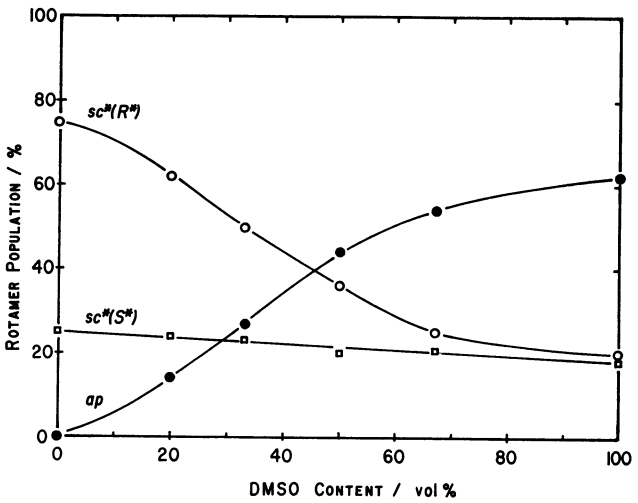
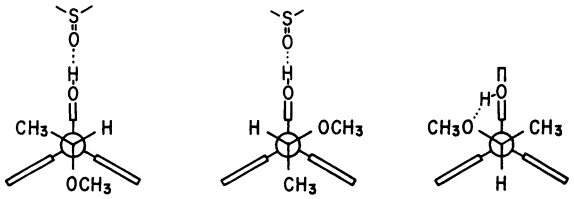


Fig. 1. Dependence of the rotamer populations in **5** upon the solvent composition in $CDCl_3$–DMSO-d_6. ●: *ap*, ○: *sc**(*R**), □: *sc**(*S**).

In a fraction of molecules of **5**, intramolecular hydrogen bonding in chloroform switches to intermolecular hydrogen bonding with a solvent molecule in DMSO. In intermolecularly hydrogen-bonded species the attractive interaction between the *peri*-hydroxyl group and the methoxyl in the side chain disappears, rendering the electrostatic repulsion between the lone pairs a ruling factor. This results in the destabilization of *sc**(*S**)-**5** and the predominance of *ap*-**5** (Scheme 1).



ap-**5** *sc**(*S**)-**5** *sc**(*R**)-**5**

Scheme 1.

It is noticed that the population ratio of the *ap* and *sc**(*S**) rotamers of **5** in DMSO is identical with that of **6** in DMSO within the experimental error (3.4 *vs.* 3.5). This suggests that the same factor dominates in controlling the distribution between the *ap* and *sc**(*S**) rotamers, *i.e.* the electrostatic repulsion between the lone pair electrons, and that the 1-hydroxyl group in the *sc**(*S**) rotamer forms an intermolecular hydrogen bonding with a DMSO molecule.

The fact that the *sc**(*R**) rotamer of **5** still exists in 20% population in DMSO, in contrast with the absence of the corresponding *sc**(*R**) rotamer of **6**, suggests that *sc**(*R**)-**5** is stabilized by a special factor which is absent in **6**, *i.e.* an intramolecular hydrogen bonding (Scheme 1).

Intra- and intermolecularity of the hydrogen bonding in **5** is also reflected in the chemical shifts, especially of the hydroxyl and methoxyl proton signals. The dependence of the chemical shifts of these signals upon the solvent composition is shown in Fig. 2. The hydroxyl

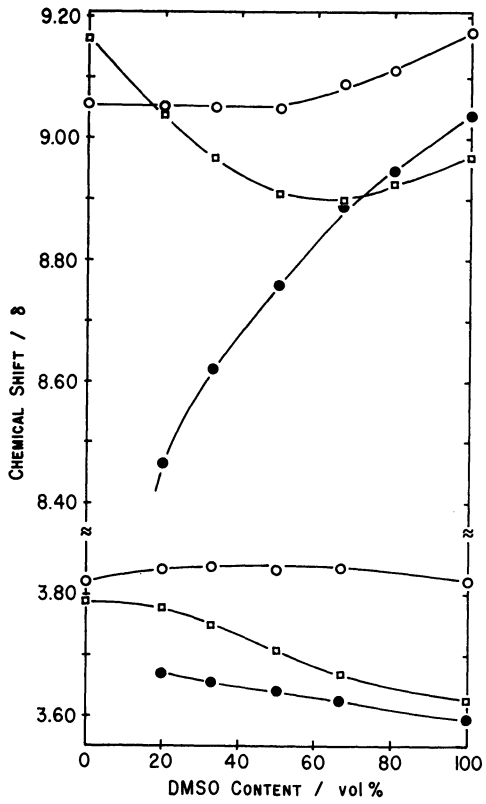


Fig. 2. Dependence of the chemical shifts of the 1-hydroxyl proton and the methoxyl protons in the 9-substituent in rotamers of **5** upon the solvent composition in $CDCl_3$–DMSO-d_6. ●: *ap*, ○: *sc**(*R**), □: *sc**(*S**).

proton signal of the *sc**(*R**) rotamer stays at the initial position of δ 9.06 and then gradually shifts downfield as the DMSO content increases. The signal retains its sharpness (a half-band width of less than 1.7 Hz) irrespective of the solvent composition reflecting the intramolecularity of the hydrogen bonding throughout the solvent range. The hydroxyl proton signal of the *sc**(*S**) rotamer, which appears at δ 9.16 in chloroform-*d*, rapidly shifts upfield and broadens as the DMSO content increases up to 50 vol%. It then moves downfield and resharpens. Appearance of the broad signal at the intermediate region of the DMSO content should be due to exchange between the intramolecular hydrogen-bonded species and the intermolecularly hydrogen-bonded ones. A small broad signal due to *ap*-**5** is observed at δ 8.45 when the DMSO content is *ca.* 20 vol%, which increases in its intensity, sharpens and shifts downfield as the DMSO content increases until it appears at δ 9.04 as a sharp singlet in DMSO.[12]

Dependence of the chemical shifts of the methoxyl protons of the 9-substituent upon the solvent composition also seems to reflect whether the methoxyl group participates in the hydrogen bonding. Although the chemical shifts of the methoxyl protons depend on several other factors, their contributions would be rather small in view of the fact that the chemical shift differences of the methoxyl protons between the rotamers in **1**—**4** is at most 0.06 ppm. The methoxyl group of *sc**(*R**)-**5** which forms the hydrogen bonding with the hydroxyl group gives its signal at a low field of δ 3.82—3.85, while that of *ap*-**5** which does not participate in hydrogen bonding appears at a high field of δ 3.59—3.67. The methoxyl proton signal due to *sc**(*S**)-**5** is located near that due to *sc**(*R**)-**5** in chloroform-*d* but it shifts upfield with the increasing content of DMSO and appears closely to that due to *ap*-**5** in DMSO, suggesting that the hydrogen bonding in *sc**(*S**)-**5** switches from intramolecular in chloroform to intermolecular in DMSO.

^{1}H NMR spectrum of **5** obtained in acetone-d_6 indicates the presence of three rotamers in a ratio of 66 : 22 : 12. The behavior of the chemical shifts and populations in mixtures of chloroform-*d* and acetone-d_6 reveals that the most abundant rotamer in acetone-d_6 is *sc**(*R**), the second abundant *sc**(*S**) and the least abundant *ap*. This ratio is almost identical with the rotamer ratio of **5** in chloroform-*d* containing 15 vol% of DMSO-d_6 (Fig. 1). Therefore the rotamer distribution in **5** may serve as a measure of the proton accepting ability of a solvent system. In benzene-d_6, **5** exists as two rotamers, *sc**(*R**) and *sc**(*S**), in a ratio of 3 : 1 just as in chloroform-*d*, indicating that benzene is as weak a proton acceptor as chloroform.

Rotational Barriers. Variable temperature ^{1}H NMR spectra of **5** and **6** were obtained in chlorobenzene. Both of them showed the presence of two rotamers in this solvent. As there is no reason to assume that the rotamer distributions significantly alter by changing the solvent from chloroform-*d* to chlorobenzene, the existing rotamers of **5** are assigned to *sc**(*R**) and *sc**(*S**) and those of **6** to *ap* and *sc**(*S**), the former predominating in each compound. Rate constants for the interconversion between the two rotamers at or near the coalescence temperatures (T_c) and the free energies of activation therefrom are given in Table 2. The barrier to the *ap*⇌*sc**(*S**) process in **6** is a little lower than that to the $+sc \rightleftarrows -sc$ process in 1,4-dimethoxy-9-isopropyltriptycene ($\Delta G_c^{\ddagger}$=23.0 kcal mol^{-1} at 140 °C),[7] both occurring through similar transition states in which the methine hydrogen in the 9-substituent eclipses the *peri*-

Table 2. Dynamic NMR data in chlorobenzene

Compound	Obsd signal	Process	T_c °C	$\Delta\nu_c$ Hz	k_c s^{-1}	$\Delta G_c^{\ddagger}$ kcal mol^{-1}	K_c
5	OCH_3	*sc**(*R**)→*sc**(*S**)	112	5.5	9.3	21.0±0.1	3.0
		*sc**(*S**)→*sc**(*R**)			3.1	21.9±0.1	
6	CH_3	*ap*→*sc**(*S**)	114	9.2	13.2	20.9±0.1	2.2
		*sc**(*S**)→*ap*			6.0	21.5±0.1	

methoxyl group. The barrier difference may be ascribed to the smaller bulkiness of a methoxyl than a methyl. The barriers in the *peri*-methoxy compound **6** are almost the same as those in the *peri*-methyl one **4**.[1] In the 9-isopropyl series, the *peri*-methoxy compound has a higher barrier than the *peri*-methyl one (ΔG_c^*: 23.0 *vs.* 22.0 kcal mol^{-1}), which was ascribed to the destabilization of the ground state in the latter due to molecular deformation. The destabilization of the ground state in **4** may be less significant because of the smaller congestion in the 9-(1-methoxyethyl) series.

Observation of the *sc**(*R**)⇌*sc**(*S**) process in **5** is unique in the point that the methoxyl group in the 9-substituent eclipses the *peri*-hydroxyl group in the transition state, because every barrier heigen hitherto examined in 9-*s*-alkyl- and 9-(1-methoxylethyl)-triptycenes has referred to the process in which the methine hydrogen eclipses the *peri*-substituent in the transition state.

Experimental

Melting points are not corrected. ^{1}H NMR spectra were obatined on a Hitachi R-20B (60 MHz) or a Varian EM-390 (90 MHz) spectrometer at *ca.* 35 °C. IR spectra were recorded on a Hitachi 260-30 or a Hitachi 260-50 spectrophotometer using a 0.1 mm KRS-5 cell for samples of *ca.* 0.1 mol L^{-1} and a 5.0 mm quartz cell for samples of *ca.* 10^{-3} mol L^{-1}.

1,4-Dihydroxy-9-(1-methoxyethyl)triptycene (9). A mixture of 944 mg (4.0 mmol) of 9-(1-methoxyethyl)anthracene (**7**)[1] and 2.1 g (20 mmol) of *p*-benzoquinone in 7 mL of acetonitrile was heated under reflux for 3 h with stirring. The mixture was cooled and the precipitate was collected by filtration. The solid was washed with diethyl ether to remove the unreacted *p*-benzoquinone. The 9,10-adduct (**8**) was obtained in 99% yield, mp 177—179 °C (decomp), which was shown by ^{1}H NMR to consist of a single diastereomer. ^{1}H NMR ($CDCl_3$, δ): 1.79 (3H, d, J=6.0 Hz), 2.97 (1H, dd, J=8.5 and 2.5 Hz), 3.45 (1H, d, J=8.5 Hz), 3.67 (3H, s), 4.43 (1H, q, J=6.0 Hz), 4.58 (1H, d, J=2.5 Hz), 5.99 (2H, s), 7.0—7.4 (7H, m), 7.95 (1H, m). A suspension of 500 mg of the adduct **8** in 50 mL of acetic acid containing 2 mL of concentrated hydrochloric acid was stirred overnight at room temperature. The solid was collected by filtration, washed with water and dried in air. Recrystallization from dichloromethane–hexane gave 475 mg (95%) of **9**, mp 166 °C (decomp). This compound was directly used for the next reaction.

1-Hydroxy-4-methoxy-9-(1-methoxyethyl)triptycene (5). A solution of 500 mg (1.45 mmol) of **9**, 3 mL (32 mmol) of dimethyl sulfate and 100 mg of benzyltrimethylammonium chloride in 50 mL of dichloromethane was stirred overnight at room temperature with 30 mL of a 1 mol L^{-1} aqueous solution of potassium hydroxide. The excess of dimethyl sulfate was decomposed by warming the organic layer with 10 mL of a 1 mol L^{-1} aqueous solution of potassium hydroxide. The organic layer was separated and concentrated by evaporation. The residue was taken up in ether. The ethereal solution was washed successively with dilute hydrochloric acid, aqueous sodium hydrogencarbonate and water, and dried over magnesium sulfate. Recrystallization of the product from chloroform–hexane gave 260 mg (50%) of **5**, mp 265—266 °C. Found: C, 80.16; H, 6.22%. Calcd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19%.

1,4-Dimethoxy-9-(1-methoxyethyl)triptycene (6). To a solution of 113 mg (0.32 mmol) of the monomethylated compound **5** in 30 mL of tetrahydrofuran was added dropwise 0.3 mL of 1.5 mol L^{-1} butyllithium in hexane and the mixture was stirred for 3 h at room temperature. To the solution was added dropwise 10 mL (160 mmol) of methyl iodide and the mixture was stirred for 24 h at room temperature. The mixture was taken up in ether and the ethereal solution was washed successively with dilute hydrochloric acid, aqueous sodium hydrogencarbonate and water. The ether layer was dried over magnesium sulfate and the solvent was evaporated. The residue was recrystallized from dichloromethane–hexane to give 62 mg (53%) of **6**, mp 204—205 °C. Found: C, 80.83; H, 6.23%. Calcd for $C_{25}H_{24}O_3$: C, 80.62; H, 6.49%.

DNMR Studies. Variable temperature ^{1}H NMR spectra were recorded on the Hitachi R-20B spectrometer. Temperatures were calibrated with the use of an ethylene glycol sample.[13] Rate constants at or near T_c were evaluated by simulating the spectra using a modified version of the DNMR 3 program by Binsch.[14] While T_c for the methoxyl proton signal in **6** was easily defined, that for the methyl signal in **5** was not definitely identified and a spectrum obtained at a temperature which was estimated to be close to T_c was simulated.

References

1) Part L: Y. Tanaka, G. Yamamoto, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **56**, 3023 (1983).

2) For nomenclature of rotamers, see Ref. 1 and also: M. Ōki, *Top. Stereochem.*, **14**, 1 (1983).

3) M. Suzuki, G. Yamamoto, H. Kikuchi, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **54**, 2383 (1981); H. Kikuchi, S. Hatakeyama, G. Yamamoto, and M. Ōki, *ibid.*, **54**, 3832 (1981).

4) A hydroxyl proton signal of phenols which do not form an intramolecular hydrogen bonding is said to appear at δ 4-7: R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectroscopic Identification of Organic Compounds," 4th ed, Wiley, New York (1981), p. 196.

5) This tendency has been observed in our previous studies for the methyl signals in 9-*t*-alkyl-[6] and 9-*s*-alkyl-triptycenes[3,7] and for the methylene protons in 9-(arylmethyl)-triptycene.[8]

6) G. Yamamoto, M. Suzuki, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **56**, 306 (1983).

7) F. Suzuki, M. Ōki, and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, **47**, 3114 (1974); G. Yamamoto and M. Ōki, *ibid.*, **56**, 2082 (1983).

8) F. Suzuki and M. Ōki, *Bull. Chem. Soc. Jpn.*, **48**, 596 (1975); G. Yamamoto and M. Ōki, *ibid.*, **54**, 481 (1981).

9) S. Zushi, Y. Kodama, K. Nishihata, K. Umemura, M. Nishio, J. Uzawa, and M. Hirota, *Bull. Chem. Soc. Jpn.*, **53**, 3631 (1980) and references cited therein.

10) a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 3rd ed, Wiley, New York (1975), Chap. 6; b) M. Tichý, *Adv. Org. Chem.*, **5**, 115 (1965).

11) The corresponding 1-deuteroxy compound shows an absorption at 2365 cm^{-1} as a sole signal ascribable to O–D stretching.

12) The hydroxyl proton of phenol in DMSO appears at δ 9.25: O. L. Chapman and K. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

13) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968).

14) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).