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INTRAMOLECULAR INTERACTIONS BETWEEN CARBONYL MOIETIES AND CHLORO OR METHOXYL GROUP IN TRIPTYCENE SYSTEMS

Michinori ŌKI,* Giichi IZUMI, Gaku YAMAMOTO, and Nobuo NAKAMURA
Department of Chemistry, Faculty of Science,
The University of Tokyo, Tokyo 113

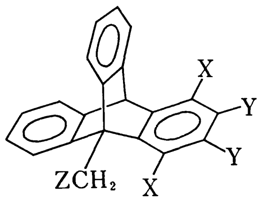
9-Substituted 1,4-dimethoxytriptycenes, where the substituents contain a carbonyl group, favor ±sc conformations relative to the ap. 9-Substituted 1,2,3,4-tetrachlorotriptycenes exist as mixtures of ±sc and ap conformations of which ratios vary according to steric and electronic effects. Some anomalies involving aldehydes and ketones are discussed with the use of ^{1}H NMR and IR spectra.

A phenomenon has been found in certain triptycene derivatives that ±sc conformers, which are otherwise disfavored because of the steric repulsion, exist as preferred forms over the ap and has been interpreted that the charge-transfer type interaction occurs in this system.1) The triptycene system appears to be useful for exploring weak interactions by the fact that a group at the bridge-head and that in the peri-position are very closely located: they are so congested that the distance between the two groups are well below the sum of normal van der Waals radii.2)

As electron acceptors, the carbonyl group is believed to be of good capacity. Intramolecular interactions involving the ketone group in medium sized rings have been well documented.3) Thus the interaction will be amplified if the carbonyl group is used in the same system. In this communication, we wish to report new findings that the cyano group can act as an electron acceptor and that the chloro group as an electron donor, if a good counterpart is present.

As a natural extension of the previous work on 9-benzyl-1,4-dimethoxytriptycenes, we chose 9-substituted 1,4-dimethoxytriptycenes, where the substituent contains a carbonyl group, as a starting point. After finding that the population of the ±sc forms overwhelms in many of the compounds, we shifted to 1,2,3,4-tetrachlorotriptycene derivatives where the chloro group must be a less potent electron-donor than the methoxyl group.4) The syntheses of the dimethoxytriptycenes were accomplished by Diels-Alder reactions between the corresponding anthracenes followed by aromatization and methylation and the tetrachlorotriptycenes by normal benzyne reactions with anthracenes, except aldehydes and ketones which were prepared by ozonolysis of the corresponding olefinic triptycenes.

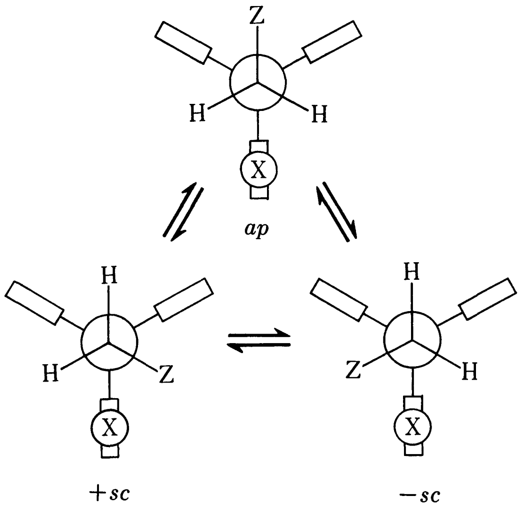
The conformational exchange of the compounds in question is schematically illustrated by the following scheme. The ap form should give a singlet signal for the methylene protons in the ^{1}H NMR spectra whereas the ±sc forms should give an AB pattern. Actually these compounds usually give a singlet signal at room or



1 : X=CH_3O, Y=H

2 : X=Y=Cl

3 : X=CH_3, Y=H, Z=CHO



higher temperatures, while they give a singlet and an AB signal, of which integrated areas give the respective populations, at low temperatures. The spectra were obtained with a Hitachi R-20B spectrometer operating at 60 MHz.

The results with the methoxy compounds (1) are compiled in Table 1. Clearly, the presence of the methoxyl group and the carbonyl group favors the ±sc forms very strongly. However, this result may not be directly interpreted that the ±sc forms is favored to that extent owing to the charge-transfer interaction, because a literature reports that even 9-ethyl-1,4-dimethoxytriptycene contains comparable amounts of ±sc and ap forms:5) it is especially so for the cyano compound (1: Z=CN) because its ±sc/ap ratio is only 1.5. Thus we prepared a 9-(2-butynyl) derivative (1: Z=C≡CCH_3) as a model to see the steric effect of the cyano group: the ±sc/ap ratio was 0.1. Thus the ap form is strongly favored if the electronic effect is negligible.

Table 1 ±sc/ap Ratios of 1 in $CDCl_3$

Z	mp (°C)	±sc/ap	Observed Temperature (°C)
CHO	252 -253	≥10	-45
$COOCH_3$	224 -225	≥10	-30
$COCH_3$	289 -290	≥10	-30
CN	273 -274	1.5	-50
C≡CCH_3	253.0-253.5	0.1	-60

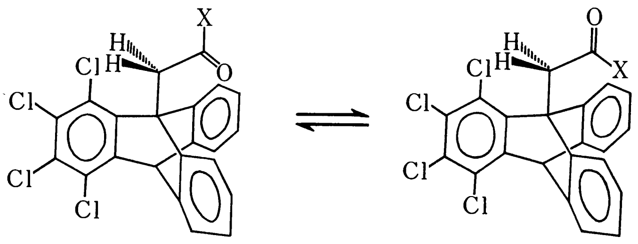
Since the results with the methoxy compounds (1) failed to show the order of electron-accepting ability of the carbonyl moieties due to the presence of negligible amount of the ap forms, we turned to the chloro derivatives (2) which should disfavor the ±sc forms relative to the methoxy compounds (1). The results are shown in Table 2:

Table 2 ±sc/ap Ratios of 2 in $CDCl_3$

Z	mp (°C)	±sc/ap	Observed Temperature (°C)
CHO	223 -224	1.1	-20
$COOCH_3$	247 -248	6	-40
$COCH_3$	273.0-273.5	≥10	-20
CN	>300	0	-40

The non-existence of the ±sc form in the cyano compound (2: Z=CN) suggests that, if the steric factor is dominating, the tetrachlorotriptycenes strongly favor the ap form and that the cyano group is a weak electron acceptor. The former point is supplemented by the fact that 9-(formylmethyl)-1,4-dimethyltriptycene (3), mp 227.0-228.5°C, exists as the ap form only, because a methyl group is a weakly electron-donating group. The data in Table 2 reveal two contrasting points also. Although, as is known in organic chemistry, an acetyl group is a better electron-acceptor than a methoxycarbonyl group, an acetyl group is a better electron-acceptor than a formyl group, contrary to the general understanding in organic chemistry. This apparently contradictory phenomenon may be attributed to the stereoelectronic effect, as is discussed below.

The conformation of 9-(acetylmethyl)-1,2,3,4-tetrachlorotriptycene is studied by X-ray analysis and is known that it exists as a carbonyl-oxygen-inside conformation.[6)] This was attributed to the steric effect: being a smaller group than the methyl, the oxygen points inside to relieve the steric strain caused by the interaction with the methyl group. The presence of two conformations (carbonyl-oxygen-inside and outside) in 9-(2-methoxycarbonyl-1-methylethyl)triptycene derivatives[7)] may be attributed to the similar size of a methoxyl and a carbonyl-oxygen group. If we continue the discussion along this line, we come to a deduction that, in the formyl compound (2: Z=CHO), the carbonyl-oxygen will point outside because it is bulkier than hydrogen.



Carbonyl-oxygen-inside conformation   Carbonyl-oxygen-outside conformation

Although evidence for the conformation must be sought in more direct methods, we tentatively measured the C=O stretching absorptions in the infrared region. The results are shown in Table 3. We can immediately point out an anomaly from the data: the $\nu_{C=O}$ of the aldehydes are at the lower frequencies than those of the methyl ketones, although the contrary is true for the normal ketones and aldehydes.[8)] If we assume, however, the carbonyl-oxygen-inside conformation for the ketones and the carbonyl-oxygen-outside for the aldehydes, we can accommodate the data in Table 3. The carbonyl stretching absorption of 9-(1-methoxycarbonyl-1-

Table 3 $\nu_{C=O}$ Data of 1 and 2 in $CHCl_3$ (cm^{-1})

Z	1	2
CHO	1720	1725
$COOCH_3$	1722, 1751	1731, 1754
$COCH_3$	1741	1741

methylethyl)triptycenes has been discussed and the absorption at a higher frequency is assigned to the carbonyl-oxygen-inside conformation.7) The high frequency for the inside-oxygen conformation is probably caused because of the steric effect of the triptycene skeleton: the high-frequency shift due to the steric effect is well documented.9)

If we assume the carbonyl-oxygen-outside form for the aldehyde (**2**: Z=CHO) and the carbonyl-oxygen-inside conformation for the ketone (**2**: Z=$COCH_3$), we find a factor which favors the ±sc forms of the ketone: since the dipole of the carbonyl is antiparallel with the C-Cl in the peri-position in the ketone whereas it is parallel in the aldehyde, the ±sc forms of the aldehyde is relatively disfavored in nonpolar solvents. The geometry of the approach of a nucleophile to a carbonyl is important10) but, as far as a molecular model can tell, there is not much difference from the requirement in both forms.

The details will be discussed in a full paper.

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