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Substituent Effects on the Populations of Rotational Isomers in 9-Benzyl-8,13-dichloro-1-methyltriptycenes. Evidence for the Presence of CH_3...π Interactions#

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Examination of population ratios, ±sc/ap, in substituted 9-benzyl-8,13-dichloro-1-methyltriptycene derivatives by ^1H NMR spectroscopy has shown that the ratio becomes larger as the substituent in the benzyl group is more electron-donating and as that in the benzeno bridge which bears the 1-methyl group is more electron-withdrawing. The results are interpreted as indicating the presence of CH_3...π interactions.

Molecular interactions involving the π-system as the proton acceptor are well documented, when the proton donor is either the hydroxyl group1) or the amino group.2) This kind of interactions is present when the proton donor is an acetylenic C-H group.3) Because the CH_3 group is the weakest proton donor among the C-H groups, the presence of the CH_3...π interactions is questionable in spite of the fact that various discussions have been made.4)

1,9-Disubstituted triptycenes comprise an interesting group of compounds in that the distance between the substituents is well within the sum of the van der Waals radii.5,6) This feature excels in finding very weak molecular interactions like between n-electrons and π*-systems of benzene rings,7) π*-systems of carbonyl moieties,8) or σ*-systems of acyloxymethyl groups.9) Recently we could even provide evidence for the presence of CH_3...O hydrogen bond by taking advantage of this system.10) We naturally sought the possibility of manifestation of CH_3...π interactions in this system.

We have had some experiences that might be interpreted by the presence of the CH_3...π interactions. In 9-(1-methyl-2-propenyl)-1,4-dimethyltriptycene, the sc/ap11) value is 1.52 which is very large relative to other compounds bearing other substituent in the 1-position instead of the methyl.12) The results might be derived because of the bulkiness of the methyl, but there could be an attractive interaction between the CH_3 group and the π system which should favor the sc conformation. In 9-substitued 8,13-dichloro-1,4-dimethyltriptycenes, the population ratio ±sc/ap is 2.0 or more if the 9-substituent bears the π-system beta to the 9-position, but it is far less 0.75 when the 9-substituent is an ethyl.13) It might be caused because the charge-transfer interactions between the chloro

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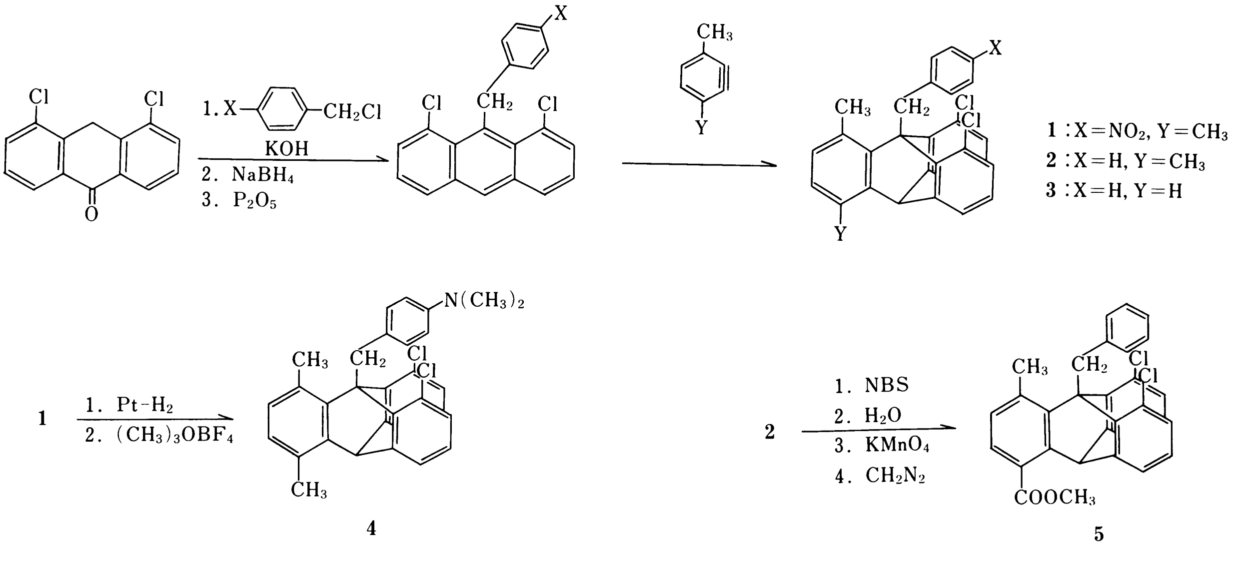
#Dedicated to Professor Teruaki Mukaiyama on the occasion of his 60th birthday.

substituent in the 8,13-positions and the π^*-system are more favorable in the ap position, but it conforms as well to a postulate that there is a $CH_3 \cdots \pi$ interaction, which should favor the ±sc conformation of the compounds that bear the π-system in the 9-substituent. Furthermore, disagreement between the EFF-calculated stability and the experimental stability of 1-methyl-9-(2,6-dimethylbenzyl)triptycenes may be cited. According to the work by Mislow et al., the EFF calculation predicts that the ±sc form of the compound is less stable than the ap by 0.6 kcal/mol, whereas the experimental value indicates that the ±sc form is more stable than the ap by 0.8 kcal/mol or more.[14] The discrepancy may be taken as that the calculation is not reliable but it is also possible to assume that there are attractive interactions in the ±sc forms which are not taken care of by the EFF calculations. These experiences together with the aforementioned backgrounds prompted us to commence a systematic study on the possibility of finding the $CH_3 \cdots \pi$ interactions in the triptycene systems.

We selected the system of 9-benzyl-8,13-dichloro-1-methyltriptycenes for two reasons. One is that it gives stable rotational isomers which are separable at room temperature,[13] and it is believed that we may obtain more reliable data by classical methods, if thermodynamic and kinetic data are required, than the NMR method. The other is that the chloro and the methyl substituents are similar in their sizes. This should give similar steric circumstances for ap and ±sc conformers. The system is composed of two series of compounds: one is 9-(4-substituted benzyl)-8,13-dichloro-1,4-dimethyltriptycenes which provide a variety of electron density in the benzyl group and the other is 4-substituted 9-benzyl-8,13-dichloro-1-methyltriptycenes which provide various acidities of the 1-methyl group. The methods of syntheses of the compounds are shown in Scheme 1. The preparation of compounds 1 and 3 is essentially the same with 9-benzyl-8,13-dichloro-1,4-dimethyltriptycene (2) which was already reported.[13] Compound 4 was prepared by reduction of 1 followed by methylation. N-Bromosuccinimide bromination of 2 followed by hydrolysis of the product, oxidation and then methylation



Scheme 1. Synthetic routes to 9-benzyl-8,13-dichloro-1-methyltriptycenes.

Table 1. Population Ratios of 9-(4-Substituted Benzyl)-8,13-dichloro-1,4-dimethyltriptycene Rotamers in $CDCl_3$ at 54.0 °C

Substituent	K(±sc/ap)	π Electron Density[a)]
$(CH_3)_2N$	2.87 ± 0.10	-0.0370
H	2.30 ± 0.04	0.0
NO_2	1.52 ± 0.04	0.0714

a) Those at 1-position of the benzyl group, as calculated by CNDO SCF method for monosubstituted benzenes.[15)]

afforded compound 5. The equilibration was carried out as $CDCl_3$ solutions and the equilibrium constants were obtained by analyzing the ±sc and ap rotamers by 270 MHz ^1H NMR spectra. The assignment of the conformers was straightforward, because the benzylic methylene protons give a singlet in the ap form and an AB quartet in the ±sc in ^1H NMR spectra. The results are shown in Tables 1 and 2.

The results in Table 1 indicate that, as the electron density on the carbon at the 1-position of the benzyl group increases, the population of the ±sc form increases. The populations of rotamers may be affected by four factors:[16,17)] charge-transfer interactions, Coulombic interactions, van der Waals repulsions, and dispersion forces. Coulombic interactions may be ruled out because no appreciable change is expected in the conformers due to the fact that the dipole which is inherent in the p-substituted benzyl group makes an angle of ca. 60° or ca. 120° with the C-Cl bonds in 8 and 13 positions. van der Waals repulsions can be rejected from the possibility because the high electron density should mean enhanced repulsions. To the first approximation, dispersion forces may be excluded because we are comparing the populations of the series of compounds.

Thus the charge-transfer interactions remain as a strong candidate for the population change observed here. However, it can be argued that the relatively high populations of the ap rotamers in the compound which carry an electron-withdrawing substituent is not caused by the destabilization of the ±sc form but by the enhanced stability of the ap form, because the electronic repulsive interactions are weak in the ap form between the chloro substituents and the π-system of the benzyl group, if the electron density in the latter is low, or the charge transfer interactions between the n-electrons on the chloro substituent and the π*-system will be enhanced. For the diagnosis of the main cause for the observed population change, we have changed the acidity of the methyl group. The acidity

Table 2. Population Ratios of 4-Substituted 9-Benzyl-8,13-dichloro-1-methyltriptycene Rotamers in $CDCl_3$ at 54.0 °C

Substituent	K(±sc/ap)	σ Value[19)]
CH_3	2.30 ± 0.04	-0.129
H	2.22 ± 0.06	0.00
$COOCH_3$	4.09 ± 0.16	0.385

of p-substituted toluenes is known to vary to a greater extent than that of substituted anilines[18)] and this should be advantageous in examining the change in populations of rotational isomers.

Table 2 clearly indicates that, as the acidity of the methyl group at the 1-position increases, the population of the ±sc form increases. Since the change in the substituent here does not cause appreciable change in the dispersion forces in the groups concerned, we may take the results as indicating that the main cause is the charge-transfer. Thus we postulate that the $CH_3\cdots\pi$ interactions which are similar to hydrogen bonds are observed. Although it is known by a theoretical study that $CH_3\cdots\pi$ interactions are extremely weak,[20)] we believe the extreme proximity of the groups concerned made it observable in the triptycene system.

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