Restricted Rotation Involving the Tetrahedral Carbon. XIV. Conformational Equilibria and Attractive Interactions in Substituted 9-Benzyltriptycenes[1]

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Several 9-benzyltriptycene derivatives were prepared by addition of benzynes to 9-benzylanthracenes. Rotation about the C_9–C_{benzyl} bond of compounds with a substituent at a *peri*-position to the benzyl group was found to be frozen at low temperatures on the NMR time scale but not at room temperature. In contrast, compounds with two substituents at two *peri*-positions to the benzyl group showed a frozen rotation about the C_9–C_{benzyl} bond at room temperature. Distribution of the conformers, as judged from the PMR intensities, showed preference to the *dl*-isomers in spite of the fact that they are the ones which are highly disfavored by steric effects. Interpretation of the phenomenon was based on the fact that attractive interactions, mainly charge-transfer type, exist between the substituted benzo group in the triptycene skeleton and the benzene ring in the benzyl group.

Many works have been carried out to elucidate the intramolecular interaction in cyclohexanes,[2] heterocyclic systems,[3] and substituted ethanes.[4] They disclosed that the steric interaction and hydrogen bonding are the important factors in determining conformational equilibria. The steric interaction may comprise van der Waals interactions including lone-pair-lone-pair interactions and dipole-dipole interactions. However, we come across examples for which the simple concept of nonbonding interelectronic repulsion does not give correct prediction.[5] In conformational equilibria, anomeric effect[6] and gauche effect[7] are notable examples. Attempts have been made to rationalize these effects on the basis of classical electrostatic interactions or the electron delocalization, but the origin of attractive interaction has remained ambiguous for a long time.

Weak attractive interactions may be present in many cases but they are usually overshadowed by strong repulsive interactions and not detectable. However, if the atoms and groups are held together at the closest proximity and other interactions are surpressed to minimum, there may be a possibility to find such interactions.[8] 9-Substituted triptycenes provide good examples since the substituents at 9- and peri-positions are held within the sum of the respective van der Waals radii.

9-Isopropyltriptycene derivatives exist as conformers of the least repulsion.[9] Thus the isopropyl group is too large to exhibit a weak attractive interaction. A group of the RCH_2 type will give less steric repulsions and there is a possibility that, if group R can possess attractive interaction with a substituent at a peri-position, such a conformation would be favored. Thus it is of interest to study the case of 9-benzyltriptycene derivatives since the phenyl group in the benzyl has relatively low-lying antibonding orbitals which may interact with bonding electrons of high levels of the substituted benzo group in triptycene.

This paper describes the conformational equilibria of 9-benzyltriptycene derivatives, giving evidence for a weak interaction between the phenyl group and the substituted benzene moiety. The phenomena are discussed in terms of orbital interactions. A preliminary report on the conformational equilibria has been published.[10]

Experimental

Syntheses. 9-Benzyltriptycenes were prepared by treating 9-benzylanthracenes with benzynes, as illustrated in the following schema. Some new 9-benzylanthracene derivatives were synthesized by the Grignard reaction of substituted benzylmagnesium chlorides with substituted anthrones, followed by dehydration of the products.

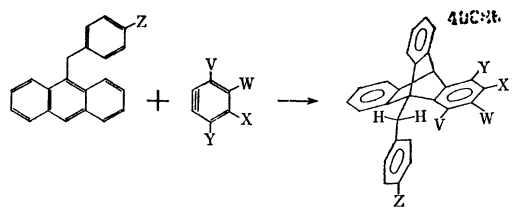
1,4-Dimethyl-9-benzylanthracene. To a solution of benzylmagnesium chloride, prepared from 3.8 g (0.03 mol) of benzyl chloride, 0.7 g (0.03 mol) of magnesium, and 100 ml of ether, was added 2.2 g (0.01 mol) of 1,4-dimethylanthrone[11] in small portions at room temperature. After 30 min, 50 ml of benzene was added and the resulting mixture was refluxed for 1 hr. The mixture was decomposed at 0 °C with dilute hydrochloric acid. The organic layer was separated, dried over sodium sulfate, and evaporated. The residue was taken up in 150 ml of carbon tetrachloride and heated on a steam bath with 30 g of phosphorus pentoxide for 2 hr. The supernatant liquid was decanted, washed with water, and dried over sodium sulfate. After removal of the solvent, the residue was chromatographed on neutral alumina. Elution with hexane gave the desired material, mp 133—134 °C, in 0.9 g (*ca.* 30%) yield. PMR (δ, $CDCl_3$): 2.78 (6H, s), 5.12 (2H, s), 6.90—8.15 (12H, m). Found: C, 93.37; H, 6.91%. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80%.

1,2,3,4-Tetrachloro-9-benzylanthracene, mp 174—175 °C, was similarly prepared from 1,2,3,4-tetrachloroanthrone[12] and benzylmagnesium chloride. The yield was *ca.* 15%. PMR (δ, $CDCl_3$): 5.17 (2H, s), 6.80—8.10 (9H, m), 8.85 (1H, s). Found: C, 62.32; H, 2.71; Cl, 35.07%. Calcd for $C_{21}H_{12}Cl_4$: C, 62.10; H, 2.98; Cl, 34.92%.

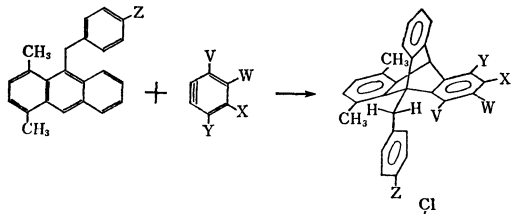
9-(4-Chlorobenzyl)anthracene, mp 124—125 °C, was prepared from anthrone and 4-chlorobenzylmagnesium chloride[13] in *ca.* 40% yield. PMR (δ, $CDCl_3$): 4.90 (2H, s), 6.80—8.25 (12H, m), 8.38 (1H, s).

1,4-Dimethyl-9-(4-chlorobenzyl)anthracene, mp 170—172 °C, was similarly prepared from 1,4-dimethylanthrone and 4-chlorobenzylmagnesium chloride. The yield was *ca.* 25%. PMR (δ, $CDCl_3$): 2.73 (6H, s), 5.00 (2H, s), 6.80—8.00 (10H, m), 8.42 (1H, s). Found: C, 83.42; H, 5.71; Cl, 10.93%. Calcd for $C_{23}H_{19}Cl$: C, 83.50; H, 5.79; Cl, 10.71%.

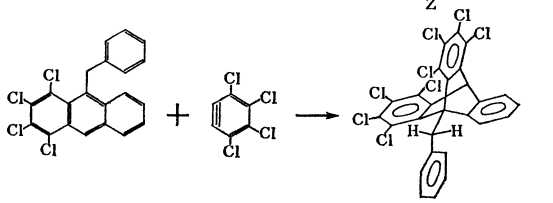
9-(4-Methoxybenzyl)anthracene, mp 138—139 °C, was prepared from anthrone and 4-methoxybenzylmagnesium chlo-



(3) V=W=X=Y=Cl, Z=H
(4) V=W=X=Y=Br, Z=H
(5) V=Y=OCH_3, W=X=Z=H
(6) V=Y=OCH_3, Z=Cl, W=X=H
(7) V=Y=Z=OCH_3, W=X=H
(8) W=Y=CH_3, V=X=Z=H



(1) V=W=X=Y=Z=H
(2) V=W=X=Y=H, Z=Cl
(10) V=W=X=Y=Cl, Z=H
(11) V=Y=OCH_3, W=X=H
(12) V=W=X=Y=Br, Z=H



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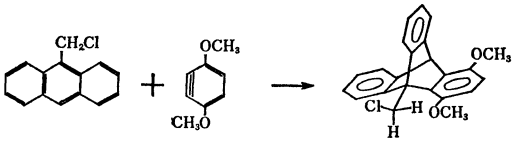

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ride[14] in 30% yield. PMR (δ, $CDCl_3$): 3.69 (3H, s), 4.93 (2H, s), 6.64—8.45 (13H, m). This compound was directly used for the preparation of a triptycene derivative **7**.

*1,4-Dimethyl-9-benzyltriptycene (**1**).* To a refluxing solution of 0.6 g (0.005 mol) of butyl nitrite and 1.48 g (0.005 mol) of 1,4-dimethyl-9-benzylanthracene in 20 ml of dichloromethane was added 0.68 g (0.005 mol) of anthranilic acid in 20 ml of acetone with stirring. Heating and stirring were discontinued after 0.5 hr and the solvent was evaporated. The residue was taken up in benzene and chromatographed on alumina. Elution with a mixture of hexane and benzene gave 0.61 g (30% yield) of **1**, mp 172—174 °C. The compound was purified by recrystallization from chloroform–ethanol. Found: C, 93.31; H, 6.47%. Calcd for $C_{29}H_{24}$: C, 93.51; H, 6.49%.

*1,4-Dimethyl-9-(4-chlorobenzyl)triptycene (**2**)*, mp 254—256 °C, was similarly prepared by treating a solution of butyl nitrite and 9-(4-chlorobenzyl)anthracene in dichloromethane with anthranilic acid in dry acetone. The yield was 28%. Recrystallization from chloroform-ethanol afforded a pure sample. Found: C, 85.80; H, 5.95; Cl, 8.73%. Calcd for $C_{29}H_{23}Cl$: C, 85.59; H, 5.70; Cl, 8.71%.

*1,2,3,4-Tetrachloro-9-benzyltriptycene (**3**)*, mp 247—248 °C, was prepared by treating butyl nitrite and 9-benzylanthracene with tetrachloroanthranilic acid.[15] The yield was *ca.* 20%. Recrystallization from benzene-hexane afforded a pure sample. Found: C, 67.82; H, 3.08; Cl, 29.31%. Calcd for $C_{27}H_{16}Cl_4$: C, 67.88; H, 3.19; Cl, 29.41%.

*1,2,3,4-Tetrabromo-9-benzyltriptycene (**4**)*, mp 237.5—239.5 °C, was prepared by treating butyl nitrite and 9-benzylanthracene with tetrabromoanthranilic acid.[16] The yield was 20%. The compound gave no satisfactory analytical results probably because of poor combustibility. Purity was checked by PMR spectrum. Mass spectrum showed molecular ion peaks at 656 for ^{79}Br compound and at 664 for ^{81}Br compound.

*1,2,3,4,5,6,7,8-Octachloro-9-benzyltriptycene (**13**)*, mp 258—260 °C, was prepared with the use of tetrachloroanthranilic acid, butyl nitrite, and 1,2,3,4-tetrachloro-9-benzylanthracene. The yield was *ca.* 7%. The compound gave no satisfactory analytical data owing to the poor combustibility. However, no impurities were detected by spectral methods. Mass spectrum showed a molecular ion peak at 616 for a compound with ^{35}Cl.

*1,2,3,4-Tetrachloro-5,8-dimethyl-9-benzyltriptycene (**10**)*, mp 233—235 °C, was prepared from tetrachloroanthranilic acid, butyl nitrite, and 1,4-dimethyl-9-benzylanthracene in 15% yield. Found: C, 68.49; H, 4.22; Cl, 28.09%. Calcd for $C_{29}H_{20}Cl_4$: C, 68.26; H, 3.95; Cl, 27.79%.

*1,2,3,4-Tetrabromo-5,8-dimethyl-9-benzyltriptycene (**12**)*, mp 233—235 °C, was prepared similarly in 15% yield. Found: C, 50.70; H, 3.05%. Calcd for $C_{29}H_{20}Br_4$: C, 50.62; H, 2.93%.

*1,4-Dimethoxy-9-benzyltriptycene (**5**).* A suspension of phenylsodium,[17] prepared from 2.25 g (0.02 mol) of chlorobenzene, 0.92 g (0.04 mol) of sodium and 50 ml of benzene, was added to a stirred solution of 1.72 g (0.01 mol) of 2-chloro-1,4-dimethoxybenzene[18] and 2.14 g (0.008 mol) of 9-benzylanthracene in 20 ml of benzene at room temperature under a nitrogen atmosphere. Stirring was discontinued after 3 hr and the mixture was treated with water. The organic layer was separated, dried over sodium sulfate, and evaporated. The residue was taken up in benzene and chromatographed on alumina. Elution with benzene gave the desired product which was recrystallized from chloroform-ethanol to give a pure sample, mp 256.5—258.5 °C, in 0.97 g (30%) yield. Found: C, 85.81; H, 5.92%. Calcd for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98%.

*1,4-Dimethoxy-5,8-dimethyl-9-benzyltriptycene (**11**)*, mp 239—240 °C, was prepared similarly by treating a mixture of 2-chloro-1,4-dimethoxybenzene and 1,4-dimethyl-9-benzylanthracene with phenylsodium. The yield was 25%. Found: C, 85.96; H, 6.22%. Calcd for $C_{31}H_{28}O_2$: C, 86.08; H, 6.52%.

*1,4-Dimethoxy-9-(4-methoxybenzyl)triptycene (**7**)*, mp 218—219 °C, was prepared from phenylsodium, 2-chloro-1,4-di-

methoxybenzene, and 9-(4-methoxybenzyl)anthracene in 20 % yield. Found: C, 83.14; H, 5.89%. Calcd for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03%.

3,6-Dimethoxyanthranilic acid was prepared according to the method of Banerjee and Chaudhury.[19] Tedious separation of isomers was avoided since products other than the desired one did not form the corresponding benzyne on treatment with nitrite esters. 2,5-Dimethoxybenzoic acid[20] (5 g or 0.027 mol) was added to 20 ml of nitric acid (d=1.38) in small portions at 0—2 °C with stirring. Stirring was discontinued after 3 hr and the mixture was poured into ice-water to precipitate yellow solids in 5.6 g yield. The PMR spectrum of the product indicated that it was a 2 : 1 mixture of 2,5-dimethoxy-6-nitro- and 2,5-dimethoxy-3-nitro-benzoic acids. The mixture in 100 ml of ethanol was hydrogenated over 1 g of 5% Pd–C under atmospheric pressure to give a viscous brown oil which was a 2 : 1 mixture of 3,6-dimethoxyanthranilic acid and 3-amino-2,5-dimethoxybenzoic acid. This mixture was used for subsequent reactions.

*1,4-Dimethoxy-9-(4-chlorobenzyl)triptycene (**6**).* To a refluxing solution of 0.6 g (0.005 mol) of butyl nitrite and 0.60 g (0.002 mol) of 9-(4-chlorobenzyl)anthracene in 20 ml of dichloromethane was added 1.15 g (0.005 mol) of the mixture of aminodimethoxybenzoic acids in 30 ml of dry acetone. Heating and stirring were discontinued after 0.5 hr and the solvent was evaporated. The residue was taken up in benzene and chromatographed on alumina. Elution with hexane–benzene followed by recrystallization of the product from chloroform–ethanol gave the desired product, mp 264—265 °C, in 30% (0.26 g) yield. Found: C, 79.05; H, 5.40; Cl, 7.95%. Calcd for $C_{29}H_{23}Cl$: C, 79.35; H, 5.28; Cl, 8.08%.

*1,4-Demethoxy-9-chloromethyltriptycene (**9**)*, mp 224—225 °C, was similarly prepared from the crude 3,6-dimethoxyanthranilic acid, butyl nitrite, and 9-chloromethylanthracene[21] in 20% yield. Found: C, 76.32; H, 5.17; Cl, 9.41%. Calcd for $C_{23}H_{19}Cl$: C, 76.12; H, 5.25; Cl, 9.77%.

*2,4-Dimethyl-9-benzyltriptycene (**8**).* To a refluxing mixture of 0.36 g (0.015 mol) of magnesium, 2.68 g (0.01 mol) of 9-benzylanthracene and 70 ml of dry tetrahydrofuran was added 2.0 g (0.01 mol) of 3,5-dimethyl-2-fluoro-1-bromobenzene[22] in 20 ml of dry ether with stirring. After 5 hr, the mixture was cooled and treated with water. The organic layer was separated after addition of 100 ml of ether, dried over sodium sulfate, and evaporated. The residue was taken up in benzene and chromatographed on alumina. Elution with hexane–benzene gave pure **8**, mp 145—147 °C, in 0.56 g (*ca.* 15%) yield. Found C, 93.21; H, 6.60%. Calcd for $C_{29}H_{24}$: C, 93.51; H, 6.49%.

The original product was a mixture of **8** and 1,3-dimethyl-9-benzyltriptycene [PMR (δ, $CDCl_3$): 2.10 (3H, s), 2.26 (3H, bs), 4.52 (2H, bs), 5.07 (1H, s), 6.60—8.20 (15H, m)] in 2 : 1 ratio. Assignments of the structure were based on the observation of coalescence at a lower temperature for **8** than the isomer.

Spectral Measurement. PMR spectra were recorded on a Hitachi R-20B spectrometer operating at 60 MHz. The samples were dissolved in appropriate solvents to make up *ca.* 10% (wt/vol) solutions. The temperatures were read by the difference in chemical shifts between methyl and hydroxy protons of methanol and are believed to be accurate within the error of ±1 °C.

The populations of rotational isomers were measured by the direct integration of the signals. The values are given as the averages of 10 integrations. The maximum deviation from the average was not greater than 7%. Logarithms of the equilibrium constants at various temperatures were plotted against $1/T$. Linearity was obtained for every case and ΔH and ΔS were calculated in the usual way.

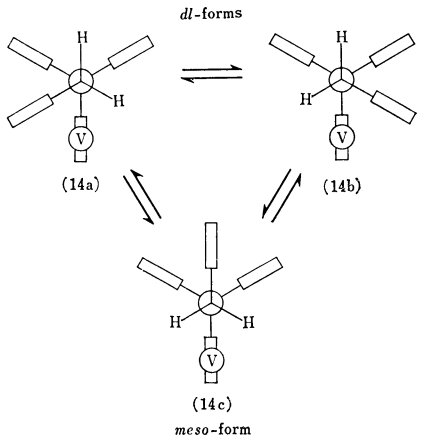
It was not possible to find a single suitable solvent for the measurements of the whole series because of the poor solubility of some compounds at low temperatures (below −55 °C). However, at relatively high temperatures, it was possible to measure the solvent effect on populations: change of the solvent from chloroform-d or carbon disulfide to acetone-d_6 did not affect the conformational equilibria within the experimental errors. The triptycenes with *p*-substituted benzyl groups or those which have two substituents at two *peri*-positions had such poor solubility that the derivation of ΔH and ΔS values was abandoned.

Results and Discussion

Peak Assignment. PMR data of the triptycene (**1**—**8**) in chloroform-*d* at 34 °C are summarized in Table 1. Compounds **1**—**7** give broadened signals for benzyl methylene groups at this temperature, indicating that the rotation about the C_9–C_{benzyl} bond is fairly slow on the NMR time scale. Lowering the temperature generally resulted in the appearance of an AB quartet and a singlet. These signals are best assigned to *dl* and *meso* forms, respectively, since the former should have two benzyl hydrogens in different magnetic environments (**14a** and **14b**) and the latter in the identical ones (**14c**). The down-

Table 1. PMR data of 9-benzyltriptycenes carrying substituents in one benzo group at 34 °C ($CDCl_3$, δ)

Compound	Methyls		Methylene	Bridge head proton	Aromatic protons
1	2.38(3H, bs)	2.48(3H, s)	4.70(2H, bs)	5.64(1H, s)	6.45—7.50(15H, m)
2	2.37(3H, bs)	2.48(3H, s)	4.65(2H, bs)	5.66(1H, s)	6.42—7.60(14H, m)
3			4.91(2H, bs)	6.08(1H, s)	6.85—7.55(13H, m)
4			4.99(2H, bs)	6.18(1H, s)	6.70—7.82(13H, m)
5	3.16(3H, s)	3.81(3H, s)	4.62(2H, bs)	5.91(1H, s)	6.38—7.46(15H, m)
6	3.19(3H, s)	3.81(3H, s)	4.60(2H, bs)	5.94(1H, s)	6.30—7.50(14H, m)
7	3.26(3H, s)	3.75(3H, s) 3.81(3H, s)	4.60(2H, bs)	5.95(1H, s)	6.32—7.62(14H, m)
8	2.11(3H, s)	2.49(3H, s)	4.43(2H, s)	5.62(1H, s)	6.62(1H, bs) 6.80—7.45(14H, m)
9	3.72(3H, s)	3.77(3H, s)	5.45(2H, bs)	5.84(1H, s)	6.47(2H, s) 6.80—7.95(8H, m)

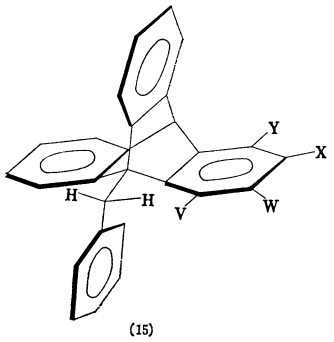


field signal of the AB quartet is reasonably assigned to the proton between the substituent at 1-position and the *peri*-hydrogen at 8-position on the basis that its chemical shift is close to that of the benzyl protons of the *meso* form, the magnetic environment of which is considered to be alike.

At −17 °C, the methyl signal of **1** comprises three signals at δ 2.03, 2.67, and 2.48. The first two are generated by the splitting of the signal at δ 2.38 at 34 °C, the last signal being split into two signals at δ 2.40 and 2.49 on further cooling. A similar phenomenon was also observed for **2** and **11**. The assignment of the signals is self-evident, if the areas of benzyl methylene protons are taken into consideration. Thus the signals at δ 2.03 and 2.49 correspond to methyls of the *dl* form and those at δ 2.40 and 2.67 to those of the *meso* form. Other factors must be taken into consideration for assignment of the signals to methyls at 1- and 4-positions.

The molecular models of these triptycenes show that the phenyl group in the benzyl (benzyl-phenyl hereafter) should take a conformation in which the phenyl group resides in the aperture made by the benzo groups in the triptycene skelton and bisects both the angles of H–C–H (benzyl methylene) and C–C–C (triptycene skelton). This type of conformation is also supported from the coupling constants (−17.4∼−18.0 Hz) of the AB protons in benzyl groups. Theoretically, the π-contribution to the geminal coupling constants is a function of the dihedral angle made by the plane of the π-system and the H–C–C plane,[23] and the π-contribution was estimated to be slightly larger than 4 Hz in a conformation in which the carbon frame of the π-system bisects the angle H–C–H. Since the coupling constant in methane is 13 Hz[24] the coupling constant should be 17 Hz or a little more, if the conformation of the benzyl group is like the one postulated from the molecular model. The observed and the calculated values agree fairly well, conformation **15** thus becoming reasonable.

In such a conformation, substituent (V) at the *peri*-position would be located in a shielding cone of the benzyl-phenyl group. Thus it is reasonable to assume that the methyl at 1-position gives the PMR signal at a higher field than the methyl at 4-position. From the foregoing discussion, the signal at δ 2.03 is assigned



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to the methyl group at 1-position of the *dl*-form and that at δ 2.49 to the methyl at 4-position. The chemical shifts of the methyl groups in the *meso* form are not self-evident, but from the coalescence-splitting behavior with the corresponding signals of the *dl*-forms the signals at δ 2.67 is assigned to the methyl groups at 1-position and that at δ 2.40 to the methyl at 4-position. Assignments along this line are carried out with other compounds and are listed in Table 2.

The situation of the methoxyl groups at *peri*-positions differs slightly from that of the methyl groups. The chemical shift difference between the methoxy-methyls at 1- and 4-positions becomes very small for the *meso* forms. This is reasonable since intervention of the oxygen between the methyl and the benzo groups makes the distance from the phenyl group larger and gives a greater freedom of rotation reducing the chemical shift difference. Nevertheless, since it is possible to assign methoxyl groups in the *dl*-forms, the methoxyl groups in the *meso* form of **6** are assigned from the coalescence-splitting behavior (Table 2).

PMR spectra of compound **9** showed a curious behavior when the temperature was varied. A signal of the chloromethyl group was a little broad at 34 °C, whereas rise and fall in temperature caused sharpening of the signal instead of further broadening or splitting at a low temperature. Sergeyev and co-workers[25] suggested that the barrier to rotation about the C_9–C_{CH_2Cl} bond in 9-chloromethyltriptycene should be higher than 15 kcal/mol. It is thus unlikely that the rotation about the C_9–C_{CH_2Cl} bond in **9** is still too fast on the NMR time scale at −30 °C. It is unrealistic to assume that the chemical shifts of the protons at three sites coincide both for methoxy and methylene protons because of the large magnetic effect of the chlorine substituent.[24,26] Solvent effect did not change the above situations. If the phenomenon is caused neither by the change in solute-solvent interaction nor by the rapid rotation about the bond in question, it is reasonable to interpret the results from the change in population of the rotamers. The internal rotation is slow enough at room temperature to be detected by the NMR technique as a broadening of the signal and the population of the *dl*-isomer is present to the extent that it can be observed. At a lower temperature, however, the less stable *dl*-isomer decreases in population and is not detected, although the rotation in question is sufficiently slow. At a higher temperature, the rotation becomes too fast for the detection of individual species, although the popula-

Table 2. PMR data of 9-benzyltriptycenes carrying substituents in one benzo group at low temperatures (δ)

Compound	Assignment	*meso*	*dl*	J_{gem} (Hz)	Temperature (°C)	Solvent
1	benzyl methylene	4.69	4.19, 4.63	−17.4	−40	$CDCl_3$-CS_2 (2 : 3)
	methyl-1	2.67	2.03			
	methyl-4	2.40	2.49			
2	benzyl methylene	4.70	4.20, 4.65	−17.5	−45	$CDCl_3$-CS_2 (2 : 3)
	methyl-1	2.71	2.06			
	methyl-4	2.41	2.50			
3	benzyl methylene	5.00	4.19, 5.07	−18.0	−50	CS_2
4	benzyl methylene	5.02	4.20, 5.10	−18.0	−23	CS_2
5	benzyl methylene	4.97	4.30, 4.94	−18.0	−56	$CDCl_3$-CS_2 (3 : 1)
	methoxy-1	3.80	2.95			
	methoxy-4	3.80	3.80			
6	benzyl methylene	4.96	4.30, 4.92	−18.0	−52	$CDCl_3$-CS_2 (3 : 1)
	methoxy-1	3.79	3.01			
	methoxy-4	3.82	3.82			
7	benzyl methylene	4.95	4.31, 4.93	−18.0	−50	$CDCl_3$-CS_2 (3 : 1)
	methoxy-1	a)	3.03			

a) Other peaks at δ 3.80 and 3.84 are not assigned because of the presence of *p*-methoxy group in the benzylbenzene.

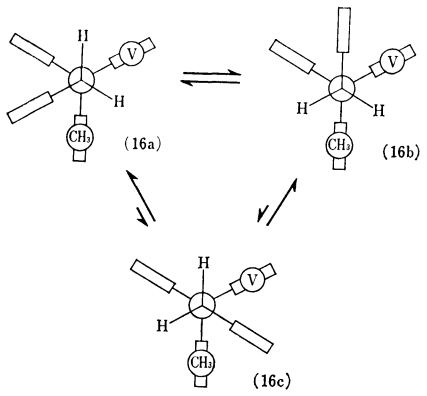
Table 3. PMR data of 9-benzyltriptycenes carrying substituents in two benzo groups at 34 °C ($CDCl_3$, δ)

Compound	Assignment	**16a**	**16b**
10	benzyl methylene	4.82, 5.60 (1.09H, J_{gem} = −17.7 Hz)	4.57, 5.75 (0.91H, J_{gem} = −17.4 Hz)
	methyl-5	2.59(1.64H, s)	2.46(1.36H, s)
	methyl-8	2.19(1.64H, s)	2.79(1.36H, s)
	bridgehead proton	6.35(1H, s)	
	aromatic protons	6.50—7.75(11H, m)	
11	benzyl methylene	4.55, 5.37 (2H, J_{gem} = −16.8Hz)	
	methyl-5	2.46(3H, bs)	
	methyl-8	2.74(3H, bs)	
	methoxy-1	2.95(3H, bs)	
	methoxy-4	3.78(3H, bs)	
	bridgehead proton	6.20(1H, s)	
	aromatic protons	6.30—7.60(13H, m)	
11[a]	benzyl methylene	4.57, 5.39[b] (2H, J_{gem} = −16.8 Hz)	
	methyl-5	2.57(0.71H, s)	2.46(2.29H, s)
	methyl-8	2.15(0.71H, s)	2.77(2.29H, s)
	methoxy-1	3.74(0.71H, s), 3.78(0.71H, s)[c]	2.94(2.29H, s)
	methoxy-4		3.81(2.29H, s)
12	benzyl methylene	4.80, 5.76 (1.05H, J_{gem} = −18.0 Hz)	4.46, 6.00 (0.95H, J_{gem} = −18.0 Hz)
	methyl-5	2.62(1.57H, s)	2.50(1.43H, s)
	methyl-8	2.21(1.57H, s)	2.81(1.43H, s)
	bridgehead proton and aromatic protons	6.40—7.10(12H, m)	
13	benzyl methylene	4.76, 6.08 (2H, J_{gem} = −18.2Hz)	
	bridgehead proton	6.38(1H, s)	
	aromatic protons	6.85—7.70(9H, m)	

a) Data obtained at 0 °C. b) A single AB quartet is observed to indicate that the chemical shifts of a pair of quartets coincide. c) Assignment of these peaks are reserved because of a small chemical shift difference.

tion of the *dl*-isomers increases. Thus the signal observed at low temperatures should be due to the *meso* form which exists as an overwhelming species among the possible conformations.

1,8-Disubstituted 9-benzyltriptycenes (**10**—**12**) showed PMR signals corresponding to two isomers at room temperature (Table 3). The results suggest that the barrier to rotation is still higher. The absence of an isomer of **16c** type is assumed since the conformation should be of high energy. The assumption is supported by the fact that compound **13** gives only one set of AB quartet, indicating that the compound solely exists as a *dl* form which has the benzyl-phenyl group at the site of the least steric interaction. The conformation **16a** should give a methyl signal at higher magnetic field than **16b**, for the methyl group at 1-position is located within the shielding cone of the benzyl-phenyl group. From the data of compounds **1** and **2**, the methyl group in a similar situation gives the signal at the highest magnetic field among other methyls. Other methyl signals are assigned by considering the signal intensities. The benzyl methylene protons due to conformations **16a** and **16b** can be assigned by taking the intensities into consideration. The downfield signal of each pair of AB protons of the benzyl group is assigned to the proton placed between the substituents at 1- and 8-positions in the Newman projection, since the proton is likely to give a signal at a lower field due to the steric compression and/or the magnetic effects of the substituents. The assignment is in line with the chemical shifts of benzylic protons in **1**—**5** in which a proton neighboring the peri-substituent gives a signal at the lower field.



Rotamer Populations. The quilibrium constants for the equilibria *meso*⇌*dl* of compounds **1**—**8**, the thermodynamic parameters obtained by the measurement of the equilibria at various temperatures, and solvent systems are listed in Table 4. The solvent system had to be varied due to the poor solubility of the compounds. However, those compounds examined in various solvents showed no solvent dependency of the population. Thus, the following discussion seems to be valid.

The data in Table 4 indicate that the *dl*-forms of benzyltriptycenes (**1**—**7**) which carry one substituent at a *peri*-position to the benzyl group are anomalously favored, particularly for compounds **5**—**7**. The equilibrium constant is even larger than 2, which value is expected from mere statistical consideration. The anomaly is striking when we compare the data with that for compound **9** which shows the presence of *dl*-isomers only to a detectable amount at room temperature (*vide supra*), giving a signal corresponding to a *meso* isomer only at lower temperatures. We may thus conclude that the *dl*-forms of the benzyltriptycenes **1**—**7** are anomalously favored.

The relative stability of conformers can be discussed on the assumption that the potential function is approximately divided into three terms: steric repulsion, electrostatic interaction including dipole-dipole interaction and electron delocalization. Such an assumption seems to be supported in simple molecules by theoretical calculations.[27]

The overwhelming relative stability of the *meso* form of compound **9** over the *dl*-form may be explained on a basis that the steric repulsion term outweighs the electrostatic interaction and the electron delocalization. The destabilization factor of dipole-dipole interaction should operate for the *meso* form of compound **9** since the dipole of C–Cl and that of the C–O–C are arranged in the same direction. Electron delocalization by transfer of an electron from the highest occupied molecular orbital (HOMO) of the *p*-dimethoxybenzene to the lowest unoccupied molecular orbital (LUMO) σ^* of the $ClCH_2$ group may occur to a limited extent, but the σ^* orbital seems to be too high to make this contribution significant. On the

Table 4. Equilibrium constants and thermodynamic parameters for 9-benzyltriptycenes **1**—**9**

Compound	Equilibrium constant $K=\frac{dl}{meso}$ (temp. °C)	ΔH (kcal/mol)	ΔS (eu)	Solvent
1	0.85±0.10 (−50)	1.1±0.1	4.9±0.9	$CDCl_3$-CS_2 (2 : 3)
2	0.84±0.10 (−50)			$CDCl_3$-CS_2 (2 : 3)
3	0.68±0.10 (−50)	1.2±0.1	4.3±0.5	CS_2
	1.0 ±0.1 (−23)			
4	1.0 ±0.1 (−23)			CS_2
5	2.8 ±0.1 (−50)	0.0±0.1	2.1±0.3	$CDCl_3$-CS_2 (3 : 1)
6	3.5 ±0.1 (−50)			$CDCl_3$-CS_2 (3 : 1)
7	2.4 ±0.1 (−50)			$CDCl_3$-CS_2 (3 : 1)
8	1.2 ±0.1 (−83)			CS_2
9	0 (−30)			$CDCl_3$

other hand, steric repulsion is very severe since the atoms in the chloromethyl and *peri*-regions are located within the sum of their van der Waals radii, and weak interactions of electrostatic nature and electron delocalization are not strong enough to overcome it.

The steric conditions of 9-benzyltriptycenes should be more severe than those of compound **9**, since the phenyl group is larger than the chlorine. As in the case of other systems such as cyclohexanes[2] and substituted ethanes,[28] we may expect such overcrowding caused by the benzyl group and the substituent to greatly increase the free energy difference of the two forms. Preference of the *dl*-form therefore cannot be explained by the steric effect. The dipole-dipole interaction also is not favorable for these compounds, since substitution of a chlorine atom by a phenyl group should result in a decrease in bond dipoles. Consequently the preference of the *dl*-form on the electrostatic basis is reduced. Benzene might have a high microscopic dielectric constant along an axis which is perpendicular to the ring. The model is supported by the anomalous behaviors of benzene as a solvent.[29] Application of this idea leads to a conclusion that *dl* isomers are provided stabilization by the electrostatic interactions between the negative benzyl-benzene ring and the oxygen or halogen at 1-position which becomes partly positive due to the electron delocalization. If this were the case, the solvent effect on the conformational equilibria would have been large. It is also difficult to explain the effect of the substituent in the benzyl group on the conformational equilibria. The electron-donating substituent would have given more *dl*-forms contrary to the observed ratio.

Thus the electron delocalization effect becomes a likely cause of the phenomenon. From the data of compounds **5**—**7** we note that the electron-donating substituent disfavors the *dl*-form, whereas the electron-attracting substituent favors it. Since the steric effect in these compounds may be assumed to be the same, the stabilization due to delocalization or through-space interaction will be the major factor, if not the only one. When the through-space interaction[30] between the benzyl-benzene and the *p*-dimethoxybenzene moities in the triptycenes is taken into consideration, the magnitude of stabilization would depend on the difference in energy between the orbitals concerned and the extent to which they overlap, if other factors such as steric repulsion, medium effects and electrostatic interactions are the same. The lower the energy level of LUMO of the benzene ring, the greater the orbital interaction with HOMO of the other moiety, provided that the level of HOMO of the donor is the same, to increase the presence of the *dl*-forms. No such stabilization is possible in the *meso* form since the orbitals lie too far apart from each other. Since the HOMO's of *p*-dimethoxybenzenes in **5**—**7** can be considered to be of the same energy, the lowering in energy of LUMO of the benzyl-benzene should result in the more preferred interaction which leads to the preference of the *dl*-form to a greater extent. The HOMO's and LUMO's of some simple benzene derivatives are given in Table 5. Since the levels of HOMO may be regarded as equal to ionization potentials to a first approximation and we are dealing with the charge transfer type interaction, the ionization potential data have been collected from those given in the literature.[31] The levels of LUMO can be estimated from those of HOMO and the data of electronic absorption spectra.[32]

Table 5. Energy levels of HOMO and LUMO of some benzene derivatives

Compound	HOMO (eV)	LUMO (eV)
Benzene	9.40	4.52
Chlorobenzene	9.31	4.72
Anisole	8.54	3.89
p-Dimethoxybenzene	7.90	3.58
p-Dichlorobenzene	9.17	4.59
p-Xylene	8.71	4.00

The observed trend is in line with what is expected from the HOMO–LUMO interactions. It may be concluded that the preference of the *dl*-forms in compounds **5**—**7** is due to the electron delocalization approximated by donation of electrons from HOMO of *p*-dimethoxybenzene to the antibonding LUMO of the benzyl-benzene. Although the effect of the alkyl substituents on the energy level is neglected here, such approximation may be accepted in a qualitative discussion.

The relative population in these compounds results from a balance between the attractive interaction due to the delocalization and the repulsive interaction due to the steric size. In compounds **5**—**7**, the former factor exceeds the latter. This will be a consequence of the high HOMO level of *p*-dimethoxybenzene moiety. If the HOMO level of the donor is lowered and other steric and electric factors are kept constant, preference for the *dl*-form will be diminished. Comparison of the equilibrium constants of compounds **1** and **5** which possess the same acceptor group indicates that the *dl*-form of **5** is more favored than that of **1**. The result is in line with the available data of HOMO (Table 5).

Stabilization of the *dl*-forms in **1** might be attributed to the interaction between the benzene ring and the electronegative methyl group, as suggested for acetonitrile–benzene system.[33] However, if this were the case, compound **2** should have disfavored the *dl*-form relative to compound **1** because of the lower electron density (or the lower HOMO level) in the chlorophenyl group. Since the equilibrium constants for both compounds are the same within the limit of error, and the phenomenon is understood in terms of orbital interactions, we prefer to attribute the phenomenon to the HOMO–LUMO interaction where the benzene moiety acts as an electron acceptor.

The effectiveness of the overlap of orbitals concerned should be considered, the difference between *meso* and *dl*-forms being a typical example. The more bulky the substituents, the more effective the overlap of orbitals is prevented since the orbitals concerned are more separated from each other. Similarly more accurate estimation for the stabilization by the electron delocalization needs coefficients of atomic orbitals

in most interacting molecular orbitals. In the *dl*-forms of dimethyl compounds **1** and **2**, the interaction may become less favorable because electrons belonging to the methyl group are relatively localized to molecular orbitals of low energy relative to those of the methoxy group in **5**—**7**.

The larger K value for compound **8** than for compound **1** can be attributed to the decrease in steric effect for the former because it has no substituent at peri-positions to interact with the benzyl group. Preference of the *dl*-forms for compound **8** is reduced, as compared with that in 2,4-dimethyl-9-isopropyltriptycene which has been reported to give an equilibrium constant of 2, a statistical factor.[9] The phenomenon can be attributed to the fact that, being an elongated group, the benzyl-phenyl group extends deeply into the aperture of the triptycene skeleton and the repulsive force between the phenyl group and 2-methyl group may become significant in some conformations: the entropy term becomes unfavorable.

In compounds **10**—**13**, the presence of a form of **16c** type is not detected at all. This may arise either by thermodynamic control or kinetic control. Thermal equilibration at 250 °C for 12 hr was attempted. Since a pair of AB quartet signals of these compounds becomes broad at a higher temperature and then collapse into a broad singlet at 120 °C, probably because of the coincidence of the chemical shifts, 250 °C is considered to be high enough to cause a full rotation about the C_9–C_{benzyl} bond and thermal equilibration will ensue to at least some extent, if the energies are feasible. However, it was not possible to detect any of the forms of **16c** by even rapid cooling after the above operation. Although the possibility that the barrier leading to **16c** form is still too high under the conditions applied cannot be ruled out completely, the results strongly suggest that **16c** is thermodynamically unstable. From the standpoint of electron delocalization, the **16c** type conformation should be favored. The steric effect seems to outweigh the electronic effect in these cases.

The data in Table 6 suggest that the conformational preference between **16a** and **16b** can be understood also from the standpoint of HOMO–LUMO interaction. In compound **11**, the conformation of **16b** type will be favored, because the HOMO of the *p*-dimethoxybenzene is higher than that of the *p*-xylene. Compounds **10** and **12** give almost the same equilibrium constants in agreement with the fact that compounds **1**, **3** and **4** give similar equilibrium constants and that the conformational energy of the *meso* forms of these monosubstituted compounds may be assumed the same.

Table 6. Relative populations of rotamers in 9-benzyltriptycenes **10**—**13** at 0 °C ($CDCl_3$)

Compound	Equilibrium constant $K=\frac{\mathbf{16a}}{\mathbf{16b}}$
10	1.2±0.1
11	$\frac{1.0}{3.2}$=0.31±0.02
12	1.1±0.1
13	1.0

In conclusion, the electron delocalization plays a significant role in determining the conformational equilibria in 9-benzyltriptycene derivatives, although the steric effect is also very important. This is an observation rarely made on the charge transfer type interaction in which a benzene ring without any strongly electron-attracting substituent acts as an acceptor in combination with donors of medium to low ability. This kind of orbital interaction is undoubtedly caused by the extreme proximity of the orbitals concerned in the overcrowded molecules.

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