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Implications of Unusual Population Ratios in Rotational Isomers of 9-(4-Substituted Benzyl)-8,13-dichloro-1,4-dimethyltriptycenes and 4-Substituted 9-Benzyl-8,13-dichloro-1-methyltriptycenes: $CH_3\cdots\pi$ Hydrogen Bond[1)]

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Population ratios of rotational isomers in substituted 9-benzyl-8,13-dichloro-1-methyltriptycenes were examined by equilibration in solution. The *sc* isomers increase in their populations as the electron density on the 9-benzyl group increases and the acidity of the 1-methyl group increases. The *sc*/*ap* ratios were larger than 2, the statistical value, in all the compounds examined, except the 4-nitrobenzyl compound. By contrast, MM2 calculations show that the *sc* isomers are less stable than the *ap* by ca. 1 kcal mol^{-1}. This discrepancy together with the substitutent effects on populations of the rotamers are attributed to the presence of $CH_3\cdots\pi$ interactions in the *sc* forms that stabilize the system mainly by charge-transfer interactions but are not included in the MM2 calculations.

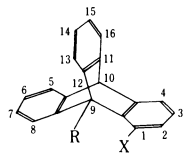
Since the π-systems act as base, though weak,[2)] it is possible to observe the presence of OH–π hydrogen bond[3)] and NH–π hydrogen bond.[4)] Because of the weakness of the basicity of the π-system, the proton donor must be rather strong to manifest the XH–π hydrogen bond. Since the CH group is a weak electron-acceptor, the CH–π interactions are seldom observed unless the C–H group is a strong acid: the presence of the interactions between the acetylenic CH group and π-systems has been reported.[5)]

Although the presence of hydrogen bond involving the CH group as an electron acceptor has been reported in various cases,[6)] evidence for the presence is often not decisive: in many cases, if a C–H group and an electron donor are placed within the sum of their van der Waals radii in crystals, the result is taken to imply the presence of the hydrogen bond.[7)] In solution, the situation is more complicated than in the solid, because there is no means to determine the distance between the two groups concerned.

Hirota and Nishio have worked for a long time in this area. Once they believed that the unusual population ratios of rotamers in 1-alkyl-2-arylethane derivatives were the indication of the presence of the CH–π interactions but later they interpreted the results by dispersion forces because MM2 calculations could reproduce the population ratios of those compounds.[8)] Although they recently reported that they observed the CD–π hydrogen bond in 2-methyl-4-phenyl-3-pentanone-2*d* by infrared spectroscopy, their experimental results are so unusual from the normal sense of hydrogen bond that it is not possible to take the results as firm evidence for the presence of the CH–π hydrogen bond: the C–D stretching absorption due to the hydrogen-bonded form appears at a higher frequency than the non-hydrogen-bonded C–D stretching and the hydrogen-bonded form is less stable than the non-hydrogen-bonded form.[9)] However, the CH–π hydrogen bond is theoretically possible, though weak.[10,11)]

It is understood that, because of the very weak nature of the CH–π hydrogen bond, if after all present, strong evidence for the presence of the CH–π hydrogen bond is difficult to obtain. The N–H stretching absorption is known not to be affected by the NH–π hydrogen bond.[12)] The CH–π hydrogen bond, being still weaker than the NH–π, is expected to not affect the C–H stretching absorption, though it is possible that the C–H stretching appears at a higher frequency than the normal C–H stretching because of the congestion.[13)] Although appearance of abnormal population ratios of rotational isomers can be taken as evidence for the presence of attractive interactions, like the *sc* isomers of 1,2-ethanedithiol,[14)] this kind of effect is manifested only when the attractive interaction is stronger than repulsive interactions in the very conformation. Because of the weak nature of the CH–π interaction, the interaction may not overcome the repulsive van der Waals interactions in a given conformer in which the CH–π interaction is possible. To observe enhanced populations due to weak CH–π interactions, we must design a system in which the van der Waals repulsion can be eliminated or balanced in various conformations.

It is not possible, of course, to construct such a system, but it is possible to construct a system that nearly conforms to the conditions mentioned above. That is the 1,9-disubstituted triptycenes (**1**). In this



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system, the atoms beta to the C_9 in the 9-substituent is placed unusually closely to the 1-substituent. X-Ray

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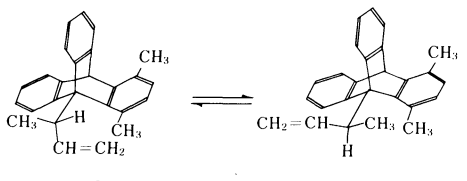
crystallographic data reveal that the distance is ca. 3.0 Å,[15] which is well within the sum of the van der Waals radii of the two groups concerned. If the 9-substituent is a primary alkyl group, it can rotate to assume another conformation, in which the atom beta to the 9-position is *ap* to the 1-substituent, when the distance between the substituent and the peri-carbon (8 or 13) is ca. 3.2 Å,[16] which is again within the sum of the van der Waals radii of the groups concerned. Although it is true that the distance between the two groups in the *ap* position is indeed a little longer than that in the *sc*[17] and the van der Waals replusion is more severe in the *sc* conformation than in the *ap*, yet it is also true that even in the *ap* conformation the van der Waals repulsion is severe, even though we neglect the presence of a hydrogen atom attached to the peri-carbon. Thus in this system, it can be expected that the severe van der Waals repulsion in the *sc* form is nearly equalled by that in the *ap*. Thus a weak interaction may be observed in this system as the unusual population ratios: that is, the *sc* form may be favored irrespective of the fact that sterically it is less favored.

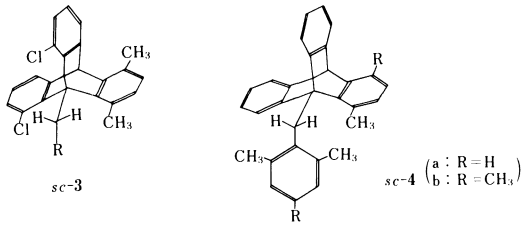
The reason why we could report the presence of weak molecular interactions by taking advantage of this system is indeed the feature of the structures mentioned above. It was possible to detect charge-transfer interactions between a methoxy-oxygen and benzene rings that do not carry electronegative groups,[18] those between a chloro or a methoxy-oxygen and a carbonyl group,[19] those between a methoxy-oxygen and a CH_2X group where the X is an electronegative group,[20] and $CH_3\cdots O$ hydrogen bond.[21] It is quite natural to expect that the system could be useful in manifesting the CH–π interactions.

We have had several experiences that might be explained by the presence of the $CH_3\cdots\pi$ interactions in the 1,9-disubstituted triptycenes. In 1,4-dimethyl-9-(1-methyl-2-propenyl)triptycene (**2**), the population ratio, *sc*/*ap*, of the rotamers is 1.52, whereas the ratio is ca. 0.8 when the 1-substituent of comound **2** is switched to a chloro, a bromo, or a methoxyl.[22] We have pointed out a possibility that the results might imply the presence of the CH–π hydrogen bond, although it is possible to argue that the unusual population could be caused by the bulkiness of the methyl group in the 9-substituent.



sc-2 *ap*-2

In 9-substituted 8,13-dichloro-1,4-dimethyltriptycenes (**3**), the *sc*/*ap* value is 2.0 or more if the 9-substituent carries a π-system beta to the 9-position, but it becomes 0.75 when the beta-substituent is a methyl.[23] Although it is possible again to argue that the results can be attributed to the steric repulsion due to the fact that a methyl is larger than a chloro and than a π-system, it is possible also to assume that the results are the indication that the *sc* conformation is stabilized by the presence of the CH–π interactions. Although the charge-transfer interaction between the chloro group and the π^*-system of the substituent may be claimed to be the cause, this interaction should favor the *ap* conformation rather than the *sc*.



sc-3 *sc*-4 (a : R=H, b : R=CH_3)

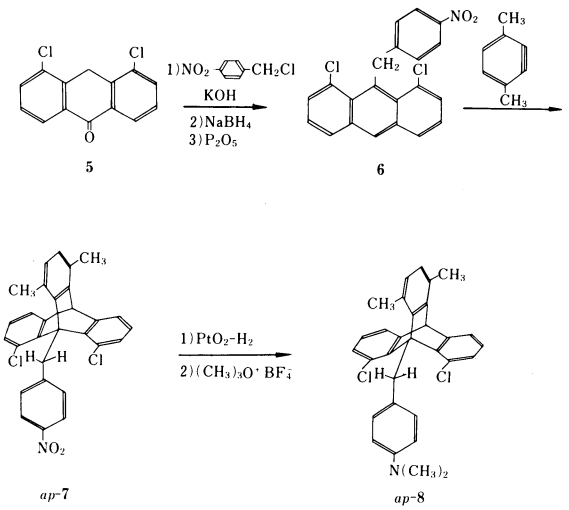
Another encouraging factor for the assumption of the presence of the CH–π interactions in this system is the failure of an empirical force field calculation in predicting the correct relative stability of the *sc* and the *ap* rotamers of 9-benzyl-1-methyltriptycene derivatives (**4**). Mislow and his co-workers calculated the stability by the empirical method to find that the *ap* conformer of 1-methyl-9-(2,6-dimethylbenzyl)triptycene (**4a**) is more stable than the *sc* form by 0.6 kcal mol^{-1} (1 cal=4.184 J). The experiment on the conformers of 1,4-dimethyl-9-(2,4,6-trimethylbenzyl)triptycene (**4b**) shows, in contrast, that the *sc* isomer is more stable than the *ap* by 0.8 kcal mol^{-1} or more.[24] The discrepancy may be taken as that the calculation is not reliable in this kind of congested molecules, but our experiences show that the calculations give correct tendency, though the value itself may not be correct.[25] It may indicate the presence of the CH–π interactions, because this type of charge-transfer interactions are not taken carè of by the empirical calculations. We have thus felt that the assumption that the CH–π interactions are observed in this system is worthwhile to examine. This paper reports the results of such an examination.

We have selected the system of 9-benzyl-8,13-dichloro-1-methyltriptycenes for two reasons. One is that the system gives stable rotational isomers that can be separated at room temperature.[23] The advantage of this system is that we can equilibrate the rotational isomers by the classical method which is believed to afford reliable data. The other is that the chloro and the methyl groups are similar in size. This should give similar steric circumstances for both the *sc* and *ap* rotamers and the cancellation of the van der Waals repulsion in both rotamers is better than the case where there are no substituents in the 8,13-positions. The system involves two series of compounds: one is 9-(4-substituted benzyl)-1,4-dimethyltriptycenes which

provide a variety of electron densities in the benzyl group and the other is 4-substituted 9-benzyl-1-methyltriptycenes which provide a variety of acidities of the 1-methyl group.

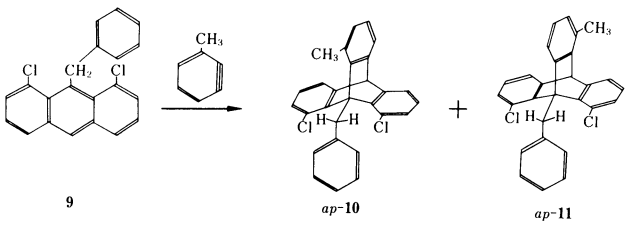
Syntheses

The method of synthesis of 1,4-dimethyl-9-(4-nitrobenzyl)triptycene (**7**) is essentially the same with that of the unsubstituted compound that has been published.[23] 4,5-Dichloro-9-anthrone (**5**) was treated with *p*-nitrobenzyl chloride and aqueous potassium hydroxide and the product was reduced with sodium tetrahydroborate and then dehydrated in the presence of phosphorus pentaoxide to afford 1,8-dichloro-9-(4-nitrobenzyl)anthracene (**6**). Treatment of the anthracene (**6**) with 3,6-dimethylbenzyne which was produced in situ from 3,6-dimethylanthranilic acid gave 8,13-dichloro-1,4-dimethyl-9-(4-nitrobenzyl)triptycene (**7**). Hydrogenation of the triptycene (**7**) in the presence of platinum oxide followed by methylation afforded 8,13-dichloro-9-[4-(dimethylamino)benzyl]-1,4-dimethyltriptycene (**8**).



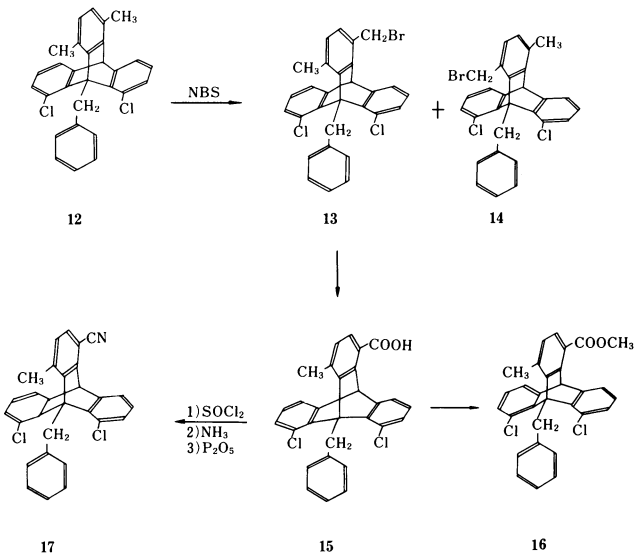
5 6 *ap*-7 *ap*-8

Similarly 9-benzyl-1,8-dichloroanthracene (**9**) was treated with 3-methylbenzyne which was generated from 3-methylanthranilic acid to afford a mixture of 9-benzyl-8,13-dichloro-1-methyltriptycene (**10**) and its 4-methyl isomer (**11**). The assignment of the structures of **10** and **11** bases on the ^{1}H NMR data: the chemical shift of the methyl protons in the *sc* form of **10** is higher than that of **11** due to the ring current effect of the benzyl-benzene ring.



9 *ap*-10 *ap*-11

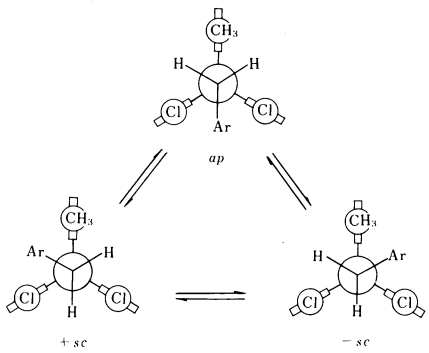
Treatment of 9-benzyl-8,13-dichloro-1,4-dimethyltriptycene (**12**) with *N*-bromosuccinimide afforded 9-benzyl-4-bromomethyl-8,13-dichloro-1-methyltriptycene (**13**) and 9-benzyl-1-bromomethyl-8,13-dichloro-1-methyltriptycene (**14**) together with other products. The identification of **13** and **14** was carried out again with the use of the chemical shift data of the methyl and the bromomethyl protons in ^{1}H NMR spectra that reflected the anisotropy effect of the benzyl-benzene ring. The 4-bromomethyl compound (**13**) was hydrolyzed and then oxidized with the Jones reagent to afford 9-benzyl-8,13-dichloro-4-carboxy-1-methyltriptycene (**15**). Compound **15** was methylated to give the methyl ester (**16**). Treatment of compound **15** with thionyl chloride followed by that with ammonia and then phosphorus pentaoxide afforded the corresponding nitrile (**17**).



12 13 14 17 15 16

Results and Discussion

The isomerization was carried out by heating solutions of the compounds in chloroform-*d* unless otherwise mentioned. The assignment of the conformations was performed by observing the singlet signal for the *ap* form and the AB quartet for the *sc* form in



Scheme 1. Rotational circuit.

the ^{1}H NMR spectra of the benzylic methylene protons as is clearly understood from the Newman-type projection in Scheme 1.

Although only one isomer was isolated by chromatography, the identity of the other isomer was confirmed by equilibration as well as their ^{1}H NMR spectra. The populations of isomers were estimated by the ^{1}H NMR spectra at 270 MHz. The equilibration data at 54 °C for the rotamers of the compounds in question are compiled in Tables 1 and 2 together with some relevant data.

In principle, the populations of one isomer can increase, if the rotamer is stabilized by an attractive interaction, or if other isomers are destabilized by a repulsive interaction or by structural deformation of the molecule. Although it is difficult to diagnose which is the case in general, the rotational barrier will give a clue for the diagnosis in this case because the transition state energy for rotation in the series of compounds can be assumed little different, if we take molecular interactions in the transition state only. Thus we decided to compare the barrier to rotation in the nitro compound (**7**) with that in the unsubstituted (**12**).[23] The kinetic data for the isomerization of the nitro compound (**7**) are compiled in Table 3.

The rate constants for isomerization, *sc*→*ap*, are ca. 1.7 times larger for the unsubstituted compound (**12**) than the nitro (**7**), whereas those for the *ap*→*sc* process are ca. 2.5 times faster for the former than the latter. Although *ap*-**7** isomerizes more sluggishly than *ap*-**12**, the tendency is also true for the *sc* conformer. The results may be interpreted to mean that the *sc* form of the nitro compound (**7**) is not specially destabilized, though its population decreases relatively from the unsusbstituted compound (**12**). We assume, therefore, that the population change in the series of compounds is mainly caused by repulsive and attractive interactions within the molecules without significant structural changes.

The main attractive forces and repulsive forces that may affect the populations of rotamers are van der Waals attractive force (dispersion force), charge-transfer interactions, van der Waals repulsions, and Coulombic interactions, both attractive and repulsive.

The data in Table 1 clearly indicate that, as the electron density on the benzyl-benzene ring increases, the *sc* form becomes favored. The results cannot be explained by the van der Waals repulsion because the high electron density on the benzyl-benzene means the bulkier π-system than the low electron-density one and

Table 1. Equilibrium Constants of the Rotational Isomers in 9-(4-Substituted benzyl)-8,13-dichloro-1,4-dimethyltriptycenes at 54.0 °C in $CDCl_3$ and Electron Densities on the Benzyl-Benzene Ring

Compd	Subst	K ($\pm sc/ap$)	Electron density[a]
8	$N(CH_3)_2$	2.87±0.10	−0.0370
12	H	2.30±0.04	0.0
7	NO_2	1.52±0.04	0.0714

a) π-Electron density at the 4-position as calculated by the CNDO method for monosubstituted benzenes.[26]

Table 2. Equilibrium Constants of the Rotational Isomers in 4-Substituted 9-Benzyl-8,13-dichloro-1-methyltriptycenes in $CDCl_3$ at 54.0 °C and Substituent Constants

Compd	Subst	K ($\pm sc/ap$)	Substituent constant (para)[27]
12	CH_3	2.30±0.04	−0.129
10	H	2.22±0.06	0.00
16	$COOCH_3$	4.09±0.16	0.385
17	CN	3.42±0.14	0.674

Table 3. Kinetic Data for the Isomerization of Rotamers in 8,13-Dichloro-1,4-dimethyl-9-(4-nitrobenzyl)triptycene in $CDCl_3$[a]

Temperature/°C	$k_{-1}/10^{-5}$ s^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1}	K ($\pm sc/ap$)
69.0	22.9	25.8	1.66
62.0	10.8	25.8	1.63
54.0	4.38	25.7	1.53
49.0	2.44	25.7	1.43

a) $ap \underset{k_{-1}}{\overset{2k_1}{\rightleftharpoons}} sc$ $\quad K=2k_1/k_{-1}$

$\Delta H^{\ddagger} = 23.8 \pm 1.2$ kcal mol^{-1}

$\Delta S^{\ddagger} = -5.8 \pm 3.7$ cal mol^{-1} K^{-1}

the methyl group is larger than the chloro group. In consideration of the Coulombic interactions, we may consider the bond dipoles of the C–Cl and the substituted benzene rings, because other parts of the molecule are hydrocarbons. Since the distance between the C–Cl bonds and the substituted benzyl-benzene rings are different in the *sc* form from those in the *ap*, the Coulombic interactions may change in one isomer from the other. However, to the first approximation, we neglect the difference, because the directions of the dipole of the substituted benzenes, 60° or 120°, relative to the C–Cl bonds do not change irrespective of the kind of rotamers. The dispersion force may be neglected to the first approximation from being the main factor that manifests the observed rotamer ratios, because the dispersion force is dependent on the polarizability and the ionization potential:[28] the high electron density means the high polarizability as well as the low ionization potential. In addition, we are comparing the rotamer distributions in a series of compounds: the comparison may cancel the change in the dispersion force. Thus the charge-transfer interactions between the CH_3 group and the π-system remain as a strong candidate that favors the *sc* conformation over the *ap*. However, it is possible to argue that, since the charge-transfer interaction[18] between the chloro group and the π^*-system of the benzyl group is expected to be stronger in the *ap* conformation than in the *sc*, especially in the case with electronegative substituents, the results are attributed to this type of charge-transfer. The argument cannot be ruled out by the data in Table 1.

The data in Table 2 suggest that, by and large, the *sc/ap* value increases as the 4-substituent becomes electronegative. Since the bulkiness of the 1-methyl group will not substantially change irrespective to the change in the electron density at the 1-position, the results cannot be explained by the van der Waals repulsions. Van der Waals attraction may also be neglected as a main factor that favors the *sc* form because the change in the force may again be small. The Coulombic interactions cannot be the factor that mainly controls the rotamer populations in this case because the dipole introduced by the 4-substituent must contribute equally to both the *sc* and *ap* rotamers. The results as well exclude the possibility that the charge-transfer interaction between the chloro substituent and the π^*-system is the main cause for the observed population ratios: if it were the case, the 4-substituent should affect the population ratios little. Thus the results strongly support the claim that we have observed the presence of the $CH_3\cdots\pi$ interactions.

Although the general trend that, as the acidity of the 1-methyl group becomes high, the *sc* form becomes favored relative to the *ap* form is apparent, close examination reveals some irregularities: the *K* value for the 4-methyl compound (**12**) is larger than that for the unsubstituted compound (**10**) and the *K* value for the 4-cyano compound (**17**) is smaller than that for the 4-methoxycarbonyl compound (**16**), even though the 4-methyl group increases the electron density on the 1-methyl group more than the 4-hydrogen and a cyano group is more electron-attracting than a methoxycarbonyl. We suspected that a small difference in dipole moments of the rotamers involved might be responsible to the irregular trend in the population ratios.

MM2 calculations show that the dipole moments of the rotamers of 9-benzyl-8,13-dichloro-1,4-dimethyltriptycene are indeed different, though the difference is small: *sc* 3.231 D and *ap* 3.157 D (1 D=3.3356×10^{-30} C m). Introduction of a substituent instead of the methyl at the 4-position will change the difference in the dipole moments of the rotamers. Thus we examined the solvent effect on the rotamer populations. The *sc/ap* values in dimethyl-d_6 sulfoxide were obtained as follows at 54.0 °C: 4-CH_3 2.0, 4-H 1.8, 4-CH_3OCO 3.0, 4-CN 2.4. Thus the *K* values all decrease in dimethyl sulfoxide relative to the value in chloroform and the irregular tendency is repeated. Thus at least dipole moments of the molecules are not the factors that cause the irregularities. Although further study is needed to clarify the point, the irregularities must be caused by the factors we have neglected in the discussion.

The total steric energies of the 4-substituted 9-benzyl-8,13-dichloro-1-methyltriptycenes as calculated by the MM2 method are shown in Table 4. The interesting point here is the fact that the *ap* forms of the series of comounds are ca. 1.0 kcal mol^{-1} more stable than the corresponding *sc* forms by calculations, irrespective of the kind of substituents, in sharp contrast to the experimental observation that the *sc* forms are more favored than the statistical value. From our experience in MM2 calculations, we under-

Table 4. Total Steric Energies of 4-Substituted 9-Benzyl-8,13-dichloro-1-methyltriptycene Rotamers as Calculated by MM2 Method

Compd	Subst	*ap*/kcal mol^{-1}	*sc*/kcal mol^{-1}	ΔE/kcal mol^{-1}
12	CH_3	28.462	29.539	1.077
10	H	28.208	29.216	1.008
16	$COCH_3$[a]	37.275	38.259	0.984
17	CN	27.397	28.445	1.052

a) This substituent was used instead of the methoxycarbonyl group, because the parameters for the latter were not available.

stand that the absolute values obtained by the method may not be reliable in the series of congested triptycenes, even for the ground states. However, it is also true that the relative values and the tendency of the stability of the ground state molecules are reproducible by the MM2 calculations.[25] Therefore, we believe the discrepancy between the MM2 calculations and the experimental results is significant. Since MM2 calculations take care of dispersion forces and the dipole interactions, the discrepancy must be attributed to the forces other than those mentioned. Thus the charge-transfer interactions are the most likely factor that stabilizes the *sc* form.

We conclude that the *sc* form of the triptycenes described in this paper is stabilized by the $CH_3\cdots\pi$ interactions. Although the $CH\cdots\pi$ interactions are known to be very weak by theoretical studies,[10,11] there are two points that render the observation of the presence of the $CH_3\cdots\pi$ interactions possible. They are the proximity of the two groups concerned that makes overlap of the orbitals concerned more effective than the normal cases and the near-cancellation of the repulsive forces in the triptycene rotamers due to the highly congested state in both rotamers. The unusual population ratios described in the introduction of this paper is now believed to include the contribution of this type of interactions at least to some extent. Although observation of normal hydrogen bonding is resulted by various factors including dipole interactions, charge transfer, and repulsive interactions, the contribution of dipole moment is rather small in the case of C–H bonds.[11] Thus the results presented in this paper can be the basis that there is the $CH_3\cdots\pi$ hydrogen bond in which charge transfer is the main stabilizing factor.

Experimental

Kinetics of Isomerization. The 4-nitrobenzyl compound (**7**) (*sc* or nearly pure *ap*) was dissolved in chloroform-*d* to make up ca. 1% (w/v) solutions. The kinetic data were obtained as described previously.[29] The analyses of the starting material and the product were performed by using a Waters HPLC apparatus (microporasil and hexane) equipped with a UV detector, *p*-nitrotoluene being used as an internal standard. The data were processed by assuming a reversible first order reaction.

Equilibration of Rotamers. The triptycenes were dissolved in either chloroform-*d* or dimethyl-d_6 sulfoxide to make up ca. 1% (w/v) solutions. The solution was sealed in an NMR sample tube and was heated by immersing into a boiling acetone bath. The populations of the rotamers were determined by integration of the methyl signals, of which assignment was confirmed by consulting the intensities of the signals due to benzylic methylene protons, in ^{1}H NMR spectra recorded on a JEOL GX270 spectrometer which operated at 270 MHz. The integration was carried out for several times and the data were treated statistically.

MM2 Calculations. The calculations were carried out with the use of an available program[30] by a HITAC M-280H computer at the Computer Center of the University of Tokyo. The parameters used for the chloro substituents were those reported from this laboratory some time ago.[31] Structural features of 1,9-disubstituted triptycenes, such as sharpening of the pyramid of which apex is C_9 with a base made up by C_{9a}–C_{8a}–C_{12} and widening of the dihedral angle that is made by two benzeno bridges flanking the beta atom of the 9-substituent (a phenyl in the cases described here), were reproducible.

4,5-Dichloro-10-(4-nitrobenzyl)anthrone. To a boiling solution of 3.29 g (12.5 mol) of 4,5-dichloroanthrone (**5**)[32] and 2.14 g (12.5 mmol) of *p*-nitrobenzyl chloride in 100 mL of methanol, was added 1.0 g (ca. 15 mmol) of potassium hydroxide (ca. 85% pure) in 40 mL of methanol in 2 h under a nitrogen atmosphere. The reaction mixture was allowed to cool with stirring and the precipitate was removed by filtration. The solvent was evaporated from the filtrate and the residue was recrystallized from tetrahydrofuran–methanol to afford pale yellow crystals, mp 200—201 °C, in 4.05 g (81%) yield. Found: C, 63.25; H, 3.30; N, 3.60; Cl, 17.33%. Calcd for $C_{21}H_{13}Cl_2NO_3$: C, 63.34; H, 3.29; N, 3.52; Cl, 17.80%. ^{1}H NMR ($CDCl_3$) δ=3.49 (2H, d, J=4.5 Hz), 5.41 (1H, t, J=4.5 Hz), 6.18 (2H, d, J=8.6 Hz), 7.2—8.0 (8H, m).

1,8-Dichloro-9-(4-nitrobenzyl)anthracene (6). To a solution of 5.58 g (14.0 mmol) of the foregoing anthrone in 200 mL of methanol, was added 3.0 g (79 mmol) of sodium tetrahydroborate in 3 portions with 10 min intervals. The mixture was stirred for further 10 min and the solvent was evaporated. The residue was treated with water and extracted with chloroform. The extract was dried over magnesium sulfate and the solvent was evaporated to give oily 4,5-dichloro-10-(4-nitrobenzyl)-9-anthranol which was apparently one isomer of the possible two according to the ^{1}H NMR spectrum ($CDCl_3$): δ=2.49 (1H, d, J=10.2 Hz), 3.21 (2H, d, J=5.6 Hz), 4.43 (1H, d, J=10.2 Hz), 5.18 (1H, t, J=5.6 Hz), 6.59 (2H, d, J=8.9 Hz), 7.1—7.6 (6H, m), 7.81 (2H, d, J=8.9 Hz).

The anthranol in 100 mL of carbon tetrachloride was heated with 15 g of phosphorus pentaoxide for 15 min. The solid was removed by filtration and was washed with hot carbon tetrachloride. The combined carbon tetrachloride solution was evaporated and the residue was submitted to silica-gel chromatography (hexane–dichloromethane eluent) to yield 1.23 g (23%) of the desired product which was purified by recrysallization from dichloromethane–hexane. Bright yellow crystals, mp 184—185 °C. Found: C, 66.14; H, 3.66; N, 3.73; Cl, 18.50%. Calcd for $C_{21}H_{13}Cl_2NO_2$: C, 65.59; H, 3.43; N, 3.66; Cl, 18.55%. ^{1}H NMR ($CDCl_3$) δ=5.71 (2H, s), 6.8—8.0 (10H, m), 8.45 (1H, s).

8,13-Dichloro-1,4-dimethyl-9-(4-nitrobenzyl)triptycene (7). To a boiling solution of 2.38 g (6.23 mmol) of the anthracene (**6**) and 6.0 mL (45 mmol) of isopentyl nitrite in 150 mL of dichloromethane were simultaneously added a solution of 3.00 g (18.2 mmol) of 3,6-dimethylanthranilic acid[33] in 80 mL of dichloromethane and that of 3.0 mL (22 mmol) of isopentyl nitrite in 20 mL of dichloromethane from two separatory funnels under a nitrogen atmosphere in 40 min and the whole was refluxed for 20 min. The solvent was evaporated and the residue was submitted to chromatography on silica gel (hexane–dichloromethane eluent). The

product was recrystallized from dichloromethane–hexane and was found to be a mixture of ca. 1:6 *sc* and *ap* isomers. Yield was 2.40 g (79%). Attempted purification of the *ap* isomer by recrystallization resulted in failure because the operation enriched the *sc* isomer. The *sc* isomer was obtained by chromatography (hexane–dichloromethane eluent) of the thermally equilibrated mixture of *sc* and *ap* forms on alumina, the mixture being obtained by heating a tetrahydrofuran solution under reflux for 6 h. The melting point was >300 °C. Found: C, 71.39; H, 4.55; N, 3.13; Cl, 14.34%. Calcd for $C_{29}H_{21}Cl_2NO_2$: C, 71.61; H, 4.35; N, 3.13; Cl, 14.58%. ^{1}H NMR ($CDCl_3$) δ=2.09 (3H, s), 2.58 (3H, s), 5.40 and 5.85 (2H, ABq, J=19.3 Hz), 5.60 (1H, s), 6.55—7.40 (9H, m), 7.65—7.8 (2H, m), 8.2—8.3 (1H, m).

The following ^{1}H NMR data ($CDCl_3$, δ) of the *ap* form were collected: 2.43 (3H, s), 2.84 (3H, s), 5.60 (2H, s), 5.64 (1H, s), 6.7—7.4 (9H, m), 7.65—7.8 (2H, m), 8.2—8.3 (1H, m).

8,13-Dichloro-9-[4-(dimethylamino)benzyl]-1,4-dimethyltriptycene (8). A suspension of 667 mg (1.37 mmol) of the nitrobenzyltriptycene (**7**, *sc*/*ap*=1.0) in 1:1 (v/v) dioxane–acetic acid was shaken under a hydrogen atmosphere in the presence of ca. 60 mg of platinum(IV) oxide for 12 h. For completion of the hydrogenation, it was necessary to add another portion of platinum oxide (60 mg) and to shake under hydrogen for 24 h. After removal of the catalyst by filtration, the solvents were evaporated and the residue was treated with aqueous sodium hydrogencarbonate. The mixture was extracted with dichloromethane and the solution was dried over magnesium sulfate. The product, after evaporation of the solvent, was used directly for the next reaction. The following ^{1}H NMR data were collected ($CDCl_3$, δ): *sc* form 2.19 (3H, s), 2.53 (3H, s), 3.38 (2H, br s), 5.13 and 5.57 (2H, ABq, J=18.9 Hz), 5.55 (1H, s), 6.1—7.4 (12H, m); *ap* form 2.37 (3H, s), 2.81 (3H, s), 3.38 (2H, br s), 5.37 (2H, s), 5.57 (1H, s), 6.1—7.4 (12H, m).

Trimethyloxonium tetrafluoroborate[34] (ca. 300 mg or ca. 2 mmol) was added to a solution of 625 mg (1.37 mmol) of the amine in 15 mL of dichloromethane and the mixture was stirred for 2 h at room temperature. The mixture was poured into a saturated solution of sodium hydrogencarbonate in water and then the aqueous layer was extracted with dichloromethane. After drying over magnesium sulfate, the solvent was evaporated and the residue was treated again with the Meerwein reagent as above. The product was chromatographed on alumina (hexane–dichloromethane eluent) to give 422 mg (64%) of the desired product, which was a mixture (*sc*/*ap*=2.0) of the rotamers.

The *sc* isomer was obtained in a pure form by semi-preparative HPLC (microporasil, 20:1 hexane-chloroform eluent), mp 280 °C (decomp). Found: C, 76.74; H, 5.32; N, 2.86; Cl, 14.43%. Calcd for $C_{31}H_{27}Cl_2N$: C, 76.86; H, 5.62; N, 2.89; Cl, 14.64%. ^{1}H NMR ($CDCl_3$) δ=2.19 (3H, s), 2.56 (3H, s), 2.87 (6H, s), 5.15 and 5.60 (2H, ABq, J=18.2 Hz), 5.56 (1H, s), 6.15—6.25 (2H, m), 6.5—7.4 (10H, m).

The following ^{1}H NMR data ($CDCl_3$, δ) of the *ap* form were collected: 2.41 (3H, s), 2.85 (3H, s), 2.88 (6H, s), 5.38 (2H, s), 5.58 (1H, s), 6.15—6.25 (2H, m), 6.5—7.4 (10H, m).

9-Benzyl-8,13-dichloro-1-methyltriptycene (10). 9-Benzyl-1,8-dichloroanthracene[23] (4 mmol) was similarly treated with 3-methylanthranilic acid[35] (9 mmol) and isopentyl nitrite in dichloromethane as described for the preparation of the nitro compound (**7**). The reaction afforded, after chromatography on silica gel (hexane–dichloromethane eluent), a 3:2:8 mixture of *sc*-**10**, *ap*-**10**, and 9-benzyl-8,13-dichloro-4-methyltriptycene (**11**). Most of the 4-methyl isomer (**11**) was removed by filtration after letting a solution of the mixture in dichloromethane to stand to evaporate the solvent. The filtrate was submitted to gel permeation chromatography (chloroform solvent) to separate **10** from **11**. The mixture of rotamers of **10** was resubmitted to GPC. Recycling 40 times did not give any of the pure rotamers. Recrystallization of the *sc*-enriched portion from 1:1 dichloromethane–hexane afforded crystals which consisted of 8:3 *sc* and *ap* rotamers and melted at 249.5—251.0 °C. Found: C, 78.36; H, 4.68; Cl, 16.88%. Calcd for $C_{28}H_{20}Cl_2$: C, 78.69; H, 4.72; Cl 16.59%. The following ^{1}H NMR data ($CDCl_3$, δ) were collected. *sc*: 2.17 (3H, s), 5.27 and 5.76 (2H, ABq, J=19.1 Hz), 6.4—7.7 (14H, m). *ap*: 2.89 (3H, s), 5.26 (1H, s), 5.51 (2H, s), 6.4—7.7 (14H, m).

The 4-methyl isomer (**11**) was submitted to recrystallization from 1:1 dichloromethane–hexane to give analytical sample, mp 227.0—228.0 °C. Found: C, 78.62; H, 4.89; Cl 16.82%. Calcd for $C_{28}H_{20}Cl_2$: C, 78.69; H, 4.72; Cl, 16.59%. This compound apparaently crystallized as *sc* forms. ^{1}H NMR ($CDCl_3$, 25 °C) δ=2.58 (3H, s), 5.60 (1H, s), 4.88 and 5.95 (2H, ABq, J=18.2 Hz), 6.50 (1H, br s), 6.7—7.5 (12 H, m), 7.58 (1H, br s). ^{1}H NMR spectra at other temperatures suggest that the isolated rotation of the benzylic phenyl group at −40 °C is slow but is taking place slowly at room temperature, whereas rotation about the C_9-to-substituent bond begins to take palce at 55 °C in chloroform-*d*: at −40 °C, δ=2.58 (3H, s), 5.60 (1H, s), 4.88 and 5.95 (2H, ABq, J=18.1 Hz), 6.49 (1H, d, J=8.5 Hz), 6.7—7.5 (12H, m), 7.68 (1H, d, J=8.5 Hz); at 55 °C, δ=2.57 (3H, s), 4.80 (1H, br d), 5.58 (1H, s), 5.94 (1H, br d), 6.6—7.4 (14H, m).

9-Benzyl-4-bromomethyl-8,13-dichloro-1-methyltriptycene (13). A mixture of 1.01 g (2.29 mmol) of 9-benzyl-8,13-dichloro-1,4-dimethyltriptycene (**12**)[23] (*sc*/*ap*=1.0), 0.45 g (2.5 mmol) of *N*-bromosuccinimide and a small amount of dibenzoyl peroxide in 60 mL of carbon tetrachloride was heated under reflux for 4 h. The mixture was cooled and the insoluble materials were removed by filtration. The solvent was evaporated in vacuo from the filtrate and the residue was submitted to chromatography on silica gel with the use of a medium-pressure liquid chromatograph (hexane–dichloromethane eluent). The order of elution was the unreacted material, *sc*-**13**, *ap*-**13**, *sc*-**14**, and *ap*-**14**. The total yield of *sc*-**13** and *ap*-**13** was 0.39 g (33%). The mixture of *sc*- and *ap*-**13** (*sc*/*ap*=2.0) was resubmitted to the medium-pressure chromatography to afford pure *sc*-**13**, mp 247.5—248.5 °C. Found: C, 66.89; H, 4.37; Cl, 13.58; Br, 15.30%. Calcd for $C_{29}H_{21}BrCl_2$: C, 66.95; H, 4.07; Cl, 13.63; Br, 15.36%. ^{1}H NMR ($CDCl_3$) δ=2.18 (3H, s), 4.73 and 4.85 (2H, ABq, J=10.3 Hz), 5.28 and 5.76 (2H, ABq, J=18.7 Hz), 5.77 (1H, s), 6.42 (1H, br d, J=8.1 Hz), 6.62 (1H, d, J=8.1 Hz), 6.8—7.6 (11H, m). The *ap*-**13** afforded the following ^{1}H NMR data ($CDCl_3$, δ): 2.89 (3H, s), 4.62 (2H, s), 5.51 (2H, s), 5.79 (1H, s), 6.42 (1H, br d, J=8.1 Hz), 6.62 (1H, d, J=8.1 Hz), 6.8—7.6 (11H, m).

9-Benzyl-4-carboxy-8,13-dichloro-1-methyltriptycene (15). To a solution of compound **13** (*sc*/*ap*=2.0, 268 mg or 0.514 mmol) in 10 mL of dimethyl sulfoxide, was added

2 mL of water and the whole was heated at 90—100 °C for 4 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 taken up in 6 mL of acetone and, to this solution, the Jones reagent[36] was added at room temperature until the yellow color of Cr(VI) became persistent. The mixture was stirred for further 30 min at room temperature and the excess of the Cr(VI) was reduced with ethanol. The solid was removed by filtration and the filtrate was poured into water. The mixture was extracted with dichloromethane and the extract was dried over magnesium sulfate. Evaporation of the solvent afforded practically pure **15**, which was directly used for the next reaction, in 229 mg (95%) yield. The *sc*/*ap* value was 4.0. The following ^{1}H NMR data were collected ($CDCl_3$, δ): *sc* 2.28 (3H, s), 5.34 and 5.81 (2H, ABq, J=19.4 Hz), 6.35—6.4 (1H, m), 6.7—7.75 (14H, m); *ap* 2.98 (3H, s), 5.55 (2H, s), 6.35—6.4 (1H, m), 6.7—7.75 (14H, m).

9-Benzyl-8,13-dichloro-4-methoxycarbonyl-1-methyltriptycene (16). To a solution of 244 mg (0.517 mmol) of the carboxylic acid (**15**, *sc*/*ap*=4.0) in 15 mL of dichloromethane, was added diazomethane in ether,[37] prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, until the solution bore yellow tinge and then the mixture was stirred for 10 min at room temperature. The excess of diazomethane was destroyed with acetic acid and the mixture was poured into aqueous sodium hydrogencarbonate. The mixture was extracted with dichloromethane and the extract was dried over magnesium sulfate. The solvent was evaporated and the residue was submitted to preparative TLC (silica gel, hexane–dichloromethane eluent) to afford 211 mg (84%) of the desired product. The *sc* isomer was isolated by medium-pressure chromatography (silica gel, hexane-dichloromethane eluent). Mp 218.5—224.5 °C. Found: C, 74.42; H, 4.82; Cl, 14.40%. Calcd for $C_{30}H_{22}Cl_2O_2$: C, 74.23; H, 4.52; Cl, 14.61%. ^{1}H NMR ($CDCl_3$) δ=2.24 (3H, s), 4.00 (3H, s), 5.32 and 5.79 (2H, ABq, J=19.1 Hz), 6.3—6.4 (1H, m), 6.65—7.6 (13H, m).

ap-**16** exhibited the following ^{1}H NMR data ($CDCl_3$, δ): 2.94 (3H, s), 3.94 (3H, s), 5.52 (2H, s), 6.3—6.4 (1H, m), 6.65—7.6 (13H, m).

9-Benzyl-8,13-dichloro-4-cyano-1-methyltriptycene (17). To a suspension of 229 mg (0.486 mmol) of the acid (**15**) (*sc*/*ap*=4.0) in 10 mL of benzene was added 0.20 mL (2.7 mmol) of thionyl chloride. The mixture was stirred at room temperature for 1 h and then heated under reflux for 4 h. The benzene and the excess of the thionyl chloride were removed in vacuo and the residue was taken up in 2.5 mL of tetrahydrofuran. The solution was treated with 2 mL of concentrated aqueous ammonia for 2 h with ice-cooling. The whole was poured into water and extracted with dichloromethane. The extract was dried over magnesium sulfate and the solvent was evaporated. The residue, taken up in 10 mL of toluene, was heated with 2 g of phosphorus pentaoxide for 2 h under reflux. The solid was removed by filtration from the cooled mixture and the solvent was evaporated from the filtrate. The residue was submitted to preparative TLC (silica gel, hexane–dichloromethane eluent) to give 95 mg (43%) of the desired product (*sc*/*ap*=3.0). The *sc* form was separated by medium-pressure chromatography (silica gel, hexane–dichloromethane), mp 300.5—301.0 °C. Found: C, 76.82; H, 4.02; N, 2.93; Cl, 15.49%. Calcd for $C_{29}H_{19}Cl_2N$: C, 77.00; H, 4.23; N, 3.10; Cl, 15.67%. ^{1}H NMR ($CDCl_3$) δ=2.22 (3H, s), 5.25 and 5.79 (2H, ABq, J=19.4 Hz), 5.83 (1H, s), 6.3—6.4 (1H, m), 6.75—7.6 (12H, m). IR (KBr disc): 2225 cm^{-1}.

The following ^{1}H NMR data for *ap*-**17** were recorded ($CDCl_3$, δ): 2.94 (3H, s), 5.50 (2H, s), 5.80 (1H, s), 6.3—6.4 (1H, m), 6.75—7.6 (12H, m).

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