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Substituent Effects on the Populations of Rotational Isomers in 9-(Aryloxymethyl)-1,4-dimethyltriptycenes. Implications for the Presence of $CH_3 \cdots O$ Hydrogen Bond

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The population ratios ±sc/ap in 9-(aryloxymethyl)-1,4-dimethyltriptycenes were determined by ^1H NMR spectroscopy. Whereas electron-withdrawing substituents favor the ap rotamer, electron-donating substituents favor the ±sc rotamer in a relative sense. The results are attributed to the presence of weak $CH_3 \cdots O$ intramolecular hydrogen bond in the ±sc form.

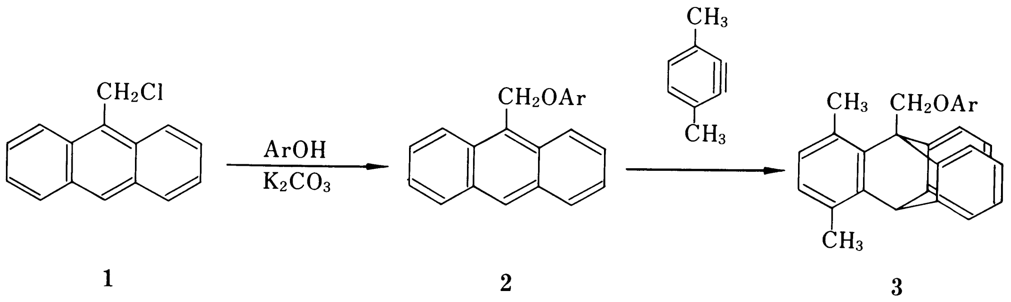
Hydrogen bond formation in which the C-H group acts as a proton donor continues to attract interests of many investigators.1,2) Yet the presence of this kind of hydrogen bond is not conclusive in many cases except for strong proton donors like hydrogen cyanide and chloroform. The methyl group, being the weakest proton donor among the C-H groups, has failed to show unambiguous evidence for the presence of such interactions, although some efforts have been expended for the search of it.3,4)

9-Substituted triptycenes comprise a unique group of compounds in which the substituents at 1- and 9-positions are very close with each other, they being actually in the contact well within the sum of van der Waals radii of the groups concerned.5,6) This is advantageous in finding weak molecular interactions as the presence of a particular conformation which is otherwise disfavored by the steric effects. We have thus shown that the charge-transfer type interactions can be detected between n-electrons and π*-systems of benzene rings,7) n-electrons and σ*-systems of acyloxymethyl groups,8) and n-electrons and π*-systems of various carbonyl moieties.9)

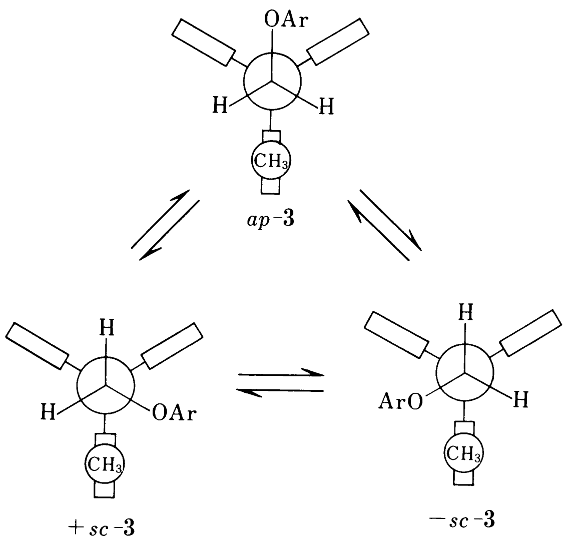
During the investigations of various triptycenes, we have come across some unusual populations of rotational isomers. Both 9-allyl- and 9-ethyl-1,4-dimethyltriptycenes show ±sc/ap values of ca. 0.7, in spite of the fact that the methyl group is believed to be larger than the π-system.10,11) 1,4-Dimethoxy-9-(1-methyl-2-propenyl)triptycene shows sc/ap value of 0.72.12) Although these can be interpreted on the basis that the repulsion between the π-system and the methoxyl group is greater than the repulsion between the methyl and the methoxyl groups, it is also possible to claim that there is an attractive interaction between a methyl group and a methoxy-oxygen atom. In 1-substituted 9-(1-methoxyethyl)triptycenes, 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 groups, all disfavor the ap rotamer to a large extent.[13)] This is another case in which the attractive interactions between the methyl group and the methoxy-oxygen are possibly operating. Thus we felt that it would be worthwhile to launch a systematic study on the possibility of experimentally demonstrating the presence of $CH_3\cdots O$ hydrogen bond. This paper is to report the outcome of such investigations in a preliminary form.

Compounds chosen for the investigation are a series of 9-(aryloxymethyl)-1,4-dimethyltriptycenes (3). They were prepared as shown in Scheme 1 except a p-dimethylamino compound: treatment of 9-chloromethylanthracene (1) with an appropriate phenol in the presence of potassium carbonate afforded 9-(aryloxymethyl)-anthracenes (2), which were treated with 3,6-dimethylbenzyne to afford the desired products. The p-dimethylamino compound was obtained by reduction of the corresponding p-nitro compound followed by methylation.



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



Scheme 2. Rotational circuit of 9-(aryloxymethyl)-1,4-dimethyltriptycenes.

The populations of ±sc and ap rotamers were determined by ^1H NMR spectroscopy at 400 MHz as $CDCl_3$ solutions. The assignment of the rotamers is straightforward, as is seen in Scheme 2: signals due to methylene protons of the ±sc form should be an AB quartet, whereas that for the ap should be a singlet. In practice, the signals due to methyl protons were used for the analysis because of the good quality of separation of signals, the rough matching of the populations being checked with the methylene signals.

The results are shown in Table 1. Although the tendency that the electron-withdrawing subsituent relatively favors the ap rotamer and the electron-donating one does the ±sc rotamers is apparent, it may be necessary to consider possibilities which might cause this type of population change other than the presence of the

Table 1. Polulations and Equilibrium Constants of the Rotational Isomers of 9-(Aryloxymethyl)-1,4-dimethyltriptycenes

Aryl	±sc/%	K[a)]	Temperature/°C
p-$(CH_3)_2NC_6H_4$	36.6 ± 0.1	0.289	-49.7
p-$CH_3OC_6H_4$	32.6 ± 1.0	0.242	-49.6
C_6H_5	30.9 ± 0.8	0.224	-49.4
p-$NO_2C_6H_4$	27.6 ± 1.4	0.191	-49.6
3,4-$(NO_2)_2C_6H_3$	24.8 ± 1.3	0.165	-49.2

a) The equilibrium constants were calculated as +(or -)sc/ap.

$CH_3\cdots O$ hydrogen bond.

Molecular interactions are observed as the consequence of the summation of various interactions. They may be charge-transfer interactions between the orbitals concerned, Coulombic interactions, van der Waals repulsions, and dispersion forces.[1)] If we are discussing the interactions by taking advantage of the population ratios of rotamers, it is necessary to confirm the stability of each rotamer, because one rotamer can be rich in population because of either its stabilization or the destabilization of other rotamers.

We may neglect the difference in Coulombic interactions between the rotamers, ±sc and ap, because the molecules are mainly composed of hydrocarbon parts, only polar part being the aryloxymethyl moiety. The latter should not change its polarity at any rotameric positions. van der Waals repulsion must be great in the series of compounds, especially in the ±sc rotamers. However, if this force were important, the ±sc form should be relatively disfavored when the electron density is high at the oxygen atom of the aryloxyl group. Since the observed trend is just the opposite of the expectation, we may reject the van der Waals repulsion from being the primary cause for the observed populations of the rotamers. Dispersion force is very hard to be ruled out because both polarizability and ionization potentials are affected by the electron density of the oxygen atom. However, since we discuss the phenomenon by comparing the population ratios of the series of compounds, we neglect, to the first approximation, the dispersion force as the main cause: when dispersion force increases in the ±sc rotamers, that kind of increase is also expected in the ap, though the distances involved are different. In addition, dispersion force cannot accommodate the fact that, in 4-substituted 9-ethyl-1-methoxytriptycenes, an electron-withdrawing substituent favors the ±sc form, the details of which will be described in a full paper. Finally, we may also neglect the gradual destabilization of the ap forms as the electron density is increased at the aryloxy-oxygen, because if it were the case, the same steric and/or the electronic effects should also operate in the ±sc form.

The above discussion then favors the presence of the $CH_3\cdots O$ hydrogen bond in the ±sc form as the main cause of the observed population change according to the substituent effects in the aryloxyl group. Since the σ^*-orbital belonging to the methyl group lies at a high energy level, the charge-transfer interaction must be a very weak one. This weakness is reflected by the populations of rotamers of 4-substituted 9-ethyl-1-methoxytriptycenes in which a repulsive rather than an attractive force is controlling the population ratios.

The $\log(K/K_0)$ values, where K_0 is the equilibrium constant of 9-(phenoxymethyl)-1,4-dimethyltriptycene, were plotted against the σ values. For the 3,4-dinitrophenyl compound, the σ value estimated from the dissociation constant of 3,4-dinitrobenzoic acid$^{14)}$ was used. The linearity was fairly good, the r value being 0.983. The interesting point is that the ρ value is very small -0.114, the normal values for the reactions which take place at the aryloxy-oxygen being 2-3.$^{15)}$ We believe this small ρ value is caused because the observed populations of the rotamers base upon the delicate balance of the weak attractive and strong repulsive forces: due to the fact that the oxygen of high electron density is bulkier than the oxygen of low electron density, the repulsive force becomes big in the former as well as the attractive force in the ±sc conformation.

We conclude that we have observed the presence of $CH_3\cdots O$ hydrogen bond in the series of 9-(aryloxymethyl)-1,4-dimethyltriptycenes. The 9-substituted triptycenes will continue to be promising in further manifesting weak interactions which are not detectable in other systems.

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