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$CH_3\cdots O$ Hydrogen Bond. Implications of Its Presence from the Substituent Effects on the Populations of Rotamers in 4-Substituted 9-Ethyl-1-methoxytriptycenes and 9-(Substituted Phenoxymethyl)-1,4-dimethyltriptycenes[1)]

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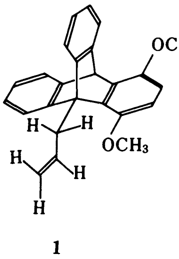
In the series of 4-substituted 9-ethyl-1-methoxytriptycenes, the populations of the *sc* conformer increase as the electron-density on the 1-methoxy-oxygen decreases. This trend was interpreted on the basis of steric repulsion which should increase as the electron density on the oxygen atom becomes high. In contrast, in the series of 9-(substituted phenoxymethyl)-1,4-dimethyltriptycenes, the high electron density on the aryloxy-oxygen favors the *sc* form. The stabilization of the *sc* form relative to the *ap* in the high electron density compounds in the latter series is attributed to the presence of $CH_3\cdots O$ hydrogen bond, since other factors like Coulombic interactions, van der Waals repulsions, and van der Waals attractions could be excluded from being the main factor for the stabilization.

Hydrogen bond is a very important phenomenon both in chemistry and in biology.[2)] Those which involve the OH and NH groups as hydrogen donors are well-documented. However, the hydrogen bond which involves the CH group as a hydrogen donor, though theoretically possible, is controversial at best, except some strong hydrogen donors like hydrogen cyanide, acetylene, and chloroform.[3)] It is a common practice to assume the presence of a hydrogen bond when two groups concerned are placed within the sum of their van der Waals radii in crystals.[4)] Nishio and Hirota have discussed the presence of this kind of interactions from the unusual populations of rotamers but their work is lacking convincing evidence.[5)] Allerhand and Schleyer investigated the presence of hydrogen bond involving the methyl group without success.[6)] As judged from the acidity of methyl groups, the electron-accepting ability of the methyl should be the lowest among the CH groups. And this makes it difficult to detect the hydrogen bond involving the methyl group as a hydrogen donor.

Molecular interactions are generally observable when one of various factors predominates. The factors may be charge-transfer interactions, Coulombic interactions both repulsive and attractive, van der Waals repulsions, and van der Waals attractions (dispersion forces).[3)] Since the charge trasfer interactions involving the methyl group are weak, the attractive forces due to charge transfer may well be cancelled by the strong van der Waals repulsive forces. This is cosidered to be the situation where we do not usually observe hydrogen bond in which the methyl group acts as a hydrogen donor.

1,9-Disubstituted triptycenes comprise a very interesting group of compounds because the substituents are placed well within the sum of the van der Waals radii, as judged from the molecular structures in crystals.[7–9)] That means that the 9-substituent cannot avoid the very strong van der Waals repulsions irrespective of their rotational positions including the otherwise stable staggered positions. In addition, this geometry will enhance the overlap of the atomic orbitals concerned. The fact that this laboratory was able to report the presence of weak molecular interactions such as charge-transfer interactions between n-electrons and π^*-systems of benzene rings,[10)] n-electrons and σ^*-systems of acyloxymethyl groups,[11)] and n-electrons and π^*-systems of various carbonyl moieties[5)] by taking advantage of the 1,9-disubstituted triptycenes owes to these particular steric situations.

We have suggested in some of the previous papers from this laboratory that there have been some phenomena that might be explained by the presence of $CH_3\cdots O$ hydrogen bond. Although the thickness of the π-system is considered to be much smaller than the van der Waals radius of a methyl group, both 9-allyl- (**1**) and 9-ethyl-1,4-dimethoxytriptycene (**2**) show the ±*sc*/*ap* value of ca. 0.7.[12–13)] Similarly, 1,4-dimethoxy-9-(1-methyl-2-propenyl)triptycene (**3**) shows *sc*/*ap* value of 0.72.[14)] Apparently the methyl group is smaller than the π-system in this case. Although it is possible to argue that these unusual population ratios of rotational isomers are caused by an unexpected instability of the conformation in which the vinyl group takes the *ap* position or the electronic repulsion between the π-system and the methoxy-oxygen is very strong, we cannot overlook a possibility that there are attractive interactions such as $CH_3\cdots O$ hydrogen bond.



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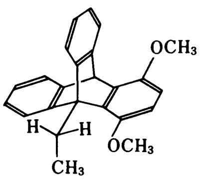

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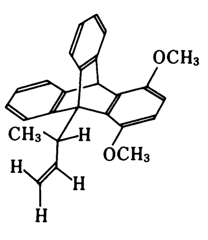

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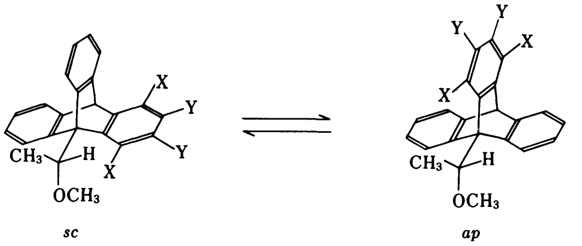
1-Substituted 9-(1-methoxyethyl)triptycenes (**4**) are another case that shows anomalous population ratios of rotamers. The *ap* rotamer becomes more favored than the statistical value of 2.0 when the 1-substituent is a methoxyl group whereas other substituents such as chloro, bromo, and methyl all disfavor the *ap* form to a large extent.[15] The results may be interpreted on one hand that the small bulkiness of the methoxyl group favors the *ap* form but on the other it is possible to assume that the $CH_3\cdots O$ hydrogen bond favors the *ap* form especially because all other substituents give small *sc*/*ap* values of 0.3—0.4. This large jump in populations might imply an attractive force in the *ap* form of the 1-methoxy compound.

In order to get further insight into the nature of the abnormal population ratios of these compounds, we have investigated the substituent effects in the population ratios, by introducing a substituent to the para position of the methoxyl group in 9-ethyl-1-methoxytriptycene (**10**) and to the para position (and in one case 3,4-positions) of the phenyl group in 9-(phenoxymethyl)-1,4-dimethyltriptycene (**16**). To the first approximation, it was expected that the lowering of the electron density on the oxygen atom should decrease the stability due to the charge-transfer interactions. The latter compounds behaved as expected, whereas the former did not. The results, however, support the presence of $CH_3\cdots O$ hydrogen bond, as will be discussed in this paper.

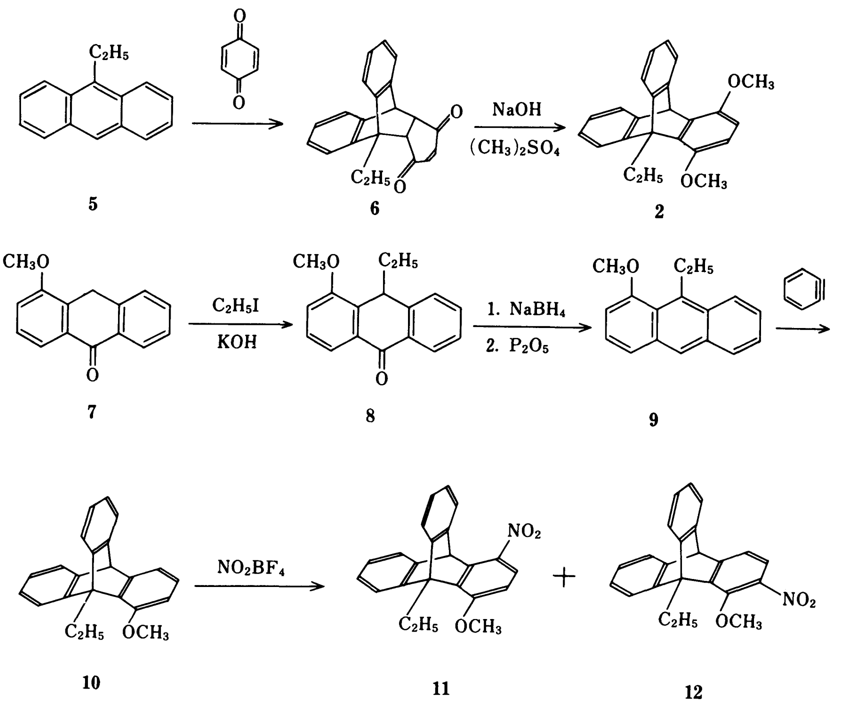


(only *R* configuration shown)

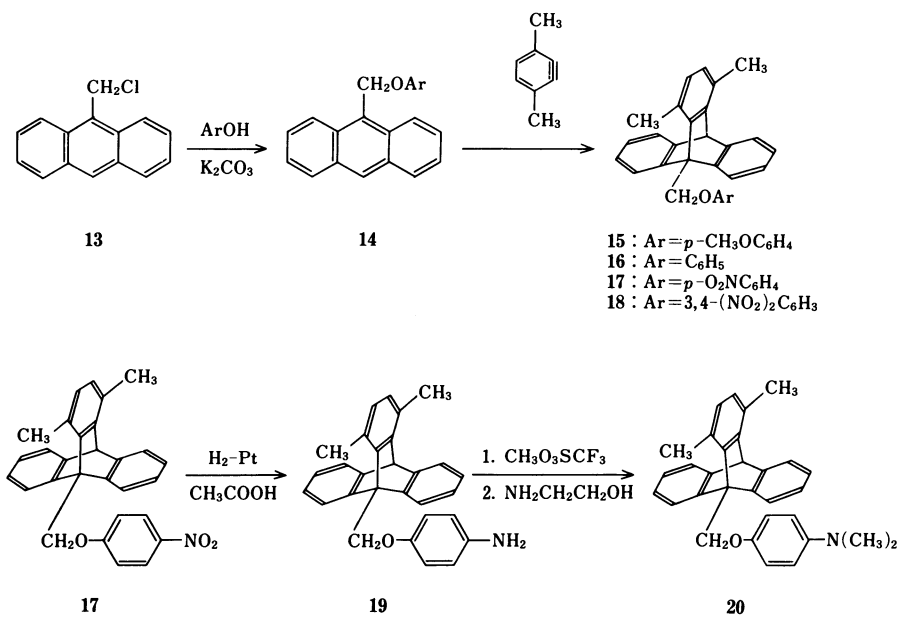
4 $\left(\begin{array}{l}X=OCH_3,\ Cl,\ Br,\ CH_3\\ Y=\ H,\ \ Cl,\ Br,\ \ H\end{array}\right)$

Synthesis and Determination of Populations

The synthetic routes for 4-substituted 9-ethyl-1-methoxytriptycenes and 9-(aryloxymethyl)-1,4-dimethyltriptycenes are shown in Schemes 1 and 2, respectively. 9-Ethyl-1,4-dimethoxytriptycene (**2**) had been prepared by treating 9-ethylanthracene with dimethoxybenzyne generated in situ by treating 2-chloro-1,4-dimethoxybenzene with phenylsodium.[12] However, the present method gave much better results including the yield and the ease of purification of the product. 9-Ethylanthracene (**5**) was heated with *p*-benzoquinone to produce the Diels–Alder adduct **6** which was then alternatively treated with aqueous sodium hydroxide and dimethyl sulfate to afford **2**. 4-Methoxy-9-anthrone (**7**) was ethylated with aqueous potassium hydroxide and ethyl iodide and the product **8** was converted to 9-ethyl-1-methoxyanthracene (**9**) by treatment with sodium tetrahydroborate and then with phosphorus pentaoxide. Treatment of the anthracene with benzyne generated from anthranilic acid afforded 9-ethyl-1-methoxytriptycene (**10**). Nitration of the triptycene (**10**) with nitronium tetrafluoroborate afforded a mixture of 2-nitro (**12**) and 4-nitro (**11**) de-



Scheme 1. Synthetic routes to 4-substituted 9-ethyl-1-methoxytriptycenes.

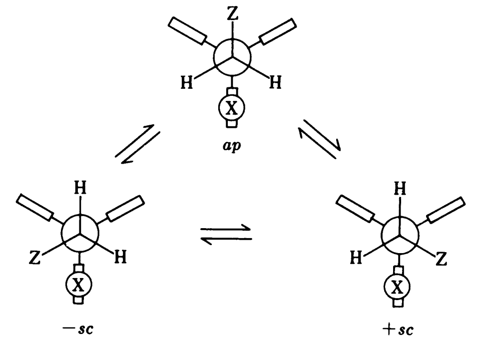


Scheme 2. Synthetic routes to 9-(aryloxymethyl)-1,4-dimethyltriptycenes.

rivatives which could be separated easily by chromatography. The structure of the 4-nitro compound was established by taking advantage of the chemical shift of 9-H in ^{1}H NMR spectroscopy. Whereas the 4-nitro compound (**11**) exhibits a large low-field shift of the 9-H signal, the 2-nitro compound **12** gives it at a normal range of 9-H signals of triptycenes.

9-(Aryloxymethyl)-1,4-dimethyltriptycenes (**15**—**18**) were preparad by treating 9-(aryloxymethyl)anthracene (**14**), which was synthesized by treatment of 9-(chloromethyl)anthracene (**13**) with substituted phenols in the presence of potassium carbonate, with 3,6-dimethylbenzyne which was generated from 3,6-dimethylanthranilic acid. 9-(Phenoxymethyl)anthracene had been prepared by treating 9-anthryldiazomethane with phenol,16) but the present method gives much better results than the reported. 9-[4-(Dimethylamino)phenoxymethyl]-1,4-dimethyltriptycene (**20**) was prepared by reduction of 1,4-dimethyl-9-(4-nitrophenoxymethyl)triptycene (**17**), which was synthesized as above, to afford the amino compound (**19**). The amine (**19**) was then methylated to the corresponding quaternary ammonium salt with methyl triflate and then demethylated with 2-aminoethanol.

Population ratios of the rotational isomers were determined by integration of ^{1}H NMR spectra at 400 MHz obtained at low temperatures. Assignment of the rotamers was straightforward, because, as is seen in Scheme 3, the *ap* form should exhibit enanthiotopic methylene signal, a singlet, and the ±*sc* form diastereotopic, an AB quartet. In practice, however, the separation of the methylene signals was not always perfect to cause errors in integration. In those cases, methyl signals were used for the estimation of populations after completion of assignments by consulting the intensity with the methylene proton signals.



Scheme 3. Rotational circuit of 1,9-disubstituted triptycenes, where the 9-substituent is ZCH_2.

Results and Discussion

4-Substituted 9-Ethyl-1-methoxytriptycenes (2, 10, and 11). The population ratios obtained at ca. −40 °C with these compounds are shown in Table 1 and thermodynamic parameters for the $ap \rightleftharpoons \pm sc$ processes in Table 2, where the populations of the ±*sc* form were divided by 2 in comparing the *ap* and the *sc* to accommodate the fact that the latter contains two degenerate positions.

The data in Table 1 are rather striking. Clearly the population of the *sc* form increases as the 4-substituent becomes more electron-withdrawing. Namely, the low electron-density on the 1-methoxy-oxygen favors the *sc* form. The changes in enthalpy and entropy were examined to find the possible cause for this phenomenon, but, as are shown in Table 2, rather small *r* values preclude any clear-cut conclusion

Table 1. Populations and Population Ratios of Rotamers of 4-Substituted 9-Ethyl-1-methoxytriptycenes at ca. −40 °C in $CDCl_3$

4-Substituent	σ Value of 4-Substituent	±*sc*/%	*sc*/*ap*[a]	Temp/°C
CH_3O	−0.268	37.7±0.7	0.302	−39.4
H	0.000	40.5±0.7	0.340	−39.4
NO_2	0.778	41.7±0.6	0.358	−39.5

a) The population of the *sc* form is taken as a half of the observed.

Table 2. Thermodynamic Parameters for the *ap*⇌±*sc* Processes in 4-Substituted 9-Ethyl-1-methoxytriptycenes

4-Substituent	ΔH°/kcal mol^{-1} [a]	ΔS°/e.u.[b]	r[c]
CH_3O	0.13±0.05	−1.8±0.2	0.998
H	0.43±0.09	−0.3±0.4	0.994
NO_2	0.18±0.44	−1.3±1.8	0.931

a) 1 cal=4.184 J. b) 1 e.u.=4.184 J mol^{-1} K^{-1}. c) Correlation coefficient in the statistical treatment.

Table 3. Populations and Population Ratios of Rotamers of 9-(Substituted Phenoxymethyl)-1,4-dimethyltriptycenes in $CDCl_3$ at ca. −50 °C

Substituent	σ Value of Substituent	±*sc*/%	*sc*/*ap*[a]	Temp/°C
4-$(CH_3)_2N$	−0.600	36.6±0.1	0.289	−49.7
4-CH_3O	−0.268	32.6±1.0	0.242	−49.6
H	0.000	30.9±0.8	0.224	−49.4
4-NO_2	0.778	27.6±1.4	0.191	−49.6
3,4-$(NO_2)_2$	1.385[b]	24.8±1.3	0.165	−49.2

a) The population of the *sc* forms was divided by 2. b) The sigma value obtained from the dissociation constant of 3,4-dinitrobenzoic acid.[20]

Table 4. Thermodynamic Parameters for the *ap*⇌±*sc* Processes in 9-(Substituted Phenoxymethyl)-1,4-dimethyltriptycenes

Substituent	ΔH°/kcal mol^{-1}	ΔS°/e.u.	r[a]
4-$(CH_3)_2N$	0.58±0.11	−0.2±0.4	0.996
4-CH_3O	0.51±0.08	−0.6±0.3	0.997
H	0.73±0.23	0.3±0.9	0.989
4-NO_2	1.19±0.06	1.7±0.3	0.999

a) Correlation coefficient in the statistical treatment.

from the data. At least, however, the results imply that there are no abrupt abnormalities associated with the change in the 4-substituent. We may discuss the results in Table 1 by taking advantage of the factors which affect the populations of rotamers.

It is unlikely that the polarity of a molecule examined here changes according to the rotameric positions taken by the substituent, because the ethyl group is the only one which rotates: The methoxyl group(s) is expected to take a coplanar position with the benzene ring[17] with the methyl group away from the 9- or 10-carbon because of the steric effect. We may neglect that Coulombic interactions comprise a main factor which controls the populations of rotamers, because rotation of the ethyl group does not cause appreciable change in dipole–dipole interactions. Charge-transfer interactions between the methyl and the methoxy-oxygen cannot be the main factor either, because if it were the case, the *sc* form should be favored when the electron density on the methoxyl group is high. Dispersion forces are known to be proportional to polarizability and to ionization potential:[18] Whereas the former increases when the electron density of the methoxy-oxygen is high, the latter decreases under the circumstance. Thus dispersion forces should not play an important role here (vide infra).

Then the important factor seems to be the van der Waals repulsion. As the electron density on the 1-methoxy-oxygen becomes high, the effective bulkiness of the group increases, thus increasing the steric repulsion between the groups concerned. It is concluded that the repulsive forces rather than attractive forces are decisive in this case.

The opposite trend seen in the populations in 4-substituted 9-ethyl-1-methoxytriptycenes to that expected for the charge-transfer interactions between the methyl group of the 9-ethyl and the oxygen atom of the 1-methoxyl group prompted us to investigate another series of compounds. The idea was that the acidity of the methyl group in an ethyl may be too low to show significant interactions with the oxygen atom. Since the pK_a value of ethane is known to be much higher than toluene,[19] changing the methyl group from that in an ethyl to that in a toluene derivative should give better chances to observe the presence of the CH_3...O hydrogen bond. Thus we shifted to 9-(substituted phenoxymethyl)-1,4-dimethyltriptycenes.

9-(Substituted Phenoxymethyl)-1,4-dimethyltriptycenes (15—18 and 20). The data of populations and the thermodynamic parameters for the process *ap* ⇌ *sc* are given in Tables 3 and 4, respectively.

The data in Table 3 clearly show that the populations of the *sc* form increase as the electron density on the aryloxy-oxygen increases. The Hammett plot (Fig. 1) gives a fairly good linearity, the *r* factor being 0.983. The ρ value is −0.114, which is very small if we compare the value with normal reactions that take place at the α-position of the aryl group.[21] Close examination of the straight line reveals that the line does not pass the point for the unsubstituted compound and the plots form a concave curve. This together with the small ρ value will mean that the observed populations base on a delicate balance of attraction and repulsion, because if attractive force is enhanced by virtue of the high electron-density, the

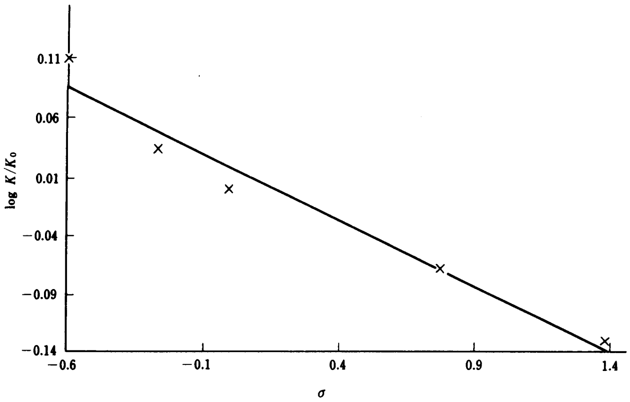


Fig. 1. The Hammett plot for the equilibrium constants of rotamers of 9-(aryloxymethyl)-1,4-dimethyltriptycenes.

same factor simultaneorsly enhances the repulsive forces.

The plot of log K vs. $1/T$ in this case affords better r factors than the case of 4-substituted 9-ethyl-1-methoxytriptycenes and shows the trend that the *sc* forms are more stabilized relative to the *ap* form as the electron-density on the aryloxy-oxygen becomes high. The data are again in conformity with the presence of attractive interactions between the 1-methyl group and the aryloxy-oxygen atom.

The above discussion all favors the presence of charge-transfer type interactions that stabilize the *sc* conformations. However, it may be better to confirm that we can reject possibilities that might favor the same conformation other than charge transfer. Steric repulsion may be excluded from the possibility, because, if it were the case, the *sc* forms in the compounds with an electron-rich oxygen should be disfavored because the high electron-density means the bulky oxygen atom. Coulombic interactions cannot be the main factor which controls the populations, because the only polar part of the molecule is the aryloxy group, that should not give much different electric interactions in different rotameric positions due to the fact that the other parts of the molecules are all hydrocarbons.

High electron density should enhance the polarizability of the oxygen atom and should lower the ionization potential. Since absolute values of these two factors are unknown, it is hard to exclude dispersion forces from the possibility of being a main factor which favors the *sc* conformation. However, since dispersion forces are inversely proportional to the sixth power of the distance concerned, enhanced dispersion forces must be more effective in the *sc* form than the *ap*. This should stabilize the *sc* form even in the 4-substituted 9-ethyl-1-methoxytriptycene series when the electron density of the methoxy-oxygen is high. Since the observed trend is just the opposite to the expectation from the dispersion forces in the said series, we conclude that the dispersion forces cannot be the main factor which controls the populations of the rotamers in the triptycenes. The results imply that, at least in triptycene series, when we compare the population ratios in a series of compounds, the effect of the dispersion forces may be disregarded from the main factor.

From the above results and discussion, we claim that we have observed the presence of $CH_3\cdots O$ hydrogen bond in the series of 9-(substituted phenoxymethyl)-1,4-dimethyltriptycenes. 1,9-Disubstituted triptycenes will continue to be a very convenient system in which we can find very weak molecular interactions that are impossible to find due to severe repulsions in other systems.

Experimental

^{1}H NMR Measurements. ^{1}H NMR spectra were recorded with a Varian EM390 instrument which operated at 90 MHz or with a JEOL GX400 which operated at 400 MHz. The data described in this experimental section are those obtained at 90 MHz at room temperature unless otherwise mentioned.

The assignment of the peaks observed at low temperature were performed by taking advantage of the population ratios and the coalescence phenomena. We assumed that the chemical shift differences for the 4-methoxy or 4-methyl protons should be smaller than those for the 1-methoxy or 1-methyl protons due to the anisotropy effect of the 9-substituent in the *sc* form. Since temperature variation measurements were not done for compounds **18** and **20**, the assignments of the methyl protons in them are tentative especially for the *sc* form.

Determination of Populations of the Rotamers. The ^{1}H NMR spectra at low temperatures were obtained with the use of the 400 MHz NMR machine. The indicated temperatures were calibrated by a thermocouple. The NMR data at low temperatures are summarized in Tables 5 and 6. For the determination of populations, the integrated intensities were obtained by cutting the chart papers and weighing the paper several times. The peaks for the integration were selected so that the best separation of the signals was observed. Signals used for the determination were those due to methyl protons for compounds **15**—**18** and **20** and methylene protons for compounds **2**, **10**, and **11**. The equilibrium data at various temperatures are given in Tables 7 and 8.

9-Ethyl-1,4-dimethoxytriptycene (2). A solution of 0.61 g (3.0 mmol) of 9-ethylanthracene (**5**)[22] and 1.60 g (14.8 mmol) of *p*-benzoquinone in 10 mL of acetonitrile was refluxed for 1 h. After cooling, the adduct **6**, which precipitated, was collected by filtration and washed with ether to remove unreacted *p*-benzoquinone. The residue was dissolved in 20 mL of dioxane and was treated alternatively with a solution of sodium hydroxide (3.00 g) in 30 mL of water and 15 mL of dimethyl sulfate under a nitrogen atmosphere. The reaction mixture was poured into 300 mL of water and the precipitate was collected. The product was purified by recrystallization from dichloromethane–hexane, the yield being 0.71 g (70%). Mp 193.5—195.5 °C (lit,[12] 179—181 °C).

Table 5. ^{1}H NMR Data (δ) of 4-Substituted 9-Ethyl-1-methoxytriptycenes in CDCl$_3$ at ca. −39.4 °C at 400 MHz

Substituent	Form	CH$_2$(Et)	CH$_3$(Et)	1-CH$_3$O	Others
CH$_3$O	*ap*	3.42 (J=6.4 Hz)	1.50 (J=6.4 Hz)	3.76	3.70 (4-CH$_3$O)
	sc	2.82, 3.40 (J=14.4, 6.5 Hz)	1.63 (J=6.5 Hz)	3.82	3.74 (4-CH$_3$O)
H	*ap*	3.45 (J=7.1 Hz)	1.50 (J=7.1 Hz)	3.73	
	sc	2.85, 3.44 (J=14.4, 6.5 Hz)	1.64 (J=6.5 Hz)	3.77	
NO$_2$	*ap*	3.46 (J=7.5 Hz)	1.51 (J=7.5 Hz)	3.83	
	sc	2.88, 3.48 (J=14.7, 6.8 Hz)	1.59 (J=6.8 Hz)	3.88	

Table 6. ^{1}H NMR Data (δ) of 9-(Substituted Phenoxymethyl)-1,4-dimethyltriptycenes in CDCl$_3$ at ca. −49.6 °C at 400 MHz

Substituent	Form	9-CH$_2$	Aromatic-2,3	1-CH$_3$	4-CH$_3$
4-(CH$_3$)$_2$N[a]	*ap*	5.72	6.66, 6.74 (J=7.7 Hz)	2.67	2.51
	sc	5.35, 5.68 (J=9.7 Hz)	6.72, 6.81 (J=8.0 Hz)	2.53	2.52
4-CH$_3$O	*ap*	5.72	6.66, 6.75 (J=7.8 Hz)	2.67	2.51
	sc	5.35, 5.69 (J=10.4 Hz)	6.72, 6.81 (J=8.1 Hz)	2.54	2.50
H[b]	*ap*	5.77	6.66, 6.75 (J=7.6 Hz)	2.68	2.51
	sc	5.40, 5.74 (J=9.8 Hz)	6.72, 6.81 (J=8.1 Hz)	2.54	2.48
4-NO$_2$	*ap*	5.88	6.69, 6.78 (J=7.6 Hz)	2.69	2.52
	sc	5.53, 5.86 (10.3 Hz)	6.73, 6.83 (J=7.8 Hz)	2.41	2.56
3,4-(NO$_2$)$_2$[a]	*ap*	5.92	6.69, 6.78 (J=7.6 Hz)	2.41	2.56
	sc	5.57, 5.91 (J=10.2 Hz)	6.73, 6.85 (J=8.0 Hz)	2.39	2.56

a) Assignment uncertain for the 1- and 4-methyls. They may be reversed. b) At −39.6 °C.

Table 7. Temperature Dependence of the Equilibrium Constants of the Rotamers in 4-Substituted 9-Ethyl-1-methoxytriptycenes in CDCl$_3$

Substituent	*sc*/*ap* (Temp/°C)[a]		
CH$_3$O	0.302(−39.4)	0.307(−29.4)	0.310(−19.4)
H	0.340(−39.4)	0.357(−29.4)	0.373(−14.5)
	0.378(−9.5)		
NO$_2$	0.358(−39.5)	0.360(−29.5)	0.369(−19.5)

a) The observed population of the *sc* form was divided by 2 to compensate the degenerate positions of the *sc* form.

Table 8. Temperature Dependence of the Equilibrium Constants of the Rotamers in 9-(4-Substituted Phenoxymethyl)-1,4-dimethyltriptycenes in CDCl$_3$

Substituent	*sc*/*ap* (Temp/°C)[a]		
(CH$_3$)$_2$N	0.262(−39.5)	0.276(−29.4)	0.292(−19.5)
	0.301(−9.7)		
CH$_3$O	0.242(−49.6)	0.265(−29.7)	0.274(−19.7)
	0.294(−4.8)		
H	0.218(−49.4)	0.243(−39.6)	0.267(−19.7)
	0.283(−4.7)		
NO$_2$	0.164(−49.6)	0.182(−39.6)	0.203(−29.7)
	0.245(−9.8)		

a) The observed population of the *sc* form was divided by 2 to compensate the degeneracy of the + and −*sc* forms.

Found: C, 84.34; H, 6.18%. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48%. ^1H NMR ($CDCl_3$) δ=1.54 (3H, t, J=6.6 Hz), 2.8—3.5 (2H, br), 3.67 (3H, s), 3.76 (3H, s), 5.81 (1H, s), 6.45 (2H, s), 6.8—7.6 (8H, m).

10-Ethyl-4-methoxy-9-anthrone (8). To a solution of 5.00 g (22.3 mmol) of 4-methoxy-9-anthrone (**7**)[23] and 34 g (0.22 mol) of methyl iodide in 130 mL of methanol, was added a solution of 1.34 g (24 mmol) of potassium hydroxide in 30 mL of methanol in 2.5 h. After stirring for 15 h, the mixture was poured into water and extracted with dichloromethane. The extract was dried over magnesium sulfate and the solvent was evaporated. The residue was chromatographed on silica gel (hexane–dichloromethane eluent) to give 0.61 g (11%) of 10-ethoxy-1-methoxyanthracene and then 3.11 g (55%) of 10-ethyl-4-methoxy-9-anthrone (**8**). ^1H NMR ($CDCl_3$) δ=0.40 (3H, t, J=9.0 Hz), 2.0 (2H, m), 3.93 (3H, s), 4.57 (1H, t, J=6.0 Hz), 7.0—8.4 (8H, m). This compound was directly used for the synthesis of 9-ethyl-1-methoxyanthracene (**9**).

The following ^1H NMR data ($CDCl_3$, δ) were recorded for 10-ethoxy-1-methoxyanthracene: 1.59 (3H, t, J=6.0 Hz), 4.03 (3H, s), 4.21 (2H, q, J=6.0 Hz), 6.67 (1H, d, J=6.0 Hz), 7.1—8.4 (6H, m), 8.61 (1H, s).

9-Ethyl-1-methoxyanthracene (9). To a refluxing solution of 2.55 g (10.1 mmol) of 10-ethyl-4-methoxyanthrone (**8**) in 100 mL of ethanol, was added a solution of 3.82 g (101 mmol) of sodium tetrahydroborate in 100 mL of 10% aqueous ethanol in 1 h. After heating for further 1 h, ethanol was removed by distillation and the mixture was poured into water. The mixture was extracted with dichloromethane and the extract was dried over magnesium sulfate. The solvent was evaporated and the residue was taken up in 250 mL of carbon tetrachloride. The solution was refluxed with 50 g of phosphorus pentaoxide for 2 h. After cooling the supernatant liquid was decanted and evaporated to give 2.29 g (96%) of almost pure 9-ethyl-1-methoxyanthracene (**9**). ^1H NMR ($CDCl_3$) δ=1.49 (3H, t, J=7.5Hz), 3.86 (2H, q, J=7.5 Hz), 4.02 (3H, s), 6.75 (1H, d, J=7.8 Hz), 7.2—8.8 (6H, m), 8.26 (1H, s). This compound was directly used for the synthesis of 9-ethyl-1-methoxytriptycene (**10**).

9-Ethyl-1-methoxytriptycene (10). To a boiling solution of 2.29 g (9.7 mmol) of 9-ethyl-1-methoxyanthracene (**9**) in 40 mL of dichloromethane, were added a solution of 2.04 g (15.0 mmol) of anthranilic acid in 40 mL of acetone and 2.60 g (22.2 mmol) of isopentyl nitrite in 40 mL of dichloromethane, from two funnels, in 3 h. After refluxing for further 30 min, the solvent was removed by distillation and the residue was submitted to chromatography on silica gel (hexane–dichloromethane eluent). The pure compound was obtained in 2.37 g (78%) yield after recrystallization from dichloromethane–hexane, mp 185—186 °C. Found: C, 88.30; H, 6.18%. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45%. ^1H NMR ($CDCl_3$) δ=1.54 (3H, t, J=6.3 Hz), 2.9—3.5 (2H, m), 3.66 (3H, s), 5.22 (1H, s), 6.48 (1H, dd, J=2.2, 7.8 Hz), 6.7—7.7 (10H, m).

Nitration of 9-Ethyl-1-methoxytriptycene (10). To a solution of 1.90 g (6.1 mmol) of **10** in 30 mL of acetonitrile, was added 7.33 g (5.5 mmol) of saturated solution (ca. 10%) of nitronium tetrafluoroborate in acetonitrile at −30 °C. The completion of the nitration was checked by TLC, and a few drops of the saturated solution of nitronium tetrafluoroborate were added if unreacted materials were detected. The mixture was poured into 500 mL of water and the precipitate was collected by filtration. After drying, the product was submitted to chromatography on silica gel (hexane–dichloromethane eluent). The desired 4-nitro compound **11** was eluted first, the yield being 0.32 g (15%). After recrystallization from dichloromethane–hexane, the pure sample melted at 260—261 °C. Found: C, 77.25; H, 5.23; N, 3.89%. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92%. ^1H NMR ($CDCl_3$) δ=1.55 (3H, t, J=5.7 Hz), 3.0—3.6 (2H, br), 3.81 (3H, s), 6.52 (1H, s), 6.54 and 7.62 (2H, ABq, J=10.2 Hz), 6.8—7.2 (8H, m).

The 2-nitro compound **12** was obtained in 0.11 g (5%) yield. Recrystallization from tetrahydrofuran–hexane afforded the pure sample, mp 235—236.5 °C. Found C, 77.38; H, 5.29; N, 3.83%. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92%. ^1H NMR ($CDCl_3$) δ=1.55 (3H, t, J=6 Hz), 3.30 (2H, q, J=6 Hz), 3.74 (3H, s), 5.33 (1H, s), 6.8—7.7 (10H, m).

9-(Aryloxymethyl)anthracenes (14). The following is a typical procedure for the syntheses of a series of compounds. Phenols were available from commercial sources, except for 3,4-dinitrophenol which was prepared according to the published procedure.[24]

A mixture of 415.7 mg (1.834 mmol) of 9-(chloromethyl)-anthracene (**13**),[25] 228.6 mg (2.429 mmol) of phenol, and 0.37 g (2.7 mmol) of potassium carbonate and 30 mL of acetone were refluxed for 48 h. After cooling, the precipitate was removed by filtration and the filtrate was poured into water. The mixture was extracted with dichloromethane and the extract was washed with aqueous sodium hydroxide. 9-(Phenoxymethyl)anthracene was obtained almost quantitatively.

These compounds were used directly for the syntheses of the corresponding triptycenes.

The following ^1H NMR data ($CDCl_3$, δ) were recorded (only aryl groups given for compounds **14**). Phenyl: 5.97 (2H, s), 6.8—8.5 (13H, m), 8.53 (1H, s). *p*-Methoxyphenyl: 3.77 (3H, s), 5.87 (2H, s), 6.86 and 7.04 (2H, ABq, J=9 Hz), 7.3—8.4 (8H, m), 8.48 (1H, s). *p*-Nitrophenyl: 6.05 (2H, s), 7.1—8.5 (12H, m), 8.54 (1H, s). 3,4-Dinitrophenyl: 6.11 (2H, s), 7.3—8.4 (11H, m), 8.60 (1H, s).

9-(Aryloxymethyl)-1,4-dimethyltriptycenes (15—18). The following is the typical procedure for the syntheses of the triptycenes. The results and analytical data are given in Table 9.

To a refluxing solution of 0.30 g (1.0 mmol) of 9-[(4-methoxyphenoxy)methyl]anthracene in 20 mL of dichloromethane, were added 0.66 g (4.0 mmol) of 3,6-dimethylanthranilic acid[26] in 40 mL of acetone and 1.14 g (9.7 mmol) of isopentyl nitrite in 40 mL of dichloromethane, from separate funnels, in 2 h. The whole was heated for further 30 min and the solvents were removed by distillation. The residue was submitted to chromatography on alumina (hexane–dichloromethane eluent). The product was recrystallized from tetrahydrofuran–hexane.

The following ^1H NMR data ($CDCl_3$, δ) were recorded except for the 3,4-dinitro compound, which was too sparingly soluble (only aryl groups given for compounds **15—17**). Phenyl: 2.57 (3H, s), 2.50 (3H, s), 5.66 (1H, s), 5.2—5.9 (2H, br), 6.64 and 6.72 (2H, ABq, J=7.8 Hz), 6.8—7.8 (12H, m). *p*-Methoxyphenyl: 2.57 (3H, s), 2.50 (3H, s),

Table 9. Yields, Melting Points, and Analytical Data of 9-(Aryloxymethyl)-1,4-dimethyltriptycenes

Compd	Yield	Mp θ_m/°C	Found			Calcd		
			C	H	N	C	H	N
15	60	216—217	86.13	6.16	—	86.09	6.26	—
16	61	176—176.5	89.84	6.15	—	89.65	6.23	—
17	67	319—321	80.27	5.22	3.27	80.35	5.35	3.23
18	42	319	72.54	4.52	5.73	72.79	4.64	5.86

3.82 (3H, s), 5.63 (1H, s), 5.3—6.0 (2H, br), 6.63 and 6.72 (2H, ABq, J=7.8 Hz), 6.8—7.8 (12H, m). *p*-Nitrophenyl: 2.55 (3H, s), 2.51 (3H, s), 5.89 (1H, s), 5.4—6.1 (2H, br), 6.64 and 6.74 (2H, ABq, J=8.0 Hz), 6.9—7.7 (10H, m), 8.35 (2H, d, J=9.0 Hz).

1,4-Dimethyl-9-[4-(dimethylamino)phenoxymethyl]triptycene (20). A solution of 97.0 mg (0.224 mmol) of 9-(4-nitrophenoxymethyl)-1,4-dimethyltriptycene (**17**) in 20 mL of acetic acid was shaken under a hydrogen atmosphere in the presence of 19.5 mg of platinum oxide for 19 h. The catalyst was removed by filtration and the filtrate was diluted with water. The mixture was neutralized with sodium hydrogencarbonate and extracted with dichloromethane. Evaporation of the solvent gave the almost pure amino compound **19**. ^{1}H NMR (CDCl$_3$) δ=2.55 (3H, s), 2.48 (3H, s), 3.89 (2H, br), 5.60 (1H, s), 5.6 (2H, br), 6.4—7.6 (14H, m).

To a solution of the amine (89 mg or 0.22 mmol) in 15 mL of dichloromethane, was added 73.4 mg (0.447 mmol) of methyl triflate in 5 mL of dichloromethane at room temperature under a nitrogen atmosphere, until the spot due to the starting amine was not detected in TLC. Water was added and the pH of the aqueous layer was adjusted to 7.0. The organic layer afforded a product which was practically insoluble in chloroform. The product was heated with 67 mg of 2-aminoethanol at 200 °C for 5 min and then poured into water. The precipitate was collected and recrystallized from tetrahydrofuran–hexane, mp 242—244 °C. The yield was 0.05 g (50%). Found: C, 86.23; H, 6.80; N, 2.97%. Calcd for $C_{31}H_{29}NO$: C, 86.27; H, 6.77; N, 3.25%. ^{1}H NMR (CDCl$_3$) δ=2.50 (3H, s), 2.57 (3H, s), 2.94 (6H, s), 5.63 (1H, s), 5.3—5.9 (2H, br), 6.63 and 6.72 (2H, ABq, J=8.4 Hz), 6.8—7.8 (12H, m).

The 400 MHz ^{1}H NMR spectra at low temperatures were measured at Institute for Molecular Science. We wish to thank Dr. Shigeru Murata of the Institute for technical assistance in the measurement.

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