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Attractive Interactions between Carbonyls and Groups Bearing Lone-pair Electrons in Triptycene Systems[1)]

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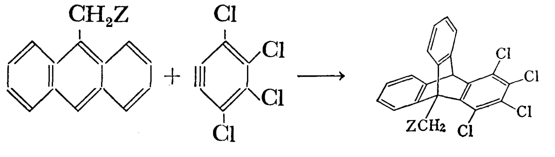
Compounds which carry a methoxyl or a chloro group in 1-position and a substituted carbonylmethyl group in 9-position of the triptycene system have been prepared to examine populations of rotamers by ^{1}H NMR spectra. The methoxy compounds favored the ±*sc* conformations, whereas the *ap* conformations were relatively favored in the chloro compounds. The results indicate that there are attractive interactions between the carbonyls and a methoxyl or a chloro group and are discussed from the electron-accepting ability of the carbonyl group and the electron-donating ability of the methoxyl and the chloro groups. An aldehyde group was apparently less able to interact with electron-donors than a ketone. This apparent anomaly was discussed from the intramolecular dipolar interactions.

Some five years ago, we encountered an unusual phenomenon that in a triptycene system a charge-transfer type interaction can occur between a phenyl and a dimethoxybenzo group, of which the former is acting as an electron-acceptor.[2)] It is not unusual to observe that a benzene derivative carrying strongly electronegative group(s) does act as an electron-acceptor; usually, benzene and its alkyl derivatives are considered to be an electron-donor. This unusual phenomenon may be considered to appear in the situation that two substituents located in the 1 and 9 positions of the triptycene skeleton are so close to each other that a weak, otherwise not-detectable interaction is made observable. This consideration aroused our interest in extending our work to find potential, weak interactions which are theoretically feasible but have not yet been observed experimentally.

Carbonyl groups are known to possess low-lying π^* orbitals[3)] which should facilitate interactions with easily ionizable electrons. Indeed, nitrogen-carbonyl interactions in medium-sized rings are well-documented.[4)] Bürgi *et al.*[5)] performed X-ray crystallographic studies of such compounds and suggested a pyramidal, rather than planar, configuration for the carbonyl group. Oxygen-carbonyl interactions, though much weaker, are also known.[6)] Although our system will not permit us to adopt a variety of electron donating groups because of difficulties in syntheses, yet it allows us at least to vary peri-substituents to some extent. This method of approach will enable us to explore possibilities of interactions involving less electron-donating systems, especially when a strongly electron-accepting group such as the carbonyl group is present in the bridgehead position. In addition, a variety of carbonyl moieties may be introduced into the bridgehead position. This introduction will afford information about the electron-accepting ability of various carbonyl derivatives and is intriguing in that the information made available so far is confined to ketones niteracting with nitrogen or oxygen atoms. Thus, we planned to introduce formyl, acetyl, methoxycarbonyl, and cyano groups as carbonyl modifications into the bridgehead position and methoxyl and chloro groups into the *peri*-position.

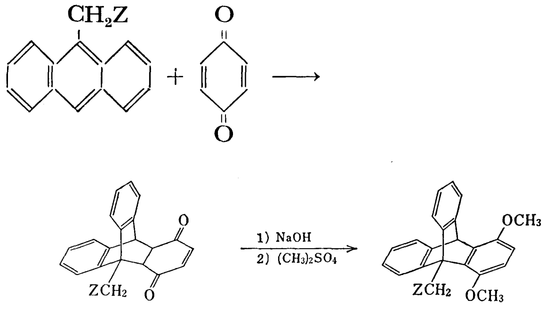
Syntheses of the compounds examined were carried out in essentially four ways. When appropriate 9-(substituted methyl)anthracenes were available, they were treated with tetrachlorobenzyne (Eq. 1).



(1)

1 $Z=COOCH_3$
2 $Z=CN$

In the syntheses of 1,4-dimethoxytriptycene derivatives, the anthracenes were treated with *p*-benzoquinone to afford Diels-Alder adducts (**3**) which were enolized by a base and were methylated with dimethyl sulfate (Eq. 2).

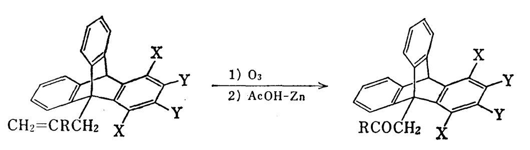


(2)

3

4 $Z=C(CH_3)=CH_2$
5 $Z=CN$
6 $Z=COOCH_3$
7 $Z=C\equiv CCH_3$

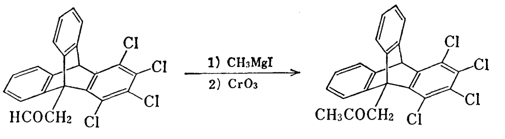
Some of the carbonyl derivatives were prepared by ozonolysis of the corresponding olefins (Eq. 3).



(3)

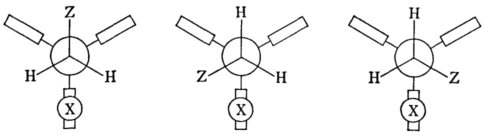
8 $X=OCH_3$, $Y=R=H$
9 $X=OCH_3$, $Y=H$, $R=CH_3$
10 $X=Y=Cl$, $R=H$
12 $X=CH_3$, $Y=R=H$
13 $X=Y=H$, $R=CH_3$

9-(Acetylmethyl)-1,2,3,4-tetrachlorotriptycene (**11**) was prepared from the corresponding aldehyde (**10**) by a Grignard reaction followed by oxidation (Eq. 4). The similar treatment of the methoxy derivative has failed to give the expected ketone because of cyclization.[7)]



10 **11** (4)

Detection of *ap* and ±*sc* isomers owes to the fact that, if the internal rotation about the C_9–C_{subst} bond is frozen on the NMR time scale, the methylene protons in the bridgehead give an AB quartet signal for the ±*sc* and a singlet for the *ap* in its proton NMR spectrum. The triptycene derivatives usually showed a broad signal due to the methylene protons in the 9-position at room temperature and the signal split into a set of AB quartet and a singlet in typical cases at low temperatures.



ap-form —*sc*-form +*sc*-form

Experimental

*9-(Formylmethyl)-1,4-dimethoxytriptycene (**8**).* To a solution of 1.6 g of 9-allyl-1,4-dimethoxytriptycene$^{7)}$ in 80 mL of dichloromethane was introduced ozone at −78 °C until the solution changed to faint blue. The solvent was removed below 30 °C and the residue was heated with 1.5 g of zinc dust, 30 mL of acetic acid, and 5 mL of water for 1 h. The acetic acid was removed and the residue was extracted with dichloromethane. Recrystallization of the product from benzene–hexane afforded the desired compound as crystals, mp 252—253 °C, in 91% yield. Found: C, 81.02; H, 5.57%. Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.65%. ^{1}H NMR ($CDCl_3$, δ): 3.63 (3H, s), 3.81 (3H, s), 3.60—4.60 (2H, br. m), 5.96 (1H, s), 6.54 (2H, s), 6.90—7.60 (8H, m), 9.96 (1H, t, J=1.8 Hz).

*9-(Formylmethyl)-1,2,3,4-tetrachlorotriptycene (**10**),* mp 223—224 °C, was similarly prepared from 9-allyl-1,2,3,4-tetrachlorotriptycene$^{8)}$ in 92% yield. Found: C, 60.71; H, 2.69; Cl, 32.10%. Calcd for $C_{22}H_{12}OCl_4$: C, 60.89; H, 2.79; Cl, 32.66%. ^{1}H NMR ($CDCl_3$, δ): 3.50—5.00 (2H, br. m), 6.11 (1H, s), 6.90—7.80 (8H, m), 9.40—10.5 (1H, br. m).

*9-(Formylmethyl)-1,4-dimethyltriptycene (**12**),* mp 227—228.5 °C, was similarly prepared by ozonation of 9-allyl-1,4-dimethyltriptycene.$^{8)}$ Found: C, 88.99; H, 5.96%. Calcd for $C_{24}H_{20}O$: C, 88.86; H, 6.21%. ^{1}H NMR ($CDCl_3$, δ): 2.46 (6H, s), 4.14 (2H, d, J=2 Hz), 5.69 (1H, s), 6.58 (1H, d, J=8 Hz), 6.62 (1H, J=8 Hz), 6.80—7.50 (8H, m), 9.92 (1H, t, J=2 Hz).

*1,4-Dimethoxy-9-(2-methyl-2-propenyl)triptycene (**4**).* A mixture of 2 g (82 mmol) of magnesium, 2 mL of 2-methyl-2-propenyl chloride, 5 mL of tetrahydrofuran, and a small amount of iodine was allowed to react. After the initial reaction subsided, 50 mL of tetrahydrofuran was added. To the mixture, 10 mL of 2-methyl-2-propenyl chloride in 50 mL of tetrahydrofuran was added in 3 h at room temperature. Anthrone (5 g or 26 mmol) was added to the mixture in small portions and the mixture was sitrred for 1 h. The mixture was treated with water and then with concentrated hydrochloric acid. The mixture formed two layers. The tetrahydrofuran layer was separated, dried over calcium chloride, and concentrated. The product was chromatographed on silica gel, hexane being used as an eluent. 9-(2-Methyl-2-propenyl)anthracene was obtained in 75% yield. ^{1}H NMR ($CDCl_3$, δ): 1.94 (3H, s), 4.26 (3H, apparent s), 4.78 (1H, br. s), 7.30—8.25 (8H, m), 8.35 (1H, s).

The anthracene (1.5 g) and 0.8 g of *p*-benzoquinone in 20 mL of toluene were heated under reflux under a nitrogen atmosphere for 3 h and allowed to stand for 24 h. A Diels-Alder adduct which crystallized out from the mixture was collected and dissolved in 50 mL of dioxane. The solution was treated with 0.5 g of sodium hydroxide in 10 mL of water and dimethyl sulfate was added until an intense color faded. The process was repeated a few times until the coloration could not be observed on addition of alkaline solutions. The mixture was poured into water and the resulted solid was collected. It was recrystallized from benzene–hexane, mp 199.5—200.5 °C. The yield was 81%. Found: C, 84.84; H, 6.40%. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.56%. ^{1}H NMR ($CDCl_3$, δ): 2.10 (3H, s), 3.62 (3H, s), 3.78 (3H, s), *ca.* 3.75 (2H), 4.21 (1H, br. s), 4.90 (1H, br. s), 5.89 (1H, s), 6.48 (2H, s), 6.80—7.50 (8H, m).

*9-(Acetylmethyl)-1,4-dimethoxytriptycene (**9**).* A solution of 1,4-dimethoxy-9-(2-methyl-2-propenyl)triptycene in dichloromethane was ozonized as above and the resulted ozonide was decomposed in the presence of zinc dust to give the product, mp 289.0—289.8 °C, in 73% yield. Found: C, 81.21; H, 5.87%. Calcd for $C_{25}H_{22}O_3$: C, 81.06; H, 5.98%. ^{1}H NMR ($CDCl_3$, δ): 2.47 (3H, s), 3.80 (3H, s), 3.60—4.70 (2H, br. m), 5.90 (1H, s), 6.51 (2H, s), 6.80—7.30 (8H, m). At −30 °C, the broad signal at *ca.* δ 4 became a distinct quartet, δ's being 4.60 and 3.81 and J being 17 Hz.

*9-(Acetylmethyl)triptycene (**13**),* mp 217—218 °C, was similarly prepared from 9-(2-methyl-2-propenyl)triptycene by ozonation. Found: C, 89.06; H, 5.97%. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85%. ^{1}H NMR ($CDCl_3$, δ): 2.55 (3H, s), 4.09 (2H, s) 5.49 (1H, s), 6.80—7.50 (12H, m).

*9-(Cyanomethyl)-1,4-dimethoxytriptycene (**5**),* mp 273—274 °C, was prepared as above: 9-(cyanomethyl)anthracene$^{9)}$ and *p*-benzo quinone were allowed to react and the product was methylated. The yield was 78%. Found: C, 81.54; H, 5.28; N, 4.26%. Calcd for $C_{24}H_{19}NO_2$: C, 81.57; H, 5.42; N, 3.96%. ^{1}H NMR ($CDCl_3$, δ): 3.80 (6H, s), 4.18 (2H, br. s), 5.92 (1H, s), 6.58 (2H, s), 6.90—7.70 (8H, m).

*9-(Methoxycarbonylmethyl)-1,4-dimethoxytriptycene (**6**).* 9-(Methoxycarbonylmethyl)anthracene was prepared from the corresponding carboxylic acid$^{10)}$ by the usual esterification. An adduct between 9-(methoxycarbonylmethyl)anthracene and *p*-benzoquinone was prepared as above and converted to the triptycene derivative, mp 223.8—224.8 °C. The yield was 85%. Found: C, 77.98; H, 5.72%. Calcd for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74%. ^{1}H NMR ($CDCl_3$, δ): 3.62 (3H, s), 3.78 (3H, s), 3.80 (3H, s), 3.40—4.40 (2H, br. m), 6.53 (2H, s), 6.80—7.60 (8H, m).

*9-(2-Butynyl)-1,4-dimethoxytriptycene (**7**).* To a solution of 2.8 g (32 mmol) of 1-chloro-2-butyne and 5.6 g (29 mmol) of anthrone in 150 mL of ethanol, was added a solution of 1.7 g (30 mmol) of potassium hydroxide in 30 mL of methanol in 3 h under a nitrogen atmosphere. The mixture was stirred for an additional hour after the addition. The solvent was evaporated and the residue was taken up in dichloromethane. The solution was washed with water and evaporated. The residue was taken up in 100 mL of methanol and to the solution was added 0.7 g of sodium borohydride in 30 mL of methanol. The solvent was evaporated and the residue was shaken with dichloromethane and dilute hydrochloric acid. The organic layer was evaporated and the residue was chromatographed on a silica-gel column. The crude anthracene derivative thus obtained was treated with *p*-benzoquinone and then converted to the triptycene derivative. The desired compound was obtained by recrystallization from benzene–hexane in 42% yield based on 1-chloro-2-butyne. Mp 253.0—253.3 °C. Found: C, 85.14; H, 5.89%. Calcd for $C_{26}H_{22}O_2$: C, 85.22, H, 6.05%. ^{1}H NMR ($CDCl_3$, δ): 1.73 (3H, t, $J=2.5$ Hz), 3.69 (3H, s), 3.75 (3H, s), 4.13 (2H, br. q, $J=2.5$ Hz), 5.89 (1H, s), 6.80—8.00 (8H, m).

*9-(Acetylmethyl)-1,2,3,4-tetrachlorotriptycene (**11**).* To a Grignard solution prepared by adding methyl iodide in ether until 0.5 g (21 mmol) of magnesium disappaered, was added 0.9 g (21 mmol) of 9-(formylmethyl)-1,2,3,4-tetrachlorotriptycene in 20 mL of dichloromethane in 20 min. After further 10 min, the mixture was decomposed with dilute hydrochloric acid. The organic layer gave 93% 9-(2-hydroxypropyl)-1,2,3,4-tetrachlorotriptycene, mp 232—234 °C. High resolution MS (observed M$^+$): 447.9933, 449.9917, 451.9940, and 453.9963. $C_{23}H_{16}OCl_4$ requires 447.9956, 449.9927, 451.9897, and 453.9868. The relative intensities of the peaks agreed well with those calculated from the natural abundance of ^{35}Cl and ^{37}Cl. ^{1}H NMR ($CDCl_3$, δ): 1.69 (1H, br. s), 1.77 (3H, d, $J=6.51$ Hz), 3.81 (2H, m), 4.31 (1H, m), 6.03 (1H, s), 7.00—7.76 (7H, m), 8.49 (1H, m).

The hydroxylic compound (0.5 g) in 30 mL of acetone–dichloromethane (2:1) was oxidized at 0 °C by mixing with 0.42 g of chromium(VI) oxide, 0.2 mL of sulfuric acid, and 0.2 mL of water for 2 h. The solvent was evaporated and the mixture was extracted with dichloromethane. The organic layer was washed with water and evaporated. The residue was recrystallized from tetrahydrofuran–hexane to afford a pure sample, mp 276—277 °C, in 95% yield. Found: C, 61.82; H, 2.94; Cl, 31.51%. Calcd for $C_{23}H_{14}OCl_4$: C, 61.64; H, 3.15; Cl, 31.64%. ^{1}H NMR ($CDCl_3$, δ): 2.56 (3H, s), 3.40—5.10 (2H, br. q), 6.01 (1H, s), 6.80—7.70 (8H, m).

*9-(Methoxycarbonylmethyl)-1,2,3,4-tetrachlorotriptycene (**1**).* To a boiling solution of 0.73 g of 9-(methoxycarbonylmethyl)-anthracene and 0.8 mL of isopentyl nitrite in 10 mL of dichlomethane, was added a solution of 0.85 g of tetrachloroanthranilic acid[11] in 5 mL of acetone in 1.5 h. The mixture was heated for further 1 h and filtered while hot to remove an acridone derivative. The solvent was evaporated and the residue was chromatographed to give a mixture of a 1,4-adduct and the desired 9,10-adduct. Since the solubility of the desired product in carbon tetrachloride was very low, the solvent could be used for separation. Recrystallization from tetrahydrofuran–hexane gave a pure sample, mp 247.3—248.0 °C, in 8% yield. Found: C, 59.25; H, 2.95%. Calcd for $C_{23}H_{14}O_2Cl_4$: C, 59.52; H, 3.04%. ^{1}H NMR ($CDCl_3$, δ): 3.81 (3H, s), 3.5—5.2 (2H, br. m), 6.05 (1H, s), 7.00—7.80 (8H, m).

*9-(Cyanomethyl)-1,2,3,4-tetrachlorotriptycene (**2**),* mp >300 °C, was prepared similarly from 9-(cyanomethyl)anthracene and tetrachlorobenzyne. Found: C, 61.58; H, 2.39; N, 3.51; Cl, 32.56%. Calcd for $C_{22}H_{11}NCl_4$: C, 61.29; H, 2.57; N, 3.25; Cl, 32.89%. ^{1}H NMR ($CDCl_3$, δ): 4.48 (2H, br. s), 6.09 (1H, s), 7.00—7.80 (8H, s).

9-(2-Hydroxypropyl)-1,4-dimethoxytriptycene. 9-(Formylmethyl)-1,4-dimethoxytriptycene was treated with a Grignard solution prepared from magnesium and methyl iodide in ether. The reaction gave 9-(2-hydroxypropyl)-1,4-dimethoxytriptycene, mp 224—225 °C. Found: C, 80.69; H, 6.31%. Calcd for $C_{25}H_{24}O_3$: C, 80.62; H, 6.49%. ^{1}H NMR ($CDCl_3$, δ): 1.50 (3H, d, $J=7$ Hz), 2.55 (1H, m), 3.45 (2H, d, $J=7$ Hz), 3.70 (3H, s), 3.77 (3H, s), 4.65 (1H, m), 5.89 (1H, s), 6.90—8.15 (8H, m).

Table 1. ±*sc*/*ap* ratios of 1,4-dimethoxytriptycene derivatives

Compound	9-Substituent	±*sc*/*ap*	Observed temp/°C
9	CH_2COCH_3	≥10	−30
6	CH_2COOCH_3	≥10	−30
8	CH_2CHO	≥10	−45
5	CH_2CN	1.5	−50
7	$CH_2C{\equiv}CCH_3$	0.1	−60

Table 2. ±*sc*/*ap* ratios of 1,2,3,4-tetrachlorotriptycene derivatives

Compound	9-Substituent	±*sc*/*ap*	Observed temp/°C
11	CH_2COCH_3	≥10	−20
1	CH_2COOCH_3	6	−40
10	CH_2CHO	1.1	−20
2	CH_2CN	0	−40

Spectral Measurements and Population Determinations. ^{1}H NMR spectra were obtained on a Hitachi R 20B spectrometer, operating at 60 MHz and equipped with a temperature variation accessory, and ^{13}C NMR spectra on a JEOL FX-60 spectrometer operating at 15 MHz. Low temperatures were calibrated by the chemical shift difference of methanol protons. Infrared spectra were obtained on a JASCO DS-402G spectrometer with a CaF_2 cell of 0.05 mm thickness. All the spectra were obtained as solution in chloroform or chloroform-*d* unless otherwise stated. Populations of rotamers were obtained by integration of the methylene signals (an AB quartet and a singlet) in the ^{1}H NMR spectra. Where proton signals, other than those of the 9-CH_2, which are split for the respective rotamers at low temperatures are available, those were used to obtain the population ratios, because they give usually clearer results. Examples are formyl protons of **8** and **10**, and dimethoxybenzo protons of **5**.

X-Ray Crystallography. Crystals of 9-(formylmethyl)-1,4-dimethyltriptycene (**12**) suitable for the X-ray diffraction study were grown from hexane–benzene. A crystal of 0.4 mm×0.4 mm×0.2 mm size was mounted on a Rigaku Automatic Structure Analysis System RASA-II and data were obtained with graphite-monochromated Cu $K\alpha$ radiation. A total of 3576 independent reflections were observed up to 135° in 2θ, and 2575 of the total was judged effective ($F \geq 2\sigma$). The crystal was orthorhombic with space group *Pbca*, having the following crystal data: $a=15.374(4)$, $b=9.801(2)$, $c=23.112(3)$, $Z=8$, $D_x=1.24$ g cm^{-3}. The structure was solved by the direct method with the use of the MULTAN program. The final *R* factor was 7.0% including hydrogens.

Results and Discussion

Population ratios obtained by integrating ^{1}H NMR signals due to the ±*sc* and the *ap* forms are listed in Tables 1 and 2.

The data in Table 1 suggest that, if an electron-accepting group is an aldehyde, a ketone, or an ester and an electron-donor is a methoxyl group, the *ap* form is not detectable. Since the steric effect is expected to disfavor the ±*sc* form, as discussed later, the results indicate that there exists a strong attractive interaction between those carbonyl groups and a methoxyl group in proximity.

In contrast, if the electron-accepting group is a nitrile, the population ratio ±*sc*/*ap* is greatly decreased. Since the ±*sc*/*ap* ratio is 2.0 from the statistical stand point, the value of 1.5 may be argued that there is no attractive interaction between a cyano and a methoxyl group. It is especially so, if one takes into account a fact that 9-ethyl-1,4-dimethoxytriptycene, in which no attractive interaction is apparent, is reported to give ±*sc*/*ap* ratio of 0.7.[12] In order to diagnose the presence or absence of the attractive interactions in the nitrile (**2**), we have used a model compound. Since the carbon atom in the cyano group is triply bonded to a nitrogen, an acetylenic bond may be used as a model for the cyano group: an acetylene group is sterically of a similar size with a cyano group but the electron-accepting ability is far less than the cyano. As is seen in Table 1, the ±*sc*/*ap* ratio of 9-(2-butynyl)-1,4-dimethoxytriptycene (**7**) is only 0.1. Thus we conclude that there is an attractive interaction, although weak, between a cyano and a methoxyl group in this system. Since the steric effect disfavors the ±*sc* form, the observed value becomes less than the statistical, reflecting the weakness of the interaction.

As to a model for other compounds, an allyl group may be used as a model for a formylmethyl group: the steric sizes of these two groups are similar as far as we discuss the steric interactions between those and the methoxyl group in 1 position, because the main effect is given by CH= groups in both cases, and the electronic interaction should be minimal between the methoxyl group and the vinyl group. The population ratio ±*sc*/*ap* of 9-allyl-1,4-dimethoxytriptycene was 0.7 to indicate that the interaction between the formyl and the methoxyl group in compound **8** is fairly strong.

The data in Table 2 are indicative of several interesting points. The most apparent phenomenon is that the ±*sc*/*ap* ratios are greatly diminished relative to the methoxy derivatives, although the existence of an attractive interaction is certain. ^{13}C NMR data obtained with $CDCl_3$ solutions were in accord with the indication by the ^{1}H NMR spectra (chemical shifts given from TMS): **1** showed a broad singlet for the methylene carbon at 34 ppm and two singlets at 170.6 and 171.7 ppm for the carbonyl carbon at −50 °C, whereas **10** gave two singlets both for methylene (41.0 and 42.4 ppm) and for carbonyl (200.7 and 202.4 ppm) carbons. Being a weak electron-acceptor, the cyano group of **2** does not make it possible to show a sign of existence of the ±*sc* isomer. A similar phenomenon was found in more congested systems.[13] The results are in conformity with the expectation from the ionization potentials of 1,4-dimethoxybenzene[14] and 1,2,3,4-tetrachlorobenzene,[15] the former being lower than the latter.

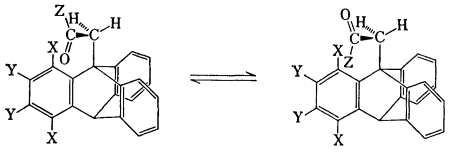
Since we are looking at the population ratios as the results of combination of electronic, steric and other effects, we may not forget the steric effect. The chloro group is known to be a little larger than the methoxyl group, if the steric effect is given by the oxygen atom only in the latter. Therefore, the steric effect of the chloro group disfavors the ±*sc* form as well, relative to the methoxyl group. The critical case is the formyl compound (**10**), since its population ratio is lower than the statistical value: there remains a problem whether we should conclude that the attractive interaction is apparent in this compound. We used 9-(formylmethyl)-1,4-dimethyltriptycene (**12**) as a model compound which has a substituent of a similar size in the peri-position, yet the electronic effect between the formyl and the substituent in the peri-position is negligible: a methyl group is known to be a little larger than a chloro group but the difference is not large. The results show that **12** exists as the *ap* form exclusively. From these, we conclude that there is an attractive interaction between the chloro and the formyl group in this system.

Table 3. Carbonyl stretching absorptions

Compound	*peri*-Substituent	Bridgehead Substituent	$\nu_{C=O}/cm^{-1}$
10	Cl	CH_2CHO	1725
1	Cl	CH_2COOCH_3	1731, 1754
11	Cl	CH_2COCH_3	1741
8	OCH_3	CH_2CHO	1720
6	OCH_3	CH_2COOCH_3	1722, 1751
9	OCH_3	CH_2COCH_3	1742
13	H	CH_2COCH_3	1732

The third and the most striking feature of the data in Table 2 is the fact that the apparent strength of the interaction between the formyl and the chloro groups is weaker than those involving a methoxycarbonyl or an acetyl group. This is rather astonishing since, in ordinary organic reactions, aldehydes are more reactive and are consequently considered to be more electrophilic than ketones and esters. There must be reasons causing this anomalous phenomenon.

When the molecules like the aldehydes (**8**, **10**, and **12**), the ketones (**9** and **11**), and the esters (**1** and **6**) are considered, the stereoisomerism about the C_{CO}–C_{α} bond is possible in addition to that about the C_9–C_{subst} bond. The possible conformations of the carbonyl moiety are depicted in the following scheme, the ±*sc* conformations being taken as examples. Indeed, the rotational isomerism of the esters of a similar system has been found by ^{1}H NMR and IR spectra.[16] In order to obtain information about the conformation of the carbonyl moieties, the infrared spectra were examined. The results are shown in Table 3.



O-inside *O*-outside

A peculiarity is immediately singled out from the

Table 4. Atomic positional parameters ($\times 10^4$) with estimated standard deviations in parentheses and anisotropic temperature factors ($\times 10^4$)[a)]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	4490 (2)	2928 (4)	2528 (1)	47	92	14	−1	0	6
C(2)	3840 (3)	3392 (4)	2914 (1)	58	115	12	−3	4	5
C(3)	3125 (3)	4111 (4)	2733 (2)	49	124	17	−2	8	−4
C(4)	2994 (2)	4409 (4)	2143 (1)	39	90	16	1	5	−2
C(4a)	3621 (2)	3944 (3)	1762 (1)	32	67	14	−4	1	2
C(5)	4428 (2)	6136 (3)	639 (1)	41	83	13	−2	−1	3
C(6)	5237 (2)	6721 (4)	529 (1)	48	94	13	−11	2	6
C(7)	5985 (2)	6092 (4)	725 (2)	38	124	16	−19	2	4
C(8)	5949 (2)	4851 (4)	1024 (1)	32	109	14	−5	0	1
C(8a)	5143 (2)	4247 (3)	1119 (1)	33	84	10	−2	1	0
C(9)	4970 (2)	2869 (3)	1421 (1)	31	80	12	6	0	4
C(9a)	4369 (2)	3229 (3)	1941 (1)	35	70	12	−3	1	2
C(10)	3566 (2)	4172 (3)	1109 (1)	28	75	13	0	0	3
C(10a)	4388 (2)	4911 (3)	939 (1)	33	73	10	−2	0	−1
C(11)	3639 (2)	2771 (3)	836 (1)	31	76	12	−4	3	2
C(12)	4373 (2)	2058 (3)	1009 (1)	35	75	12	−4	4	3
C(13)	4494 (2)	731 (4)	807 (2)	44	85	18	4	6	−1
C(14)	3893 (3)	167 (4)	418 (2)	57	90	20	−15	8	−9
C(15)	3178 (3)	904 (4)	239 (2)	46	113	17	−25	3	−5
C(16)	3037 (2)	2211 (4)	453 (1)	37	96	13	−17	1	1
C(17)	5248 (3)	2149 (5)	2793 (2)	71	189	14	36	−2	16
C(18)	2207 (3)	5207 (5)	1957 (2)	51	164	24	33	9	−2
C(19)	5819 (2)	2104 (4)	1547 (2)	34	110	17	15	0	7
C(20)	6332 (2)	1822 (4)	985 (2)	28	111	46	19	5	−10
O	6937 (2)	1136 (5)	982 (2)	70	367	43	43	12	−1

a) The form of the anisotropic temperature factor is: $T=\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-2B_{12}hk-2B_{13}hl-2B_{23}kl)$.

data in Table 3. Whereas the esters show two absorptions, other carbonyls give only one absorption. Although it is clear that there are two conformations, *O*-inside and *O*-outside, for the esters from the analogy of the similar system,[16)] it is not apparent that other carbonyls exist in a single conformation. Especially because there is only one band in spite of the fact that at least there are two conformations concerning the rotation about the C_9–C_{subst} bond, there is a possibility that the infrared spectra cannot distinguish the rotamers which are actually present. The infrared spectra do suggest, however, that the data in Table 3 are anomalous in that the aldehydes show absorptions due to the C=O stretching at lower frequencies than those of ketones. This is the opposite of normal trends[17)] and the anomaly is caused because the ketones absorb at abnormally high frequencies.

There may be various reasons for raising frequencies of C=O stretching vibrations. The most commonly encountered reason is the syn-parallel arrangement of two strong dipoles. For example, 2-halocyclohexanone is known to show C=O stretching absorptions at higher frequencies when the halogen is equatorial.[18)] This kind of effect is considered to be stronger if the conformation is ±*sc* than the case of *ap* conformation in the systems examined here because the distance between the two parallel dipoles, C–Cl and C=O, is smaller in the former. Thus if the diople interaction is the cause for the IR results, the ketones should take *O*-inside conformations and the aldehydes *O*-outside conformations. Another possible cause is the steric effect. 2,6-Di-*t*-butylphenols are known to show abnormally high frequencies for the O–H stretching vibration[19)] and the shift to the high frequency is attributed to the steric effect of the *t*-butyl groups. Schleyer *et al.* used this interpretation for the assignment of the two O–H stretching absorptions of cyclohexanol derivatives.[20)] Birdcage compounds are known to show ν_{C-H} absorptions at abnormally high frequencies[21)] and bicyclo[3.3.1]nonane systems show high C–H stretching absorptions as well.[22)] If it is the *O*-inside conformation, the carbonyl stretching vibration will absorb at higher frequencies, as judged from the analogous phenomena presented above. Then the ketones take *O*-inside conformations and the aldehyde *O*-outside conformations, if the steric effect is the cause.

These discussions lead to a prediction that, if we can see the real conformation of these compounds and if the carbonyl absorptions correspond to one conformation, we can see the real reason for the phenomenon. Consideration of the steric effect gives, although not definite, a clue for judging the probability of the two possible causes. The reason for the existence of the two conformers, *O*-inside and *O*-outside, of the esters in the literature[16)] is the similar bulkinesses of a methoxyl and an oxo group of the ester moiety. If the bulkiness of one side of a plane is much different from the other side, a conformation, in which the bulkier side is outside of the triptycene skeleton, is favored to a great extent relative to another which

Table 5. Bond lengths and bond angles involving nonhydrogen atoms of **12** with estimated standard deviations in parentheses

Bond lengths(l/Å)			
C(1)-C(2)	1.4147(52)	C(8a)-C(10a)	1.3895(47)
C(1)-C(9a)	1.4015(44)	C(9)-C(9a)	1.5556(42)
C(1)-C(17)	1.5207(58)	C(9)-C(12)	1.5443(43)
C(2)-C(3)	1.3712(56)	C(9)-C(19)	1.5335(46)
C(3)-C(4)	1.4079(49)	C(10)-C(10a)	1.5075(44)
C(4)-C(4a)	1.3833(46)	C(10)-C(11)	1.5143(45)
C(4)-C(18)	1.5031(56)	C(11)-C(12)	1.3980(45)
C(4a)-C(9a)	1.4094(44)	C(11)-C(16)	1.3821(45)
C(4a)-C(10)	1.5295(43)	C(12)-C(13)	1.3947(47)
C(5)-C(6)	1.3939(50)	C(13)-C(14)	1.4027(54)
C(5)-C(10a)	1.3874(45)	C(14)-C(15)	1.3791(56)
C(6)-C(7)	1.3807(52)	C(15)-C(16)	1.3909(53)
C(7)-C(8)	1.3996(52)	C(19)-C(20)	1.5448(59)
C(8)-C(8a)	1.3895(47)	C(20)-O	1.1475(57)
C(8a)-C(9)	1.5443(43)		
Bond angles(ϕ/°)			
C(2)-C(1)-C(9a)	116.7(0.3)	C(12)-C(9)-C(19)	111.9(0.3)
C(2)-C(1)-C(17)	116.7(0.3)	C(1)-C(9a)-C(4a)	119.8(0.3)
C(9a)-C(1)-C(17)	126.6(0.3)	C(1)-C(9a)-C(9)	128.4(0.3)
C(1)-C(2)-C(3)	126.6(0.3)	C(4a)-C(9a)-C(9)	111.8(0.3)
C(2)-C(3)-C(4)	122.6(0.3)	C(4a)-C(10)-C(10a)	106.3(0.2)
C(3)-C(4)-C(4a)	116.6(0.3)	C(4a)-C(10)-C(11)	106.0(0.2)
C(4a)-C(4)-C(18)	123.4(0.3)	C(10a)-C(10)-C(11)	105.9(0.2)
C(4)-C(4a)-C(9a)	123.1(0.3)	C(5)-C(10a)-C(8a)	121.0(0.3)
C(4)-C(4a)-C(10)	122.8(0.3)	C(5)-C(10a)-C(10)	125.6(0.3)
C(9a)-C(4a)-C(10)	114.0(0.3)	C(8a)-C(10a)-C(10)	113.3(0.3)
C(6)-C(5)-C(10a)	119.2(0.3)	C(10)-C(11)-C(12)	112.7(0.3)
C(5)-C(6)-C(7)	119.9(0.3)	C(10)-C(11)-C(16)	125.7(0.3)
C(6)-C(7)-C(8)	121.1(0.3)	C(12)-C(11)-C(16)	121.5(0.3)
C(7)-C(8)-C(8a)	118.9(0.3)	C(9)-C(12)-C(11)	113.9(0.3)
C(8)-C(8a)-C(9)	126.7(0.3)	C(9)-C(12)-C(13)	127.3(0.3)
C(8)-C(8a)-C(10a)	119.7(0.3)	C(11)-C(12)-C(13)	118.7(0.3)
C(9)-C(8a)-C(10a)	113.5(0.3)	C(12)-C(13)-C(14)	119.5(0.3)
C(8a)-C(9)-C(9a)	104.7(0.2)	C(13)-C(14)-C(15)	120.8(0.3)
C(8a)-C(9)-C(12)	105.9(0.2)	C(14)-C(15)-C(16)	120.0(0.3)
C(8a)-C(9)-C(19)	111.5(0.3)	C(11)-C(16)-C(15)	119.4(0.3)
C(9a)-C(9)-C(12)	103.9(0.2)	C(9)-C(19)-C(20)	111.3(0.3)
C(9a)-C(9)-C(19)	118.0(0.3)	C(19)-C(20)-O	121.6(0.5)

has the bulkier group inside.[23] Since the sizes of a hydrogen and an oxo group in a formyl group are different to a large extent, the formyl group in compounds **8**, **10**, and **12** will take an *O*-outside conformation. Similar consideration suggests that the acetyl group in compounds **9**, **11**, and **13** will take *O*-inside conformations. Thus the steric effect hypothesis is more likely than the dipole interaction hypothesis.

If the charge-transfer type interaction is responsible to the observed population ratios, the interacting carbonyl groups are expected to have elongated C=O bond, thus shifting the carbonyl stretching frequencies to the low side. The fact that the C=O stretching absorption of compound **8** is at a little lower frequency than that of compound **10** may be taken as an indication of this effect, but we failed to obseve any bifurcation of absorptions in the ordinary measurements. The tetrachloroaldehyde (**10**) was shown to exist as a mixture of almost 1 : 1 *ap* and ±*sc* conformations. Therefore this compound was considered to have the highest possibility of showing two bands in the $\nu_{C=O}$ region. A detailed study of this compound did show two absorptions at 1725 and 1720 cm^{-1}, the latter being a shoulder. This fact suggests that the carbonyls in these compounds absorb at similar frequencies if their types, aldehydes or ketones, are given, irrespective to the presence or absence of the interaction. Alternatively, the interaction is not so strong as to cause a large shift in C=O stretching vibrations in these compounds.

The final and strongest support to the conformation of the ketones and the aldehydes can be obtained by X-ray crystallography. Accordingly X-ray-diffraction study was carried out on crystals of 9-(acetylmethyl)-1,2,3,4-tetrachlorotriptycene (**11**)[24] and 9-(formylmethyl)-1,4-dimethyltriptycene (**12**). The details of

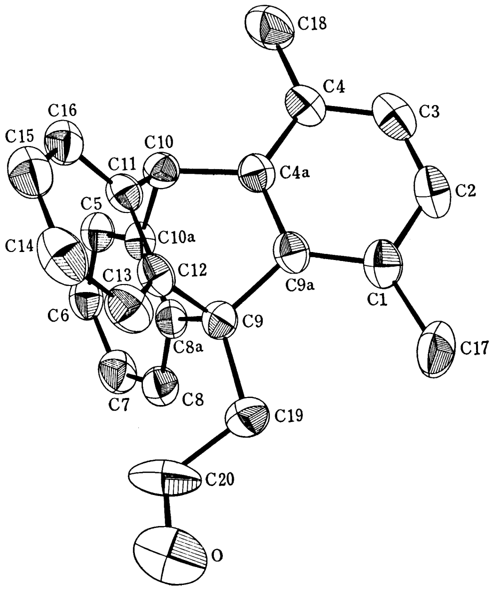


Fig. 1. An ORTEP diagram of 1,4-dimethyl-9-(formylmethyl)triptycene.

the results of the former will be described elsewhere but it is clear that the acetyl group takes an *O*-inside conformation both in ±*sc* and *ap* forms of **11**. The results of the X-ray structural determination of compound **12** are shown in Tables 4 and 5 and in Fig. 1, where carbon atoms are numbered, as shown in the figure for the convenience of discussion.

The feature of the structure of **12** is that the formyl group takes the *O*-outside conformation among others which follow. The steric strain caused by the substituents in 1- and 9- positions is released by deformation of the molecule throughout, as was the case of 9-*t*-butyl-1,2,3,4-tetrachlorotriptycene.[25] Although ∠C(4a)–C(4)–C(18) is widened from the normal value due to the steric effect of C(10), the angle is smaller than ∠C(9a)–C(1)–C(17). The 9-substituent is tilted against C(17) as well to relieve the steric strain. Consequently, ∠C(19)–C(9)–C(9a) is considerably widened. It is interesting to note also that the trigonal pyramid, of which apex is C(9) and base atoms are C(9a), C(8a), and C(12), has a smaller apex angle than that composed of an apex of C(10) and a base of C(4a), C(10a), and C(11). This may be attributed to the steric effect caused by the two substituents. The steric strain is also eased by widening angles, which are made by the bonds connecting C(9) (and C(10) to a lesser extent) and aromatic rings, and the aromatic C–C's which are outside of the triptycene skeleton. Finally the lengths of the bonds connecting C(9) with aromatic carbons are definitely longer than those connecting C(10) with aromatic carbons, although the degree of elongation is much less than those in 9-*t*-butyl-1,2,3,4-tetrachlorotriptycene. The dihedral angles made by benzene rings are as follows: $\phi(C_{8a}\text{–}C_9\text{–}C_{12}) = 121.0°$, $\phi(C_{9a}\text{–}C_9\text{–}C_{12}) = 119.4°$, $\phi(C_{8a}\text{–}C_9\text{–}C_{9a}) = 119.5°$. The hydrogen of the aldehyde group, being small, does not seem to affect the dihedral angle, in contrast to the case of 9-(acetylmethyl)-1,2,3,4-tetrachlorotriptycene.[24] Although we do neither have any piece of evidence that the structure in the solid state is retained in solutions, nor that the structure is common in all compounds of the same type, we may conclude, from pieces of evidence given by various sources discussed above, that the aldehydes take *O*-outside conformations and the ketones *O*-inside conformations.

After establishing the conformations of the aldehydes and the ketones, we may now discuss the cause for the unexpected stability of the ±*sc* conformation of ketone **11**. In the ketone, if the acetyl group takes the *O*-inside conformation, we realize that the bond dipoles of the C=O and the C–Cl in the *peri*-position are anti-parallel in the ±*sc* conformation. In contrast, the bond dipoles of the C=O in the aldehyde (**10**) and the C–Cl in the *peri*-position are syn-parallel. These arrangements of the dipoles will make the ±*sc* conformation of **10** less stable in nonpolar solvents and that of **11** favorable in the same solvents: the relative arrangements of the bond dipoles are the same in *ap* conformations as well, but the long distance will diminish the interaction probably due to the solvent intervention. Although the charge-transfer itself is of polar nature, this polar effect is very small on the populations, probably because of the weakness of the interaction. In conclusion, the apparently unusual phenomenon that the acetyl group stabilizes ±*sc* conformations more than the formyl group is mainly caused by the dipolar interaction within the molecules. The methoxycarbonyl compound (**1**) may be in the same category with ketone **11** because it can take the *O*-inside conformation.

Further support for the above discussion should be obtained by examining the population ratios in solvents of different polarity. Thus population ratios of compounds **5** and **10** were examined in mixed solvents. The examination of the populations of the ketones and others was abandoned because the populations were lop-sided. The results are shown in Table 6.

It may be difficult to compare the polarities of rotamers of compound **5** but we can assume that the group dipoles of the cyano and the methoxyl in the *ap* conformation is close to syn-parallel, because the methoxyl group is within the plane of the benzo-bridge and the methyl of the methoxyl group will be away from the bridgehead substituent: this conformation of the methoxyl group is probable if one considers the steric effect. Thus the *ap* form will be more polar than the ±*sc* form. The population ratios in solvents of different polarity agree with these considerations. The behaviors of the chloro-aldehyde (**10**) are in accord with expectation as well. Being more polar than the *ap* form, the ±*sc* conformation is favored in the more polar solvents.

Finally we wished to obtain thermodynamic parameters of the compounds examined. Unfortunately, however, it was not possible for many compounds to do so because of the lop-sided population of one isomer. The only compound we could examine its populations at various temperatures was 9-(formylmethyl)-1,2,3,4-tetrachlorotriptycene (**10**). The ±*sc*/*ap* ratios of this compound were 1.1 at 0, −20, and −50 °C: the populations were temperature independent. The

Table 6. ±*sc*/*ap* ratios of triptycenes in various solvents

Compound	Substituents		±*sc*/*ap*	Temperature	Solvent
	9-	*peri*-		°C	(vol/vol)
10	CH_2CHO	Cl	1.1	−20	$CDCl_3$
			1.5	−25	$CDCl_3$-$(CD_3)_2CO$ (2 : 3)
			1.7	−25	$CDCl_3$-CD_3CN (7 : 10)
5	CH_2CN	OCH_3	1.5	−50	$CDCl_3$
			1.3	−45	$CDCl_3$-$(CD_3)_2CO$ (5 : 6)
			1.2	−45	$CDCl_3$-CD_3CN (5 : 7)

ΔH and ΔS were obtained as 0.0 kcal/mol (1 kcal= 4.18 J) and +1.0 e.u.

In conclusion we wish to point out that, for the first time, we have demonstrated that attractive interactions can be detected experimentally between carbonyl moieties, like cyano, formyl, and methoxycarbonyl, and a chloro or a methoxyl group. It is especially noteworthy because the presence of the interaction between ketones and oxygen was questionable by means[26,27] other than X-ray crystallography.[6,28] This finding is possible because two groups in *peri*- and bridgehead positions are well within the sum of van der Waals radii.[25] Therefore this triptycene system is considered very good in revealing an interaction experimentally which is not otherwise possible to do so because of its weakness. We wish to search other weak interactions with the use of this system in the future. Nitrogen carbonyl interactions were studied by X-ray crystallography and treated as an incipient transition state for the addition of a nucleophile to a ketone.[29] This work extends the possibility of studying the transition state of other systems. This aspect of the present work may have further extension.

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