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Restricted Rotation Involving the Tetrahedral Carbon. XXV. Barriers to Exchange between *dl* and *meso* Forms of 9-(Arylmethyl)triptycenes[1)]

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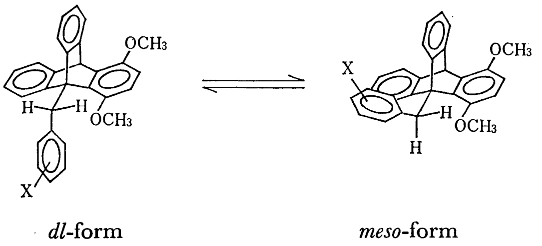
Barriers to exchange between *dl* and *meso* forms *via* rotation about the C_9–C_{subst} bond of 9-(arylmethyl)-1,4-dimethoxytriptycenes are obtained by the use of the methoxyl signals in the ^1H NMR spectra. It is found that, although the population ratios are affected by the substituent in the 9 position, the enthalpy of activation for the rotation is almost invariant at *ca.* 10 kcal/mol.

9-Substituted triptycenes constitute a unique system in that unusually high barriers are observed for rotation about the C_9–C_{subst} bond.[2)] Thus freezing the rotation of even methyl groups on the NMR time scale has been realized[3)] and stable rotational isomers isolated at room temperature.[4)] Whereas barriers to rotation about the C_9–C_{subst} bond are known in the cases where the substituent is a tertiary alkyl,[5)] an isopropyl,[6)] or a methyl group,[3)] barriers to rotation about the C_9–CH_2 bond have not been known except for one case, 9-(chloromethyl)triptycene, where signals due to ring protons[7)] and ring carbons[8)] have been used for the analysis.

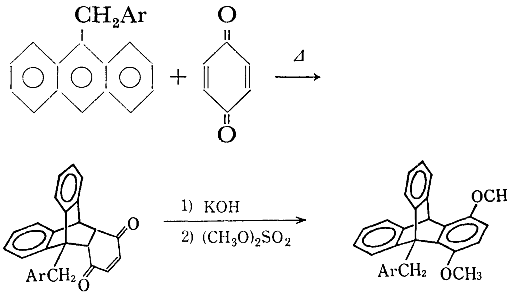


(**1**)

9-Benzyltriptycenes are interesting in that there is an attractive interaction between the 9-benzyl group and the benzo group of the triptycene skeleton:[9)] the *dl* forms are unusually favored if there is an electron-attracting substituent in the benzyl group and the benzo group has a group of low ionization potential. The interaction should affect the enthalpy of activation for rotation if other conditions are the same. This paper describes the reinvestigation of the population ratios of the *dl* and the *meso* forms of 9-(arylmethyl)-1,4-dimethoxytriptycenes (**1**) using the FT NMR technique to obtain better data and the study of the barrier to exchange between the *dl* and the *meso* forms by internal rotation using the line shapes of the methoxyl signals in ^1H NMR spectra.

Experimental

Syntheses of Triptycenes. The substituted benzyltriptycenes were prepared by the Diels-Alder reaction between the corresponding 9-benzylanthracenes (**2**) and *p*-benzoquinone followed by enolization and methylation.



(**1**)

*9-(*m*-Nitrobenzyl)anthracene.* *m*-Nitrobenzylideneanthrone[10)] (3 g) was heated under reflux with 10 ml of ethanol and 3 ml of water and 3 g of sodium borohydride was added in small portions. The mixture was heated for 1 h and cooled. The insoluble material was removed by filtration and the mother liquor was concentrated. The residue was taken up in 200 ml of carbon tetrachloride and the solution was heated for 2 h with 20 g of phosphorus pentaoxide. The solution was decanted and evaporated. The residue was chromatographed on silica gel, using benzene as an eluent. The desired product was obtained in 70% yield and used directly for subsequent reactions.

9-(Arylmethyl)-1,4-dimethoxytriptycenes. These compounds were prepared by the following general procedure. The compounds were known unless otherwise stated and their physical properties agreed well with those reported.

A solution of 1.3 g (0.005 mol) of 9-benzylanthracene and 1.1 g (0.01 mol) of *p*-benzoquinone in 20 ml of acetonitrile was refluxed for 24 h and evaporated. The residue was chromatographed on silica gel and eluted with benzene–chloroform (10: 1). An adduct was obtained in over 90% yield. To a solution of the adduct (0.6 g) in 20 ml of dioxane was added 20 ml of 1 M aqueous potassium hydroxide in 10 min and the mixture was treated with 5 ml of dimethyl sulfate in small portions. The potassium hydroxide solution was added in small portions to the mixture until the addition caused no color change. After 10 min stirring, the precipitate was collected and purified by alumina chromatography using hexane–benzene (4: 1) as an eluent. The yield was over 90%.

*1,4-Dimethoxy-9-(*p*-methylbenzyl)triptycene:* Mp 223—224 °C. Found: C, 85.94; H, 6.25%. Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26%. ^1H NMR ($CDCl_3$) $\delta=2.28$ (CH_3), 3.21 (CH_3O), 3.80 (CH_3O), 4.64 (CH_2), 5.95 (bridgehead), 6.47 (AB quartet for dimethoxybenzo H's, $J_{AB}=9.0$ Hz, $\Delta\nu_{AB}=6.3$ Hz), 6.8—7.5 (aromatic H's).

*1,4-Dimethoxy-9-(*m*-nitrobenzyl)triptycene:* Mp 301—305 °C (dec). Found: C, 77.34; H, 4.95; N, 3.10%. Calcd for $C_{29}H_{23}NO_4$: C, 77.48; H, 5.16; N, 3.12%. ^1H NMR ($CDCl_3$–CS_2, integrated for 70 times) $\delta=3.19$ (CH_3O), 3.85 (CH_3O), 4.70 (CH_2), 5.92 (bridgehead), 6.48 (AB quartet for dimethoxybenzo H's, $J_{AB}=9.0$ Hz, $\Delta\nu_{AB}=11.0$ Hz), 6.8—7.6 (aromatic H's).

^{1}H NMR Spectra. The spectra were obtained on a JEOL FX60 spectrometer equipped with FT facilities. The solvent was a 3:1 mixture of chloroform and carbon disulfide and sample tubes were of 10 mm diameter. In one case dichloromethane-d_2 was used as a solvent. The temperature was read by a thermocouple directly dipped into the mixed solvent placed in the probe. The error in reading the temperature was ±0.6 °C. Pulses of 20 μs duration was used with 5 s intervals. The data were accumulated *ca.* 40 times except for the *m*-nitro derivative which required 400 time accumulation.

Total Line Shape Analysis. It was performed with the use of a modified Binsch program,[11] treating the spectra as a pair of uncoupled A⇄B exchanges. Populations were obtained as described in Results and Discussion and the rate constant (k_1) of the *meso*→*d* (or *l*) process was varied in the calculation, the rate constant (k_{-1}) of the reverse process being put outside of the consideration. Since there are two identical processes transforming the *meso* to the *dl* form, $2k_1[meso]=k_{-1}[d \text{ and } l]$ is obtained: namely $K(dl/meso)=2k_1/k_{-1}$. Thus the rate obtained by the computer simulation was divided by 2 to obtain k_1. Chemical shift differences were used as observed. T_2 was calculated from the half band width of the tetramethylsilane signal added as an internal standard.

The signal due to the 4-methoxyl group was always included in the calculation. *p*-Chloro and *m*-nitro compounds gave excellent results by this method. The presence of the *p*-methoxyl group in the *p*-methoxybenzyl compound gave a strong drawback to this method. Thus the line shape analysis was performed only at the higher field. The spectra of the *p*-methylbenzyl and the benzyl compounds were analyzed similarly. The calculated spectra were compared with the observed and the best fit spectra were chosen by visual fitting. The agreement between the observed and the calculated spectra was excellent.

Results and Discussion

Assignment of the Spectra. Fig. 1 shows ^{1}H NMR spectra of 9-(*p*-chlorobenzyl)-1,4-dimethoxytriptycene at three temperatures. Apparently the methoxyl and the methylene signals broaden on lowering the temperature. The latter splits into a quartet signal and a singlet. Assignments of the spectral peaks of the methylene part is straightforward: a quartet is due to the *dl* form and a singlet the *meso* form (see Newman projections). The former has two singlets which split into two large singlets and a small singlet at the lower temperature. The former two singlets are assigned to the *dl* forms and the latter to the *meso* form from the intensity considerations. The methoxyl groups of the *dl* form in 1- and 4-positions suffer from a large difference in magnetic environment because of the presence of the benzylic phenyl group in the proximity of the 1-position: the signal at the higher field is thus assigned to the 1-methoxyl group. In contrast, the two methoxyl groups of the meso form seem to be in similar magnetic environments.

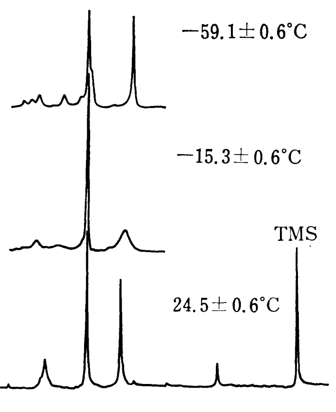


Fig. 1. ^{1}H NMR spectra of 9-(*p*-chlorobenzyl)-1,4-dimethoxytriptycene at three temperatures.

The aromatic region of the *p*-chloro compound showed temperature dependence in its spectrum but the change was too complicated to analyze.

Other compounds showed similar behavior in the ^{1}H NMR spectra at various temperatures. The assignments were performed similarly.

Populations of Rotamers. In principle, it should be possible to obtain population ratios at various temperatures by calculation, because the ratios can be used as variants in the total line shape analysis. In practice, however, it will add another uncertainty in the simulation. It was also hoped to reduce the number of parameters in simulations of the line shapes of the methylene part.[12] Thus we decided to obtain the ratios from other sources.

There are two signal pairs to be used for the population analysis. The methylene signals appear as an AB quartet and a singlet. Integration of these signals should produce the population ratio at a given temperature. However, in practice, there are some overlaps in the down-field part of the AB signal with that of the *meso* and in the up-field part of the AB signal with that of the methoxyl signal. The signal due to the methoxyl groups of the *meso* form heavily overlaps with that due to the 4-methoxyl of the *dl* form in the down-field. Thus integration of the methoxyl signals is less hopeful.

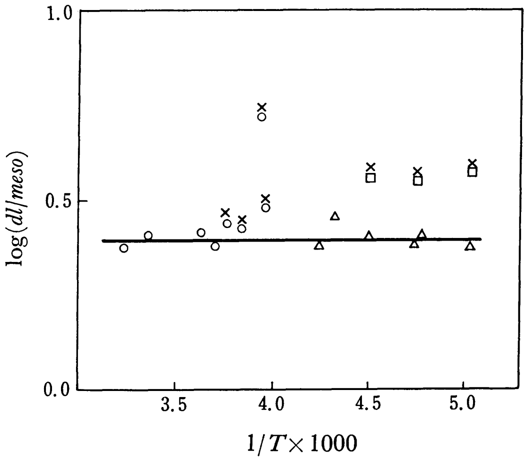


Fig. 2. Population ratios (*dl*/*meso*) of 9-(*p*-methylbenzyl)-1,4-dimethoxytriptycene at various temperatures: □ by integration of the methylene region, △ by integration of the methoxyl region, ○ by the drift in the chemical shift of the methoxyl signal after coalescence. Those with cross marks are rejected in drawing the straight line. See text for the reasons.

TABLE 1. EQUILIBRIUM CONSTANTS AND THERMODYNAMIC PARAMETERS PERTAINING TO ROTAMERS OF 9-ARYLMETHYL-1,4-DIMETHOXYTRIPTYCENES

Aryl	Representative K's ($dl/meso$) (Obsd)		$-\Delta H$ (kcal/mol)	ΔS (e.u.)
	−20 °C	−50 °C		
p-$CH_3OC_6H_4$	2.7±0.2	3.0±0.2	0.32±0.02	−1.5±0.5
p-$CH_3C_6H_4$	2.5±0.2	2.5±0.2	0.05±0.01	−1.1±0.2
C_6H_5	2.8±0.2	2.8±0.2	0.57±0.03	+0.3±0.1
p-ClC_6H_4	4.1±0.2	4.5±0.2	0.44±0.06	−1.6±0.1
m-$NO_2C_6H_4$	4.4±0.2	4.9±0.2	0.36±0.12	−0.7±0.1

To avoid these uncertainties, we decided to use the cross-check method of using both the methylene and the methoxyl signals. For the latter, both the integrated intensities and the chemical shift drift at temperatures higher than the coalescence were used. The results are shown in Fig. 2, taking the case of the *p*-methylbenzyl compound as an example. As is seen in the figure, the chemical shift method gives apparently absurd values at temperatures close to the coalescence, which are rejected as the unreliable. Those data obtained by integration of the AB signals were found to give apparently larger values in the cases where the population of the *meso* form was large. Therefore these were also abandoned in the least squares treatment.

The equilibrium constants and thermodynamic parameters thus obtained are tabulated in Table 1. The equilibrium data are in general accordance with those reported,[9] but we take the values reported here to be more reliable because of the better S/N ratios relative to the previously reported. The results confirm that the *dl* form is stabilized relative to the *meso* form and the stabilization is enhanced when the benzyl part carries an electronegative substituent.

Barriers to Exchange between the dl *and the* meso *Forms.* There are 6 rotational processes as depicted in Fig. 3. However, since we are looking at the signals due to the *dl* forms as a package, we can neglect the $d \rightleftharpoons l$ processes. Thus there remain 4 processes of which $meso \rightarrow d$ and $meso \rightarrow l$ are identical and so are the reverse processes, because *d* and *l* forms are not distinguishable.

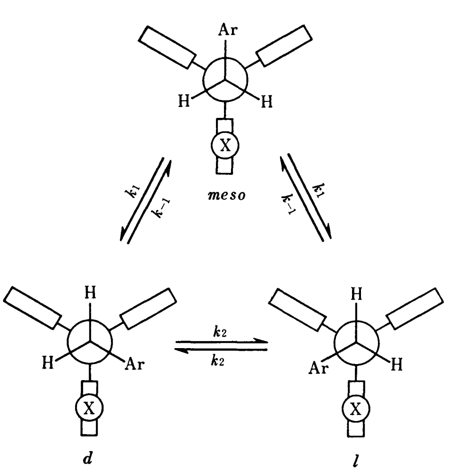


Fig. 3. Processes of mutual exchanges among *meso*, *d*, and *l* forms.

For the *m*-nitro compound, it is possible to take two conformations for the *meso* and the *dl* forms with respect to the nitrophenyl group, although that phenyl group will assume the conformation in which the π-system bisects the H–C–H angle of the α-methylene group.[9] They are NO_2-inside and NO_2-outside conformations. However, these species were not distinguishable by the present technique. We tentatively assume that the average processes are observed, although it is likely that the NO_2-inside conformations are unstable and we are observing processes which involve the NO_2-outside conformations.

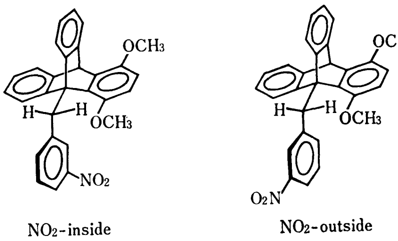


Fig. 4. NO_2-inside and NO_2-outside conformations of a *d* (or *l*) form.

Fig. 5. Computed and observed spectra of 9-(*p*-chlorobenzyl)-1,4-dimethoxytriptycene at various temperatures.

In Fig. 5 the results of computer simulation of the line shapes of the *p*-chloro compound are shown with the rate constants and compared with the observed spectra. These results were put into the Eyring's plot and excellent linear relationships were obtained. From the slopes and the intercepts, the activation parameters were obtained as shown in Table 2.

It is interesting to note that the ground state stabilities seen in the equilibrium constants $K(dl/meso)$ is

Table 2. Activation parameters for the exchange between the *meso* and the *dl* forms of 9-arylmethyl-1,4-dimethoxytriptycenes in $CDCl_3$–CS_2 (3: 1)

Aryl	$\Delta H^{\neq}$(kcal/mol)		$\Delta S^{\neq}$(e.u.)		$\Delta G^{\neq}$ (kcal/mol) (−15 °C)	
	meso→*dl*	*dl*→*meso*	*meso*→*dl*	*dl*→*meso*	*meso*→*dl*	*dl*→*meso*
p-$CH_3OC_6H_4$	8.8±0.3	9.1±0.3	−13.6±0.3	−12.9±1.4	12.3±0.5	12.4±0.5
p-$CH_3C_6H_4$	11.8±0.4	11.8±0.4	−2.6±0.5	−2.8±1.5	12.4±0.3	12.5±0.3
p-$CH_3C_6H_4$[a]	11.3±0.4	12.1±0.4	−4.4±1.4	−1.5±1.8	12.4±0.1	12.4±0.1
C_6H_5	10.0±0.1	10.7±0.2	−7.7±0.6	−5.5±1.0	11.9±0.2	12.1±0.2
p-ClC_6H_4	11.8±0.3	12.1±0.3	−3.4±1.3	−3.7±1.3	12.6±0.2	13.0±0.2
m-$NO_2C_6H_4$	9.6±0.1	10.0±0.1	−12.3±0.4	−12.3±0.4	12.8±0.2	13.2±0.2

a) These values were obtained with a solution in CD_2Cl_2.

not reflected in the $\Delta H^{\neq}$'s. All the compounds examined show almost the same $\Delta H^{\neq}$'s irrespective to the substituent. Since the ground state stability of the compounds with electronegative substituents is ascribable to the charge transfer interaction, it should be reflected in the $\Delta H^{\neq}$'s, if the other factors are the same. Although we must carefully discuss the entropy of activation derived by the total line shape analysis,[13] it is tempting to consider that in the transition state of rotation the *m*-nitro compound suffers from the decrease in entropy probably due to change in solvation which counterbalances the enthalpy factor in the ground state.

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