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Intramolecular Interactions between a Group Bearing *n*-Electrons and a CH_2-X Where X is an Electronegative Group[1]

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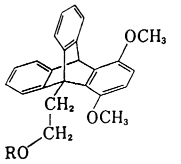
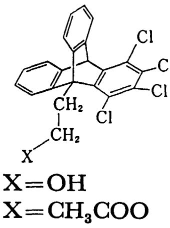
Conformational equilibrium of 9-(2-acyloxyethyl)-1,4-dimethoxytriptycenes in chloroform-*d* suggests that the stability of the ±*sc* conformation increases as the electronegativity of the acyl group increases. The results together with other pertinent data are discussed from the stand point that there is an attractive interaction between the acyloxymethyl and the methoxyl groups in proximity. Reflecting its high ionization potential, the chloro group in 1-position showed no stabilization of the ±*sc* conformation, although mass spectra and some chemical properties indicate that there is an interaction between the chloro group and highly electronegative CH_2X group. A possible correlation of these results with the incipient transition state for S_N2 reactions is suggested.

During the course of investigations on the reactivity-conformation correlations, we have encountered a striking difference in reactivities of 1,2,3,4-tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene rotamers: the ±*sc* conformation reacted in the presence of titanium tetrachloride to afford Friedel-Crafts cyclization products, whereas the *ap* conformation remained intact under the conditions.[2] The results suggest that there may be a kind of interaction between the CH_2–Cl group in the substituent at the bridgehead and the chloro group in the peri-position: the peri-chloro group stabilizes the transition state by delocalizing the partially developed positive charge on the carbon atom of the CH_2–Cl group. Although this phenomenon is concerned with the transition state of the reaction, the ground state of the molecule may be stabilized as well if we consider a charge-transfer interaction between the *n*-electrons of the chloro group and the σ^* orbital of the CH_2–Cl group.

Since we have succeeded in detecting the attractive interactions of *n*-electron-phenyl[3] and *n*-electron-carbonyl[4] in triptycene systems by looking at the population ratios of rotamers, we thought the same technique may be applied to the present case to diagnose the presence or absence of the interaction involving the CH_2–Cl group and a group carrying a lone pair of electrons. At the outset, it was thought that the attractive interaction could easily be observed if the group in 1-position of the triptycene system had a low ionization potential. Thus we first attempted to synthesize 9-(2-chloroethyl)-1,4-dimethoxytriptycene from the corresponding alcohol and thionyl chloride and observed that the treatment afforded only a cyclized product:[5] it seemed that the interaction between a CH_2–Cl (or possibly the corresponding ion pairs) and a methoxyl group in this system was so strong that it caused a reaction. The results suggest that if we wish to find interactions instead of reactions, we should use a combination of a weaker electron acceptor than the CH_2–Cl group and a methoxyl group or that of CH_2–Cl group and a weaker electron donor than the methoxyl. Our choice was acyloxymethyl groups instead of the CH_2–Cl in combination with the methoxyl because the electronegativities and consequently the electron-accepting power of the former group can be easily modified by changing the acyl group. This paper reports the results of such investigations together with those of the interaction between a chloro group and a CH_2–X where X is either a chloro or a *p*-toluenesulfonyloxyl group.



(**1**) R=H
(**2**) $R=CH_3$
(**3**) $R=CH_3CO$
(**4**) $R=C_6H_5CO$
(**5**) $R=p\text{-}CH_3OC_6H_4CO$
(**6**) $R=p\text{-}O_2NC_6H_4CO$
(**7**) $R=ClCH_2CO$
(**8**) $R=Cl_2CHCO$
(**9**) $R=Cl_3CCO$
(**10**) $R=F_3CCO$



(**11**) X=OH
(**12**) $X=CH_3COO$
(**13**) X=Cl
(**14**) $X=p\text{-}CH_3C_6H_4SO_3$

Syntheses of the compounds were straightforward. 9-(Formylmethyl)-1,4-dimethoxytriptycene or 1,2,3,4-tetrachloro-9-(formylmethyl)triptycene was reduced to the corresponding alcohol (**1** and **11**). They were converted to esters by ordinary methods or to chloride by treatment with thionyl chloride.

Experimental

^1H NMR spectra were measured on a Hitachi R-20B spectrometer equipped with a temperature variation accessory. The temperature was read by the chemical shift differences of methanol protons. High resolution mass spectra were recorded on a JEOL JMS-D300 spectrometer.

9-(2-Hydroxyethyl)-1,4-dimethoxytriptycene (1). To a boiling solution of 1.3 g (3.7 mmol) of 9-(formylmethyl)-1,4-dimethoxytriptycene[4] in 20 mL of dichloromethane and 20 mL of methanol, 0.5 g (13 mmol) of sodium tetrahydridoborate in 20 mL of methanol was added in 15 min. The mixture was heated for additional 30 min and evaporated. The residue was treated with dilute hydrochloric acid and extracted with dichloromethane. The alcohol, mp 220.8—221.5 °C, was obtained in 95% yield. Found: C, 80.30; H, 6.01%. Calcd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19%. ^1H NMR ($CDCl_3$, δ): 2.00 (1H, m), 3.50 (2H, t, J=7 Hz), 3.68 (3H, s), 3.77 (3H, s), 4.20 (2H, t, J=7 Hz), 5.88 (1H, s), 6.50 (2H, s), 6.80—7.70 (8H, m).

1,2,3,4-Tetrachloro-9-(2-hydroxyethyl)triptycene (11), mp 251—252 °C, was similarly prepared by sodium tetrahydridoborate reduction of 1,2,3,4-tetrachloro-9-(formylmethyl)triptycene.[4] High resolution MS (M^+): 433.9798, 435.9763, 437.9694, and 439.9718. $C_{22}H_{14}OCl_4$ requires 433.9799, 435.9770, 437.9740, and 439.9708. The intensities of these observed M^+ peaks agreed well with those calculated from the natural abundance of ^{35}Cl and ^{37}Cl.

1,4-Dimethoxy-9-(2-methoxyethyl)triptycene (2). To a solution of 0.5 g (1.4 mmol) of 9-(2-hydroxyethyl)-1,4-dimethoxytriptycene (**1**) in 30 mL of tetrahydrofuran, was added 0.2 g (8 mmol) of sodium hydride which had been washed with hexane. The mixture was stirred for 1 h and then 0.5 mL (0.8 mmol) of methyl iodide was added to the mixture. Stirring was continued in a sealed system for 24 h and the solvent was evaporated. The residue was treated with dilute hydrochloric acid and extracted with dichloromethane. Evaporation of the solvent followed by recrystallization of the residue from benzene–hexane afforded the desired compound, mp 226—227 °C, in 92% yield. Found: C, 80.91; H, 6.66%. Calcd for $C_{25}H_{24}O_3$: C, 80.62; H, 6.49%. ^1H NMR ($CDCl_3$, δ): 3.45 (3H, s), 3.66 (3H, s), 3.74 (3H, s), *ca.* 3.5 (2H), 3.98 (2H, br t), 5.88 (1H, s), 6.46 (2H, s), 6.80—7.70 (8H, m).

Esters of 9-(2-Hydroxyethyl)-1,4-dimethoxytriptycene. A general procedure is given for acetylation. The other compounds were similarly prepared from the alcohol and acyl chloride except trifluoroacetate, in the preparation of which the acid anhydride was used.

A mixture of 0.6 g of the alcohol and 0.2 mL of acetyl chloride in 3 mL of pyridine was shaken for 5 min. To the mixture were added 30 mL of dichloromethane and dilute hydrochloric acid. The organic layer afforded, after chromatography on silica gel (benzene–hexane), the acetate (**3**), mp 167—168 °C, in 82% yield. Found: C, 77.77; H, 5.94%. Calcd for $C_{26}H_{24}O_4$: C, 77.98; H, 6.04%. ^1H NMR ($CDCl_3$, δ): 2.21 (3H, s), 3.56 (2H, br t, J=7 Hz), 3.70 (3H, s), 3.77 (3H, s), 4.78 (2H, t, J=7 Hz), 5.88 (1H, s), 6.50 (2H, s), 6.90—7.70 (8H, m).

Benzoate (4), mp 170.4—171.2 °C. Found: C, 80.56; H, 5.52%. Calcd for $C_{31}H_{26}O_4$: C, 80.50; H, 5.67%. ^1H NMR ($CDCl_3$, δ): 3.71 (3H, s), 3.79 (3H, s), 3.50—4.00 (2H), 5.07 (2H, t, J=7 Hz), 5.90 (1H, s), 6.51 (2H, s), 6.90—7.70 (11H, m), 8.10—8.30 (2H, m).

p-*Methoxybenzoate (5)*, mp 192.5—193.0 °C. Found: C, 77.86; H, 5.53%. Calcd for $C_{32}H_{28}O_5$: C, 78.03; H, 5.73%. ^1H NMR ($CDCl_3$, δ): 3.73 (3H, s), 3.80 (3H, s), 3.89 (3H, s), 3.50—4.00 (2H), 5.02 (2H, t, J=7 Hz), 5.90 (1H, s), 6.52 (2H, s), 6.90—7.70 (10H, m), 8.19 (2H, d, J=9 Hz).

p-*Nitrobenzoate (6)*, mp 254—255 °C. Found: C, 73.52; H, 4.71; N, 2.58%. Calcd for $C_{31}H_{25}NO_6$: C, 73.36; H, 4.97; N, 2.76%. This compound was so scarcely soluble in chloroform-*d* that the NMR measurement was not carried out.

Chloroacetate (7), mp 166—167 °C. Found: C, 71.80; H, 5.33; Cl, 8.15%. Calcd for $C_{26}H_{23}O_4Cl$: C, 71.69; H, 5.30; Cl, 8.10%. ^1H NMR ($CDCl_3$, δ): 3.56 (2H, br t, J=7 Hz), 3.71 (3H, s), 3.79 (3H, s), 4.20 (2H, s), 4.90 (2H, t, J=7 Hz), 5.88 (1H, s), 6.50 (2H, s), 6.90—7.60 (8H, m).

Dichloroacetate (8), mp 166.5—167.0 °C. Found: C, 66.39; H, 4.75; Cl, 14.97%. Calcd for $C_{26}H_{22}O_4Cl_2$: C, 66.53; H, 4.72; Cl, 15.11%. ^1H NMR ($CDCl_3$, δ): 3.60 (2H, br t), 3.72 (3H, s), 3.79 (3H, s), 5.00 (2H, t, J=6.5 Hz), 5.90 (1H, s), 6.62 (2H, s), 6.90—7.60 (8H, m).

Trichloroacetate (9), mp 178—179 °C. High resolution MS (M^+): 502.0485, 504.0471, 506.0357, and 508.0418. $C_{26}H_{21}O_4Cl_3$ requires 502.0507, 504.0477, 506.0448, and 508.0418. The observed intensities of the molecular ions agreed well with those calculated from the natural abundance of ^{35}Cl and ^{37}Cl. The base peak was 326.1292 to indicate that the loss of a trichloroacetoxyl and a methyl group occurred. ^1H NMR ($CDCl_3$, δ): 3.72 (3H, s), 3.80 (3H, s), *ca.* 3.75 (2H), 5.08 (2H, t, J=6.5 Hz), 5.90 (1H, s), 6.53 (2H, s), 6.90—7.60 (8H, m).

Trifluoroacetate (10), mp 170.0—170.3 °C. Found: C, 68.94; H, 4.86%. Calcd for $C_{26}H_{21}O_4F_3$: C, 68.72; H, 4.66%. ^1H NMR ($CDCl_3$, δ): 3.60 (2H, br t, J=6.5 Hz), 3.70 (3H, s), 3.79 (3H, s), 5.08 (2H, t, J=6.5 Hz), 5.85 (1H, s), 6.52 (2H, s), 6.90—7.60 (8H, m).

9-(2-Acetoxyethyl)-1,2,3,4-tetrachlorotriptycene (12), mp 192—193 °C, was similarly prepared from the corresponding alcohol (**11**). Found: C, 60.40; H, 3.58%. Calcd for $C_{24}H_{16}O_2Cl_4$: C, 60.28; H, 3.37%. ^1H NMR ($CDCl_3$, δ): 2.23 (3H, s), 3.86 (2H, t, J=7 Hz), 4.61 (2H, t, J=7 Hz), 6.01 (1H, s), 7.00—7.70 (8H, m).

1,2,3,4-Tetrachloro-9-(2-chloroethyl)triptycene (13). A solution of 0.1 g of the alcohol (**11**) in 30 mL of dichloromethane and 0.2 mL of thionyl chloride were stirred at 0 °C for 30 min and then refluxed for 30 min. The mixture was mixed with dilute aqueous sodium hydroxide and shaken. Evaporation of the organic layer followed by recrystallization of the residue from tetrahydrofuran–hexane afforded the desired material, mp 270—271 °C, in 93% yield. High resolution MS gave M^+ peaks at 451.9515, 453.9501, 455.9610, and 457.9221. Peaks corresponding to the loss of a hydrogen chloride and a chlorine were observed. The intensity ratios were in agreement with the calculated from the natural abundance of ^{35}Cl and ^{37}Cl. $C_{22}H_{13}Cl_5$ requires 451.9445, 453.9431, 455.9401, and 457.9372. ^1H NMR ($CDCl_3$, δ): 3.91 (2H, br t, J=6.5 Hz), 4.51 (2H, br t, J=6.5 Hz), 6.03 (1H, s), 6.90—7.70 (8H, m).

*1,2,3,4-Tetrachloro-9-[2-(*p*-tolylsulfonyloxy)ethyl]triptycene (14).* A mixture of 0.1 g of the alcohol (**11**), 10 mL of pyridine and 0.1 g of *p*-toluenesulfonyl chloride was stirred at room temperature for 24 h. The mixture was shaken with 40 mL of dichloromethane and dilute hydrochloric acid. The desired product was rather labile and hydrolyzed to the starting material on standing and on chromatography. ^1H NMR ($CDCl_3$, δ): 2.45 (3H, s), 3.88 (2H, t, J=7 Hz), 4.60 (2H, t, J=7 Hz), 5.99 (1H, s), 6.90—7.60 (10H, m), 7.88 (2H, d, J=8 Hz).

Deuterated Compounds. 9-Allyl-1,4-di(methoxy-d_3)triptycene was prepared as described elsewhere[5] from the Diels-Alder adduct between 9-allylanthracene and *p*-benzoquinone and di(methyl-d_3) sulfate. It was ozonized as reported to produce 9-(formylmethyl)-1,4-di(methoxy-d_3)triptycene which was reduced with sodium tetrahydridoborate. The alcohol (**1**-d_6) thus obtained was transformed into esters as described above.

The ^1H NMR spectrum of a chloroform-*d* solution of the acetate at −55 °C showed an AB quartet (δ 3.08 and 3.74, J=15 Hz) and a singlet (δ 3.74), whose relative intensities were 2.1 ± 0.4, on irradiation at δ 4.76 corresponding to $AcOCH_2$ protons. Under the same conditions, the peak at δ 6.50 split into two peaks (δ 6.48 and 6.58). The intensity ratio (the low field peak over the high field peak) was 1.6 ± 0.2.

The ^1H NMR spectrum of the trifluoroacetate at −50 °C gave the following data. 9-CH_2: quartet δ 3.28 and 3.82, J=15 Hz; singlet δ 3.74; intensity ratio (quartet/singlet) 2.9 ± 0.8. Dimethoxybenzo protons: δ 6.51 and 6.42; intensity ratio (low/high) 3.1 ± 0.3.

Results and Discussion

Determination of Conformations and Population Ratios.

Since the compounds studied here all carry a CH_2 group at the bridgehead of the triptycene skeleton, it should exhibit, in principle, a set of AB quartet if it is the ±*sc* conformation and a singlet if it is the *ap*. In practice, however, the determination of conformation poses difficult questions. Firstly, since the CH_2 (α) group at the bridgehead is connected to another CH_2 (β) group, it is necessary for seeing clearly a set of AB quartet and a singlet to irradiate the β-CH_2 protons for decoupling. Then, if the chemical shifts of these two methylene protons are very close, the α-CH_2 protons are partially saturated to make it difficult to obtain good data for the intensity. Secondly, the compounds carrying methoxyl groups give the methoxyl signals in the range of those due to α-CH_2 to cause heavy overlaps. And finally irradiation of β-CH_2 protons may not cause saturation completely because of its range.

These difficult situations were overcome by the following procedures. Since the overlap of the α-CH_2 signals can be avoided by deuterating the methoxyl groups, we first synthesized two triptycenes (acetate and trifluoroacetate) carrying the fully deuterated methoxyl groups in 1,4-positions. Their population ratios were observed by irradiating the β-CH_2 protons. We found that the population ratios obtained by integrating the AB quartet and the singlet due to ±*sc* and *ap* conformations, respectively, involve rather large errors but are in agreement with those obtained by integrating singlets which are formed by splitting of the signal at δ 6.5, if we assume that the signal at a higher magnetic field is due to the *ap* form and that at a lower field to the ±*sc* form. The protons which give a signal at δ 6.5 at room temperature are assigned to the aromatic protons of the dimethoxybenzeno bridge from the electronic density considerations. Since the splitting of the signal at δ 6.5 is definitely caused by freezing of the conformations, it is reasonable to assume that the intensities of these signals reflect conformational populations. Since the correspondence of the higher field signal to the population of the *ap* conformation and that of a lower field signal to the ±*sc* were unaltered in the cases examined, we may assume that the tendency is common in the series examined here, although the exact cause for the chemical shifts is unknown. As discussed later, this assumption afforded reasonable data about the conformational populations.

Conformational Equilibria. The population ratios of conformers of 1,4-dimethoxytriptycenes are listed in Table 1 together with pK_a values of the corresponding acids. Since the population ratio ±*sc*/*ap* of 9-ethyl-1,4-dimethoxytriptycene is known to be 1.0,[6] we cannot take the appearance of the ±*sc* conformer as evidence for the presence of attractive interactions as are the other cases.[4] Thus we take the 9-(2-methoxyethyl) compound (**2**) as a reference. This compound exhibits a low ±*sc*/*ap* value which is close to that of 9-ethyl-1,4-dimethoxytriptycene and can be taken that the attractive interaction between the methoxymethyl and the methoxyl groups is absent because of the low electron-accepting power of the former: thus this much of population ratio is expected in the absence of the attractive interaction.

Table 1. Populations ratios (±*sc*/*ap*) of 9-(2-acyloxy- or alkoxyethyl)-1,4-dimethoxytriptycene and pK_a's of the corresponding acids

Acyl (or Alkyl) group (R)	±*sc*/*ap*	Temp/°C	pK_a of ROH[7]
CH_3	0.7	−50	14.4
CH_3CO	1.5	−45	4.76
C_6H_5CO	1.7	−50	4.20
p-$CH_3OC_6H_4CO$	1.7	−50	4.47
$ClCH_2CO$	2.0	−45	2.86
Cl_2CHCO	2.5	−45	1.26
Cl_3CCO	3.0	−50	0.65
F_3CCO	3.0	−50	0.23

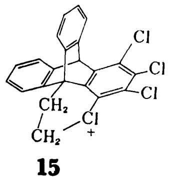
Inspection of the data in Table 1 reveals that all the compounds examined here exhibit larger ±*sc*/*ap* values than that of the 9-(2-methoxyethyl) compound (**2**). The results cannot be attributed to the electric effect although it was the case for some carbonyl-substituted triptycenes.[4] Although the conformation of the acyloxyl group is not well known, the important contribution for the interaction with the dipole of the peri-methoxyl group should be given by the CH_2–O group. Then the ±*sc* form is considered to be more polar since the two dipoles are arranged in a closer proximity: there cannot be an important compensation by solvent molecules. Therefore, if it is the electric nature which dominates as a factor in controlling the population, the ±*sc* form should be disfavored in nonpolar solvents such as chloroform. The difference between the methoxy (**2**) and acyloxy compounds cannot be accommodated by the steric repulsion either, because the steric sizes are, by and large, the same among the conformers examined.

The favoredness of the ±*sc* conformation relative to the *ap*, when an electronegative acyl group is introduced, should be attributed to the increased stability of the ±*sc* conformation, because no instability factor associated with the *ap* form is apparent. The results correspond to the fact that the acyloxyl group is more electronegative than the methoxyl and consequently the former group is more electron-accepting. pK_a values of carboxylic acids are associated with the electronegativities of the acyl group.[8] The fact that, among carboxylic esters, the larger is the pK_a of the corresponding acid, the smaller is the ±*sc*/*ap* value, although a minor change in pK_a does not seem to affect the ±*sc*/*ap* value to a significant extent, clearly shows that the attracting interaction is occurring between the acyloxymethyl group and the methoxyl group. The nature of the interaction is of the charge-transfer type, the acyloxymethyl group acting as an electron acceptor and the methoxyl group as an electron-donor.

Since the acyloxymethyl group should possess at least two low-lying vacant orbitals, it may be worthwhile to discuss the orbitals involved in the interaction here. Our choice is the σ^* orbital, which involves mainly the CH_2–O group, that is responsible to the interaction. It may be argued that the π^* orbital of the carbonyl group is responsible because of its electron-accepting ability. Indeed, the C–T interaction involving the carbonyl moiety is well documented.[4,9] However, we rule out this possibility for the following reasons. The first is the fact that if the interaction between the carbonyl of the acyl group and the methoxyl had occurred, the ring formed there must be 8-membered. This kind of interaction is usually very unfavorable because of the decrease in entropy. It is especially so if we consider the weakness of the interaction discussed here. The second is indirect but is more convincing. Namely the attempt at synthesizing the tosylate of 9-(2-hydroxyethyl)-1,4-dimethoxytriptycene ended in the formation of a cyclic ether.[5] In this case, the result is best accommodated by assuming that the interaction between the SO_3–CH_2 and the methoxyl groups was so strong that it resulted in a reaction. Several phenomena related to this may be cited: that is the reactivities of 9-(2-chloroethyl) compound (**13**) which will be discussed later in this paper, where it becomes apparent that an interaction between a CH_2–Cl and a chloro group can take place. Finally the behavior of the trichloroacetate (**9**) may be taken into consideration. An attempted purification of the compound on a TLC plate which was inpregnated strongly activated silica gel ended in failure because a part of the compound reacted to give a cyclized compound, 6-methoxy-7,11b-*o*-benzeno-7,11b-dihydronaphtho[1,2,3-*de*]chromene.[5] The results together with the fact that the loss of a trichloroacetoxyl and a methyl groups was observed in the MS support the idea that it is the trichloroacetoxy-CH_2 group that is interacting with the methoxyl group in the peri-position. These considerations lead to a conclusion that σ^* orbital of the CH_2–O group is responsible to the interaction.

In contrast to the population ratios of the 1,4-dimethoxytriptycenes, 9-(2-acetoxyethyl)-1,2,3,4-tetrachlorotriptycene (**12**) showed the sole presence of the *ap* form at −50 °C. It was not possible to obtain a $\pm sc/ap$ ratio of 1,2,3,4-tetrachloro-9-(2-chloroethyl)-triptycene (**13**), since the NMR signals of α-CH_2 and β-CH_2 in this compound were too closely located to perform a decoupling experiment. 1,2,3,4-Tetrachloro-9-[2-(*p*-tolylsulfonyloxy)ethyl]triptycene (**14**) did show a sign of the presence of the $\pm sc$ form but the $\pm sc/ap$ value was practically zero. These results indicate that, being a weak electron-donor than a methoxyl group,[10] the chloro group is not a good enough electron-donor for the detectable interaction: that is best illustrated by the fact that compound **14** was prepared at room temperature in contrast to the facile cyclization of 1,4-dimethoxy-9-[2-(*p*-tolylsulfonyloxy)ethyl]triptycene.[5] The size of the chloro group is also responsible to the absence of the interaction.

Although the interaction between the CH_2–X and the chloro groups in compounds **12**, **13**, and **14** was not spectroscopically detectable, the chemical properties of the latter two compounds do indicate the presence of such an interaction. The CH_2–Cl compound (**13**) afforded 1,2,3,4-tetrachloro-9-(2-hydroxyethyl)triptycene (**11**) on chromatography on silica gel. Namely, the hydrolysis of the CH_2–Cl group in **13** is very easy. Probably the stabilization of a chloronium cation (**15**)[11] or the incipient transition state (**16**) for the formation of the chloronium cation is responsible to the phenomenon. A similar situation is found for the tosylate (**14**) as well: chromatography of this compound on silica gel or standing a solution of **14** in tetrahydrofuran–hexane in atmosphere caused hydrolysis to afford **11**. Fragmentation of **13** in mass spectroscopy is a further support to the above discussion: those corresponding to the chloronium ion (**15**) and to the loss of a hydrogen chloride molecule were observed as strong peaks, whereas the molecular ion peaks were rather weak in this compound.



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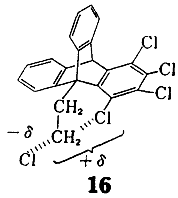

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Establishing that there is an attractive interaction between the CH_2–Cl and the chloro group, we can now discuss the population ratios of 1,2,3,4-tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene and 1,2,3,4-tetrachloro-9-(2-chloro-1-chloromethyl-1-methylethyl)triptycene.[12] As were discussed elsewhere,[13] the $\pm sc/ap$ ratio of 1,2,3,4-tetrachloro-9-(2-phenyl-1,1-dimethylethyl)triptycene is 0.48.[14] Being larger than a methyl, the chloromethyl group in 9-(2-chloro-1,1-dimethylethyl)- and 9-(2-chloro-1-chloromethyl-1-methylethyl)-1,2,3,4-tetrachlorotriptycenes should disfavor conformations in which the chloromethyl group is close to the peri-chloro group. In practice, however, the *ap* form of the latter which has two chloromethyl groups flanking the peri-chloro is unusually favored: $\pm sc/ap$ for the former is 0.96 and that for the latter is 1.80. We may attribute this anomaly to the attractive interaction between the CH_2–Cl and the chloro group.

Incipient Transition State for S_N2 *Reactions.* The above discussions reveal that the interaction as depicted by **16** is important. Then it implies that the molecules investigated here present models for the incipient transition state for S_N2 reactions. Here the peri-chloro or peri-methoxyl group acts as a nucleophile and the chloro or acyloxyl group in the 9-substituent as the leaving group in S_N2 reactions. This view is in conformity with the idea that pK_a values of acids corresponding to the leaving groups parallel with the leaving ability.[15] As we predicted before, the triptycene system has proved to be a good one in finding weak interactions which are otherwise not detectable. Dunitz *et al.* were able to show that the intramolecular nucleophile-carbonyl interaction could be taken as models for the nucleophilic addition to the carbonyl group.[16] We now add that the intramolecular interaction between a chloro or a methoxyl group and a CH_2–X group where X is an electronegative group can be considered as models for the incipient transition state of S_N2 reactions.

S_N2 reactions had originally been considered that it involves a single transition state.[17] However, data are accumulating for these days which suggest that S_N2 reactions may involve multisteps. Sneen *et al.* postulated that S_N2 reactions involve prior ionization from product distributions and rates of reaction studied as a function of nucleophile concentration in competitive substitutions by solvent and nucleophile.[18] Ion cyclotron resonance study by Brauman and coworkers revealed that organic halides form complexes with nucleophiles before reaching the transition state for the S_N2 reactions.[19] Roberts *et al.*, using high-pressure mass spectrometry, have shown that various alkyl halides form complexes with nucleophiles.[20] Hayami and his coworkers have shown that a mixture of an organic halide and a nucleophile shows a definite shift in ^{1}H NMR spectroscopy and attributed this phenomenon to the formation of a hydrogen bond.[21] Since our system is a primary halide or a primary alkyl ester, the phenomenon may be attributed to the hydrogen bonding as well. However, we take the fact shown by Roberts *et al.* that even *t*-butyl bromide or carbon tetrachloride can form a complex significant. We prefer to state that, during the course of S_N2 reactions, there is a point which is stable due to interactions between *n*-electrons of a nucleophile and the σ^* orbital of a substrate.

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