Rotation of the Benzene Rings in Paracyclophane Derivatives, studied by Nuclear Magnetic Resonance Spectroscopy

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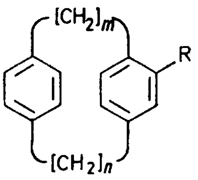
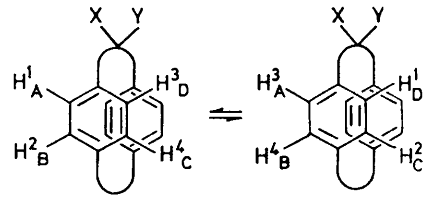
Summary The rates of rotation of the benzene rings in [*m*,*n*]paracyclophanes having suitable substituents on the aliphatic bridges may be measured by n.m.r. line-shape methods.

Restricted rotation of the benzene rings in [*m*,*n*]paracyclophanes (**1**) has previously been studied[1] by the optical resolution of suitably substituted compounds such as the acid (**1**; $m = 4$, $n = 3$, $R = CO_2H$). We report here a general and convenient method for studying this phenomenon using n.m.r. spectroscopy.[2]

The n.m.r. spectra of the aromatic protons of [*m*,*n*]paracyclophanes which have asymmetrical bridge substitution [see groups X and Y in (**2**)] should be observable as ABCD systems if rotation of the benzene rings is slow on the n.m.r. time scale. Fast rotation of the benzene rings (**2a**) ⇌ (**2b**) results in rapid exchange of the hydrogen atoms 1 and 3 between the sites A and D and of hydrogen atoms 2 and 4 between the sites B and C, so that under these conditions the aromatic protons would give rise to an AA′BB′ system. Thus ring rotation may be studied by examining the temperature dependence of the aromatic proton spectra and this is exemplified by the following study of the n.m.r. spectra of the paracyclophane derivatives† (**3**) and (**4**).



(1)



(2a) (2b)

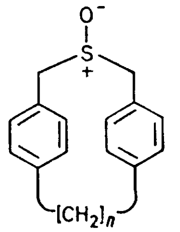
The aromatic protons of the sulphoxides (**3b** and **c**) give a single ABCD spectrum at low temperatures which changes to an AA′BB′ spectrum at high temperatures; the line-shape changes were analysed in the usual way[2,3] to give the rates and free energies of activation for the process (**2a**) ⇌ (**2b**) (Table). The line-shape calculations were based upon site exchange between appropriate sites of two

Table

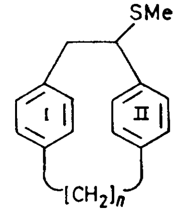
Rate constants and free energies of activation for rotation of the benzene rings in thiaparacyclophane derivatives (**3**) *and* (**4**)

Compound		Solvent	Temperature/ °C (±2)	k/s^{-1}	$\Delta G^‡$/(kcal mol^{-1})[a] (±0·3)
(**3a**)		$(CD_3)_2SO$	180	<6[b]	>25[b]
(**3b**)		$(CD_3)_2SO$	158·5	16·9	23·2
(**3c**)		$CDCl_3$	11·5	117·5	13·9
(**3d**)		$CDCl_3$–CS_2 (1:4)	−100	>30[c]	<9[c]
(**4a**)	Rings I and II	$(CD_3)_2SO$	160	<6[b]	>24[b]
(**4b**)	Ring I	$(CD_3)_2SO$	82	121·0	17·5
	Ring II	$(CD_3)_2SO$	82	10·9	19·2
(**4c**)	Ring I	CS_2–$CDCl_3$ (1:1)	−41	60·0	11·4
	Ring II	CS_2–$CDCl_3$ (1:1)	−14	18·8	13·6
(**4d**)	Ring II	CS_2–$CDCl_3$ (1:1)	−80	*ca.* 89[d]	*ca.* 9·4[d]

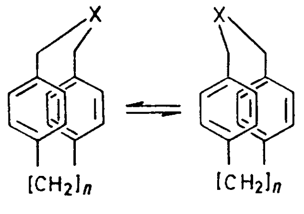
[a] For compounds (**3**) the spectral changes involve rotation of both benzene rings; for compounds (**4**) rotation of the two different benzene rings can be observed separately. [b] < 2 Hz line-broadening at the stated temperature. [c] Line width 4 Hz, ($\nu_A - \nu_B$) estimated as 8 Hz. [d] Based upon signal coalescence at −80°; the data refer to ring II only.



(3)
a; $n = 4$
b; $n = 5$
c; $n = 6$
d; $n = 7$



(4)
a; $n = 6$
b; $n = 7$
c; $n = 8$
d; $n = 9$



(5a) (5b)

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† These and other new compounds cited in this communication were synthesised by standard procedures and had analytical and spectral properties consistent with the proposed structures.

AB systems; this ignores the small *meta*-coupling constants but this simplification should not lead to significant errors in exchange rates.‡ The spectral changes observed for the thioethers (**4b** and **c**) were more complex (two ABCD systems at low temperatures and two AA′BB′ systems at high temperatures) and different rates of rotation were observed for the two different aromatic rings [I and II, see (**4**)]. Line-shape calculations for the four protons of each ring were carried out using the same simplified approach as for the sulphoxides (**3**). The rapid increase in the free-energy barrier to rotation of the benzene rings as the length of the polymethylene bridge is decreased in both series of compounds is qualitatively understandable in terms of the increase in non-bonded interactions in the transition state for ring rotation. The thiomethyl substituent in (**4**) evidently has a considerable effect on the rate of rotation of the adjacent benzene ring [ring II in (**4**)] and $\Delta G^{\ddagger}$ is increased by *ca.* 2 kcal mol^{-1}. A more detailed discussion of rotational rates and the steric interactions in the transition states for rotation will be presented in the full paper.

The above approach to the study of rotation of the benzene rings in paracyclophanes depends upon conformational changes associated with the aliphatic bridges (*cf.* ref. 5) being fast on the n.m.r. time-scale at temperatures where the aromatic proton spectra are affected by the rotational process (**2a**) $\leftrightharpoons$ (**2b**). This was readily shown to be the case. Changes in the n.m.r. spectra of the thiaparacyclophane derivatives (**5**; X = S or SO$_2$, *n* = 3—6) associated with a bridge inversion process (**5a**) $\leftrightharpoons$ (**5b**) can be observed at low temperatures but the free energies of activation associated with these processes ($\Delta G^{\ddagger}$ 8·9—10·8 kcal mol^{-1}) are lower than those associated with ring rotation (Table) and are even lower ($\Delta G^{\ddagger} < 8{\cdot}4$ kcal mole^{-1}) if $n > 6$. Conformational changes associated with the [CH$_2$]$_n$ bridge are only observable by n.m.r. line-shape methods for $n = 3$ ($\Delta G^{\ddagger}$ *ca.* 11·5 kcal mol^{-1}) and $n = 4$ ($\Delta G^{\ddagger}$ *ca.* 8·9 kcal mol^{-1}).

The results presented in this paper show that the rotation of benzene rings in suitable [*m,n*]paracyclophane derivatives may conveniently be studied by n.m.r. line-shape methods. Different approaches using paracyclophanes with substituents on the benzene rings have also been reported.[6,7]

(*Received*, 18*th April* 1972; *Com.* 665.)

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‡ In fact activation parameters were not found to differ significantly from those obtained using very simple approximations (*cf.* ref. 4).

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