

RESTRICTED ROTATION INVOLVING THE TETRAHEDRAL CARBON. XII.
ANOMALOUS CONFORMER DISTRIBUTION IN 9-BENZYLTRIPTYCENES
CARRYING SUBSTITUTENT AT PERI-POSITION.¹⁾

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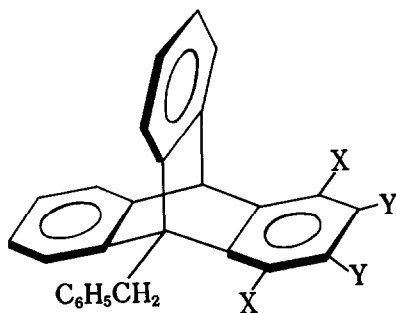
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As a part of our interest in restricted rotation, 9-benzyltriptycenes are interesting as a model showing intermediate barrier to rotation and complex signal patterns on freezing the rotation. If it is a meso conformer, it will give a singlet methylene signal, whereas the corresponding signal will be of the AB type if the conformation is chiral.

Along lines of this sort, 9-benzyltriptycenes were prepared and their PMR spectra determined at various temperatures. Examination of the spectra at low temperatures disclosed the anomalous distribution of the conformers: the dl conformers were anomalously favored from the stand point of steric interference. We wish to report these findings and compare them with other sterically similar compounds.

Three 9-benzyltriptycenes were prepared by Diels-Alder reactions of appropriate combinations of 9-benzylanthracenes and benzyne. Their melting points are given in the following page.

PMR spectra of these compounds at room temperature showed a singlet for the benzyl methylene protons. However, the signal broadened on lowering the temperature and separated into a singlet and an AB quartet, as shown in Table 1. By integrating these signals at various temperatures, we can obtain the equilibrium (meso \rightleftharpoons dl) constants (K) and consequently differences in thermodynamic



	X	Y	mp (°C)
(1)	C1	C1	247 - 248
(2)	OCH ₃	H	256.5-258.5
(3)	CH ₃	H	172 - 174

Table 1 PMR data of 9-Benzyltritycenes at Low Temperatures
(δ from internal TMS)

Compound	Form	CH ₂	J _{gem}	Other Protons ^{b)}	Temperature (°C)	Solvent
<u>1</u>	meso	5.00			-50.2	CS ₂
	racemic	4.19, 5.07	-18.0			
<u>2</u> ^{a)}	meso	4.97		3.80 (OCH ₃)	-56.2	CDCl ₃ -CS ₂ (3:1)
	racemic	4.30, 4.94	-18.0	2.95 (1-CH ₃ O) 3.80 (4-CH ₃ O)		
<u>3</u>	meso	4.69		2.67 (1-CH ₃) 2.40 (4-CH ₃)	-29.8	CDCl ₃ -CS ₂ (2:3)
	racemic	4.19, 4.63	-17.4	2.02 (1-CH ₃) 2.49 (4-CH ₃)		

a) The methoxy proton signal of this compound was apparently doublet. The signal at 3.80 ppm is a composite of signals involving two methoxy groups in the meso form and another methoxy group of the racemic form.

b) A signal at a higher magnetic field in a pair of methyl or methoxy signals of the racemic form may be assigned to the one at 1-position by considering the anisotropy of the benzene ring. (See structure 5.) Assignment of the methyl or methoxy signals of the meso form was performed by observing coalescence of the signals with those of the racemic form.

parameters between the meso and the dl forms. The results are shown in Table 2.

Evidently, the dl form of the methoxy compound (2) is abnormally favored, compared with the other two. Enthalpy difference between the dl form and the meso form of 2 is almost zero. This seems to be anomalous at the first look, because, having the bulkier phenyl group in the proximity of the peri-substituent,

Table 2 Thermodynamic Data for Equilibria between Meso
and Racemic Forms of 9-Benzyltriptycenes

Compound	K ($\frac{\text{racemic}}{\text{meso}}$)	ΔH (kcal/mole)	ΔS (eu)	Solvent
<u>1</u>	0.68 \pm 0.1	1.2 \pm 0.1	4.3 \pm 0.5	CS ₂
<u>2</u>	2.8 \pm 0.2	0.0 \pm 0.1	2.1 \pm 0.3	CDCl ₃ -CS ₂ (3:1)
<u>3</u>	0.85 \pm 0.1	1.1 \pm 0.1	4.9 \pm 0.5	CDCl ₃ -CS ₂ (2:3)

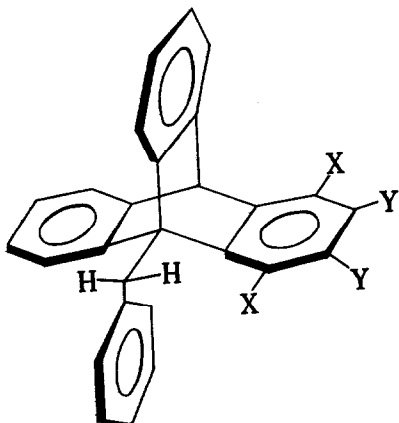
the dl form is a more crowded form. This anomaly is not caused by the specific solvent-solute interactions, because changing the solvent to acetone-d₆ did not cause any appreciable change in distribution of the conformers of 1-3.

There might exist an attractive interaction between the methoxy group and the phenyl in benzyl group. However, uv-visible spectra of these compounds could not detect any charge-transfer band: the uv-visible spectrum of 2 was almost the same with that of 9-isopropyl-1,4-dimethoxytriptycene. Therefore, the charge-transfer type interaction is not present to the extent which uv spectra can detect.

Considering a yet unidentified attractive interaction, it seemed interesting to see the conformational equilibria of compounds in which such attractive interaction is impossible. Thus 9-chloromethyl-1,4-dimethoxytriptycene (4), mp 224-225°C, was prepared, which carry chloro-substituent instead of the phenyl. To our surprise, this compound showed PMR signals attributable to a meso isomer only: a solution of 4 in 3:2 CDCl₃-CS₂ gave a methylene signal at 5.28 ppm from internal TMS at room temperature and the signal essentially unchanged even at -70°C. No other signals attributable to methylene protons were found. In the case of compound 4, repulsive force between methoxy and chloro groups predominates to allow the presence of meso conformer only, as was the case of 9-isopropyl-1,4-dimethoxytriptycene.¹⁾

Accordingly, even compounds 1 and 3 must be considered to have some kinds of attractive interaction between the substituent and the phenyl group. If the repulsive interaction between the phenyl group and the substituent were the decisive factor, these compounds should have existed as a meso form exclusively, because phenyl group is considered to be larger than the chloro.²⁾

Generalization of these phenomena seems to be a very difficult one. It could be derived by considering structures of the molecules in detail. Since it is suggested that the π -contribution to the geminal coupling constants is a function of the dihedral angle between the methylene group and the adjacent π bond,³⁾ conformation of the benzyl group may be deduced from the J values in



(5)

Table 1. The coupling constants of these compounds are larger than that of methane⁴⁾ by ca 5 Hz. By theoretical consideration, the π -contribution was estimated to amount to a little larger than 4 Hz in a conformation that the carbon frame of the π -system bisects the angle H-C-H. Therefore the most probable conformation of the benzyl group is such that the phenyl group is inserted into an aperture made by two benzene rings of the triptycene skeleton (5).

In such a conformation, an attractive interaction between a methyl group and a benzene ring might be possible, as suggested by Abraham.⁵⁾ If there existed such an interaction, it would favor the dl form which is otherwise very unstable. Charge-transfer type interaction between a benzene ring and substituents (CH₃O and Cl) having lone pair electrons could exist in such conformations also, although too weak to detect by the conventional uv-visible absorption method. Investigations are in progress along these lines.

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