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The Intramolecular OH---π Bonding in [*n*]Paracyclophanols[1)]

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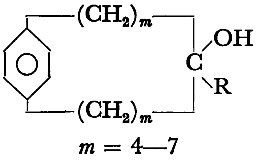
The intramolecular OH···π bonding, the probable conformations, and the internal rotation in two series of [*n*]-paracyclophanols, I (**1**—**4**) and II (**5**—**8**), are investigated by means of IR, UV, and PMR spectroscopies. The IR results indicate that (1) there is the OH···π bonding in **1**, **2**, **3**, **5**, and **7** in CCl_4, and (2) the integrated intensity ratio of the π-bonded OH species to the free OH, (A_b/A_f), hardly changes in going from **1** to **3**, while it decreases in going from **5** to **7**. The ratio is, then, related to both ΔH and ΔS. In the PMR spectra, aliphatic-proton signals are assigned by means of the spin-decoupling and/or the shift-reagent technique; the results agree with those predicted, with a few exceptions. In the aromatic region, **3**, **4**, and **8** show singlets, while the others show AB-like quartets. These results are discussed in relation to the internal rotation of the benzene ring and/or the alkylene chain.

Intramolecular hydrogen bondings have been observed in many systems of open chains and medium-size rings,[2)] and the spectral shifts of the bonded OH bands have been measured. There have, though, been surprisingly few reports on thermodynamic measurements for the intramolecular hydrogen-bond formations, and these have been for only a few acylic systems of β-phenylalkanols,[3)] 1,3-diols,[4)] and ω-methoxyalkanols.[5)] Only the last system has been examined in relation to the alkylene-chain length. In this system, the loss of entropy accompanying the hydrogen-bond formation increases greatly with the increasing chain length, but the enthalpy term hardly changes at all.

In the present work, we will examine the intramolecular OH···π bonding in two series of [*n*]paracyclophanols, I and II, by means of IR spectroscopy, and thermodynamic parameters, ΔH and ΔS, for the hydrogen-bond formation will be obtained from measurements of the temperature dependence of the ν_{OH} spectra.



$m = 4$—7
Series I: R=H
Series II: $R=CH_3$

The reasons why paracyclophanols are selected are that their conformations are partially fixed around the benzene rings and that at least some of them are expected to be internally hydrogen-bonded with a relatively slight loss of entropy.

On the other hand, there have been presented several experimental or theoretical approaches to estimate the probable conformations of [5]—[12]paracyclophane compounds. These include an examination of molecular models,[6)] a free-electron model calculation,[7)] X-ray diffraction,[8,9)] and a force-field calculation.[10)]

In the present work concerning probable conformations in Series I and II, the degrees of bending of the benzene rings are predicted by a comparison of the UV spectral shifts with the theory,[11)] and the magnitudes of magnetic shielding for the aliphatic protons are estimated by a calculation using the Johnson and Bovey method.[12)] Furthermore, the PMR spectra of the aromatic protons are simulated by assuming an A_2B_2 type of proton system, and the internal rotation of the benzene rings and/or the alkylene chains is discussed.

Experimental

Samples. All the paracyclophanols examined were unknown compounds, except for [9]paracyclophane-5-ol,[13)] **1**. [11]Paracyclophane-6-ol, **2**, and its 6-methyl derivative, **6**, were prepared by the $LiAlH_4$ reduction or by the Grignard reaction of the corresponding ketone, which had itself been obtained by the Dieckmann reaction[14)] of dimethyl benzene-1,4-dihexanoate. The others were similarly obtained from the corresponding known ketones.[13,14)] The alcohols thus obtained were purified by recrystallization from hexane; their melting points and analytical results are summarized in Table 1.

IR Spectra. The ν_{OH} spectra were recorded on a JASCO DS-403G spectrometer; the solvent used was CCl_4, and the concentrations selected were *ca.* 0.003 mol/l or less so as to give apparent peak intensities of *ca.* 1.4 and to avoid an intermolecular association (cell length: 50 mm). The tem-

Table 1. Melting points and analytical data of the paracyclophanols

Compound				Mp, °C (Uncorrected)	Calcd (%)		Found (%)	
	No.	*m*	R		C	H	C	H
I	**1**	4	H	111 —111.5				
	2	5	H	60.0— 61.0	82.87	10.64	83.33	10.76
	3	6	H	51.5— 52.0	83.15	11.02	83.09	10.95
	4	7	H	79.6— 80.2	83.38	11.33	83.49	11.18
II	**5**	4	CH_3	43.2— 43.7	82.70	10.41	82.68	10.32
	6	5	CH_3	101.0—101.6	83.02	10.84	83.38	11.00
	7	6	CH_3	*ca.* 76[a)]	83.27	11.18	83.25	11.16
	8	7	CH_3	88.0— 89.0	83.48	11.47	83.14	11.37

a) A waxy solid which was homogeneous according to its GC and TLC and according to its PMR spectrum.

perature dependence of the spectra was also examined at different temperatures ranging from 10 to 60 °C (error: ±1 °C in each case); correction was made for the thermal expansion of the solvent at each temperature. The calculated spectral slit width was 1.5 $\mathrm{cm^{-1}}$ at about 3600 $\mathrm{cm^{-1}}$.

UV Spectra. Measured in concentrations of *ca.* 0.002 mol/l in hexane, using a Hitachi EPS-3T spectrometer.

PMR Spectra. Recorded in concentrations of 5—10 w/v% in CCl_4 on a JEOL JNM4H-100 spectrometer operating at 100 MHz; TMS was used as an internal reference and a lock signal. Dilution experiments were carried out in the concentration range of 1—20 w/v%, and the chemical shifts for concentration-dependent protons were obtained at an infinite dilution. Lanthanoid-induced shift measurements were performed by the step-by-step addition of either $Pr(fod)_3$ or $Eu(fod)_3$ to $CDCl_3$ solutions of substrates in the molar-ratio ranges of 0—0.6, until enough magnitudes of the induced shifts were obtained to assign the proton signals. The temperature dependence of the aromatic proton spectra was examined in dimethyl-d_6 sulfoxide or acetone-d_6 which proved to be suitable for obtaining an appropriately high resolution at the higher or lower temperatures examined.

The above measurements were carried out at room temperature (*ca.* 25 °C) unless otherwise noted.

Results and Discussion

IR Spectra. Three paracyclophanols, **4**, **6**, and **8**, show single, unsymmetric or symmetric OH bands characteristic of the monomers of ordinary secondary or tertiary alkanols.[15] The other paracyclophanols show doublets, which are ascribed to the presence of at least two OH species, free and internally bonded, but to other causes such as Fermi resonance, overtone, conformational heterogeneity, or intermolecular association. If the latter causes were predominant, **4**, **6**, and **8** could be expected to show similar doublets. Each doublet can be graphically separated into two almost symmetric bands; the higher-frequency band corresponds to the free OH group, so the lower-frequency one should then be assigned to the π-bonded one. The integrated intensity of each band is calculated using the following equation:

$$A = (\pi/2cl)\ln(I_0/I)_{\max}\Delta\nu_{1/2} \quad (\text{in l mol}^{-1}\,\text{cm}^{-2})$$

The spectra of **1**, **4**, and **5** are shown in Fig. 1 as typical examples, and the results are summarized in Table 2.

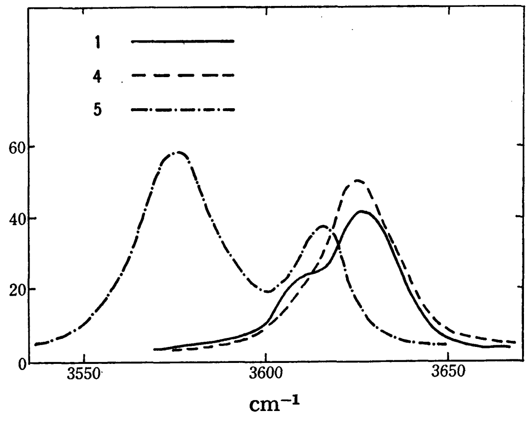


Fig. 1. OH spectra of **1**, **4**, and **5** in CCl_4 at room temperature.

TABLE 2. IR DATA OF THE PARACYCLOPHANOLS AT *ca.* 25 °C

	Compound No.	$\nu_{\max}$ ($\mathrm{cm^{-1}}$)	$\Delta\nu_{1/2}$ ($\mathrm{cm^{-1}}$)	$A\times10^{-3}$ (l $\mathrm{mol^{-1}}$ $\mathrm{cm^{-2}}$)	A_b/A_f[a]
I	**1**	3628.0	19.6	2.850	0.27
		3608.0	12.6	0.769	
	2	3627.5	20.7	2.802	0.23
		3606.8	15.1	0.645	
	3	3630.0	21.3	2.443	0.33
		3609.0	16.6	0.805	
	4	3625.0	21.0	3.833	
II	**5**	3616.3	17.1	2.068	2.5
		3578.0	26.1	5.178	
	6	3616.9	14.4	2.876	
	7	3616.9	17.0	2.634	0.13
		3566.9	18.7	0.354	
	8	3616.9	15.5	3.022	

a) A_b and A_f denote the integrated intensities of bonded and free OH bands respectively.

The A values for **1**, **2**, and **3** may be less accurate than those for the others, because their doublet-components so overlap that it is not easy to separate them. On raising the temperature, ν_{OH} becomes slightly higher and the sum of A_b and A_f becomes smaller, as is usually observed.[16] From these data, the thermodynamic parameters can then be calculated using the following equation:[16]

$$\ln A_b/A_f = -\Delta H/RT + (\Delta S/R - \ln a)$$

where a is the ratio of the true molecular extinction coefficients of the bonded and the free OH groups. Good linear relationships are obtained between $\ln A_b/A_f$ and $1/T$, as Fig. 2 shows. The results are summarized in Table 3.

It can be seen in Table 2 that, in Series I (**1**—**3**), the shifts ($\Delta\nu_{OH}$) of the π-bonded OH frequencies from the

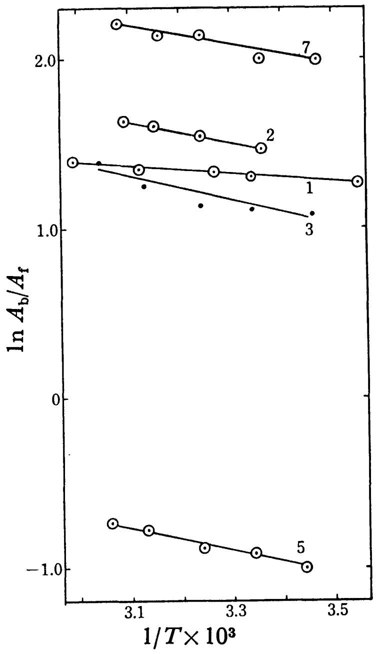


Fig. 2. Linear relationship between $\ln A_b/A_f$ and $1/T$.

corresponding free OH ones are almost the same, *ca.* 20 cm^{-1}, comparable to those in α-phenylalkanols.[17] In Series II (**5** and **7**), $\Delta\nu_{OH}$ is *ca.* 40 or 50 cm^{-1}; these values correspond to those in β- and γ-phenylalkanols.[8,18] The difference in $\Delta\nu_{OH}$ must be related to the distance (r) between the π-bonded OH group and the π-site.[2] However, the relationship between $\Delta\nu_{OH}$ and r can not be examined in the present case, because the paracyclophanols are in very complicated conformations with sterically unfavorable dihedral and bond angles[9,10] and the geometries of the internally bonded conformations can not be estimated.

As an approximate measure of the r, one may assume a magnitude of magnetic shielding for the OH proton. However, the observed magnitude ($\Delta\delta_{OH}=\delta_{ref.OH}-\delta_{OH}$) is not related to the $\Delta\nu_{OH}$, probably because each δ is the weight-average for all the OH species in all conformations.

An inspection of Table 3 reveals that, in Series I, both $-\Delta H$ and $-\Delta S$ tend to increase in going from **1** to **3** and are, therefore, contributable to the A_b/A_f ratio. In Series II also, the ratio is related to ΔH and ΔS, because $-\Delta H$ decreases in going from **5** to **7**, while $-\Delta S$ increases. In this connection, it is noteworthy in Table 2 that, in I and II, the A_b/A_f ratios alternate with m. The alternation in I is noticeable and is attributable to the ΔH's, but not to the ΔS's, because $-\Delta H$ in **5** is greater than that in **1** and $-\Delta H$ in **7** is less than that in **3**, while the ΔS's in **5** and **7** are almost the same as those in **1** and **3**. In **6**, ΔS is expected to be not greatly different from the ΔS in **3**; therefore, the absence of hydrogen bonding should be attributable to ΔH, which would be negligibly small or be positive in sign.

Table 3. Thermodynamic data for the internally bonded paracyclophanols

	Compound No.	$-\Delta H$ (kcal/mol)	$-(\Delta S/R - \ln a)$	$-\Delta S$[a] (e.u.)	$-AI$ (kcal/mol)	RI (kcal/mol)
I	**1**	0.4±0.1	2.1±0.1	4.2	0.94	0.54
	2	1.2±0.1	3.6±0.1	7.2	0.95	−0.25
	3	1.3±0.2	3.3±0.1	6.6	0.95	−0.35
II	**5**	1.4±0.1	1.5±0.1	3.0	1.22	−0.18
	7	0.5±0.1	3.8±0.2	7.6	1.42	0.92

a) Approximate values, assuming $a=1$.[16]

We will now discuss the ΔH by separating it into its two components: the interaction between the OH group and the π-site (AI) and the combined interactions between the other non-bonded atoms (RI). AI can be approximately estimated from $\Delta\nu_{OH}$, using the Joesten and Drago equation[19] for intermolecular hydrogen bonds:

$$-AI \pm 0.5(\text{kcal/mol}) = 0.016\Delta\nu_{OH} + 0.63$$

The values of AI and RI calculated in this manner are also listed in Table 3. The accuracy of these values is considerably poor, but it is at least possible to ascertain the tendency of their change through the whole series. Of interest is the fact that, in I and II, $-\Delta H$ is inversely proportional to RI. In other words, the OH···π bond formation is less exothermic in **1**, but more exothermic in **2** and **3**, than expected, because RI increases in **1** but decreases in **2** and **3**. This means that, the longer the alkylene chain is, the more feasible it is for the conformational change in forming the hydrogen bond to occur; this could be a reflection of the theoretical results[10] that, in [5]—[10]paracyclophanes, the conformation is less strained when the alkylene chain is longer.

In Series II, the reverse is true and the OH···π bond formation is more exothermic in **5**, but much less exothermic in **7**, than expected. This may be explained in terms of the flexibility of the alkylene chain being more decreased in II than in I. Because of the methyl group attached to the central bridge atom, the alkylene chains in II are more rigid than those in I. Taking this expectation together with the A_b/A_f ratios into consideration, it seems reasonable that the conformation of **5** is so fixed that the OH···π bond formation is accompanied by only a slight change in RI and that the conformation of **6** is so fixed that the hydrogen-bond formation requires an excessively large increase in RI. The large RI in **7**, as compared to that in **3**, may similarly be explained in terms of the less flexible conformation. This is supported by the observation that the internal rotation of the benzene ring and/or the alkylene chain is more restricted in **7** than in **3**, as will be described later. An examination of molecular models indicates that the C–OH bond in **5** is situated inside the alkylene loop, with its O–H toward the face of the benzene ring, while the C–OH bonds in the other paracyclophanols must be in such conformations as to be less favorable for the OH···π interaction.

Table 4. UV data in hexane solutions

	Compound No.	m	λ_{max} (log ε)	
I	**1**	4	270.8(2.57)	225.5(2.85)
	2	5	268.0(2.56)	222.5(2.85)
	3	6	266.2(2.65)	220.5(2.89)
	4	7	266.0(2.66)	220.5(2.88)
II	**5**	4	271.5(2.54)	—[a]
	6	5	267.3(2.57)	—[a]
	7	6	265.3(2.61)	—[a]
	8	7	265.5(2.57)	—[a]
	9[b]		271 (3)	224 (3)
	10[c]		268 (2)	223 (3)
	12[d]		265 (2)	214 (3)

a) Not observed. b) [9]Paracyclophane. c) [10]-Paracyclophane. d) *p*-Diethylbenzene. The data for b), c), and d) are taken from Ref. 9.

UV Spectra. The spectra of **1**—**8** are quite similar to those of the corresponding [*n*]paracyclophanes;[20,21] hence, the OH and/or CH$_3$ substituents at the central bridge carbon and also the OH···π bonding involved seem to have no detectable effect on the electronic transitions. Table 4 lists the spectral properties of the 1st and 2nd electronic transitions. As m decreases from 7 to 4, the absorption maxima shift toward longer wavelengths with lower intensities. This tendency is associated with an increasing bending of the benzene ring from planarity,[9,20] the extent of which is related to the magnitude of

TABLE 5. CHEMICAL SHIFTS FOR THE ALIPHATIC PROTONS OF PARACYCLOPHANOLS IN CCl_4 AT ROOM TEMPERATURE (in ppm from TMS downfield)[a)]

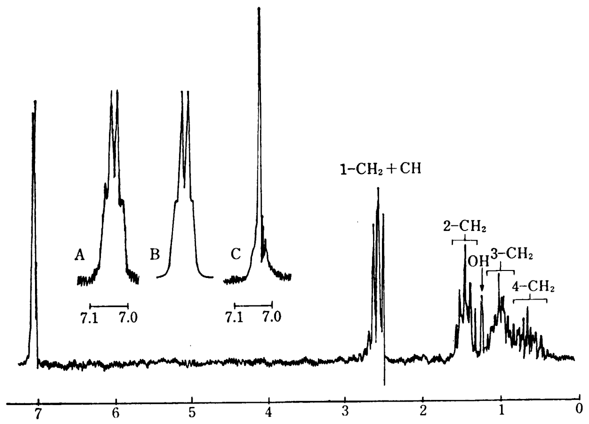
No.	OH	CH	CH_3	CH_2 at the position of						
				1	2	3	4	5	6	7
1	0.26	2.70		2.57 (t, 4H)	1.45 (m, 4H)	1.00 (m, 4H)	0.60 (m, 4H)			
	0.04	2.55		2.61	1.44	0.95	0.55			
2	0.53	2.80		2.60 (t, 4H)	1.61 (m, 4H)	1.23 (m, 4H)	0.82 (m, 8H)			
	0.09	2.72		2.59	1.49	1.12	0.90	0.80		
3	0.54	3.00		2.58 (t, 4H)	1.60 (m, 4H)	1.10 (range: 0.95—1.30) (bm, 16H)				
	0.53	2.98		2.57	1.62	1.12	1.13	1.15	1.19	
4	0.63	3.40		2.59 (t, 4H)	1.60 (m, 4H)	1.15 (range: 0.9—1.4) (bm, 20H)				
	0.68	3.48		2.59	1.56	1.23	1.25	1.18	1.17	1.33
5	0.37		0.74	2.60 (t, 4H)	1.52 (m, 4H)	0.99 (m, 4H)	0.40 (m, 4H)			
	−0.55		0.77	2.61	1.44	0.95	0.45			
6	0.41		0.88	2.60 (t, 4H)	1.63 (m, 4H)	1.22 (m, 4H)	0.45 (m, 4H)	0.82 (m, 4H)		
	0.49		0.89	2.56	1.52	1.28	0.36	0.82		
7	0.50		0.90	2.58 (t, 4H)	1.60 (m, 4H)	1.12 (bm, 8H)		1.00 (bm, 8H)		
	0.33		0.93	2.57	1.55	1.08	1.27	1.22	1.08	
8	0.57		1.00	2.58 (t, 4H)	1.60 (m, 4H)	1.12 (range: 0.75—1.38) (bm, 20H)				
	0.50		0.91	2.60	1.57	1.24	1.30	1.28	1.08	1.16
9[b)]				2.58 (t, 4H)	1.42 (m, 4H)	0.96 (m, 4H)	0.60 (m, 4H)	0.33 (m, 2H)		
				2.61	1.44	0.95	0.55	0.44		
11[c)]				2.55	1.55	1.18	0.79	0.79	0.68	
				2.59	1.49	1.12	0.90	0.80	0.65	
13[d)]	0.76	3.68		1.50[e)]	1.33[f)]					
14[g)]	0.67		1.08	1.40[e)]	1.33[f)]					

a) The numerical data in the upper row: observed; those in the lower row: predicted. In parentheses, t=triplet, m=multiplet, bm=broad multiplet, and the number of protons are cited. b) [9] Paracyclophane. c) [11]-Paracyclophane; the observed values are taken from the data presented at the 8th symposium on Structural Organic Chemistry, Kyoto, October 1975, No. 1A03 (T. Kamata, T. Inoue, and S. Misumi). d) Cyclooctadecanol. e) CH_2 at the α-position to OH. f) CH_2's other than e). g) 1-Methylcyclooctadecanol.

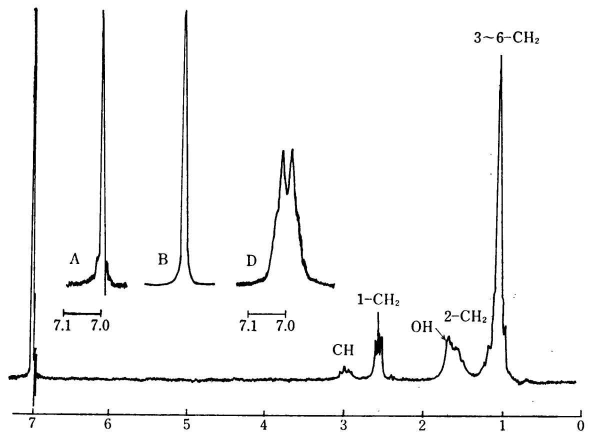
the red shift from the λ_{max} of *p*-diethylbenzene.[11)] According to this relationship, the angles of bending of the benzene rings in I and II are equal to those in the parent hydrocarbons[11)] and may be less than 5 degrees with $m=6$ and 7, equal to *ca.* 5° with $m=5$, and *ca.* 15° with $m=4$.[22)]

PMR Spectra. In the aliphatic region, the OH, CH, and CH_3 signals could easily be confirmed by their characteristic patterns, chemical shifts, relative intensities, and/or concentration-dependence. For the CH_2 signals, **1** and **2** (and also **9**, for comparison) were first examined by spin-decoupling. The signals thus assigned showed lanthanoid-induced shifts (LIS) obeying the general rule[23)] that, in alkanols, CH_2 groups at greater distances from their positions of attachment to an OH group have smaller LIS values. For this reason, the CH_2 signals of the other paracyclophanols were assigned by means of the shift-reagent technique. The results are summarized in Table 5, while the spectra of **1**, **3**, and **5** are shown in Fig. 3 as typical examples.

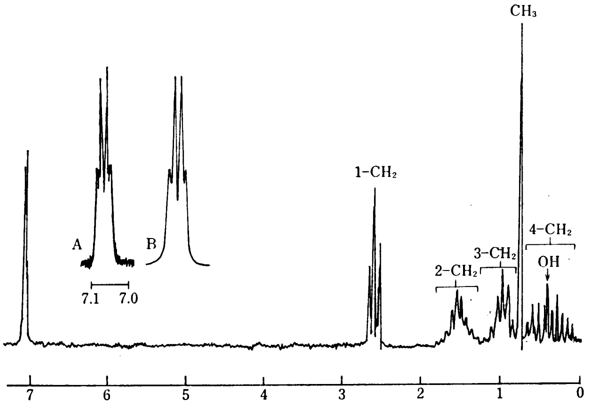
A calculation was then made using the Johnson and Bovey method[12)] in order to estimate the probable conformations. The magnitudes of chemical shielding for the 1-CH_2 and the other protons were assumed to be equal to the averaged chemical shifts (δ: 2.11 ppm) for the 3-CH_2 groups of cycloheptene and cyclooctene and to those for the corresponding protons in **13** and **14** respectively. The magnitudes of shielding for all the aliphatic protons by the π-current were predicted by constructing molecular models[24)] to establish the probable conformation of the alkylene bridge and by measuring the positions of the protons involved. After this procedure has been repeated several times, the average positions were finally obtained. The angles of bending of the benzene rings were taken as 15 and 5 degrees for only $m=4$ and 5 respectively. However, the Johnson



Compound 1



Compound 3



Compound 5

Fig. 3. PMR spectra of **1**, **3**, and **5** in CCl_4 at room temperature. A: five-fold expanded spectrum; B: calculated spectrum; C: in DMSO-d_6 at 130 °C; D: in acetone-d_6 at —60 °C.

TABLE 6. PMR DATA OF THE AROMATIC PROTONS IN PARACYCLOPHANOLS IN CCl_4 AND THE PARAMETERS USED IN SIMULATION

No.	δ (ppm)	$\Delta\delta_{A-B}$ (Hz)	J_{AB} (*para*) (Hz)	J_{AB} (*meta*) (Hz)
1	7.03(q)	2.6	0.2	1.2
2	7.01(q)	7.0	0.2	1.2
3	6.99(s)	0	0.2	1.2
4	6.98(s)	—	—	—
5	7.05(q)	2.8	0.2	1.2
6	7.01(q)	2.2	0.2	1.2
7	6.97(q)	2.0	0.2	1.2
8	6.97(s)	0	0.2	1.2
9[a)]	7.07(s)			
11[b)]	7.03(s)			
15[c)]	6.99(s)			

a), b) The same compounds as those in Table 5.
c) *p*-Diethylbenzene.

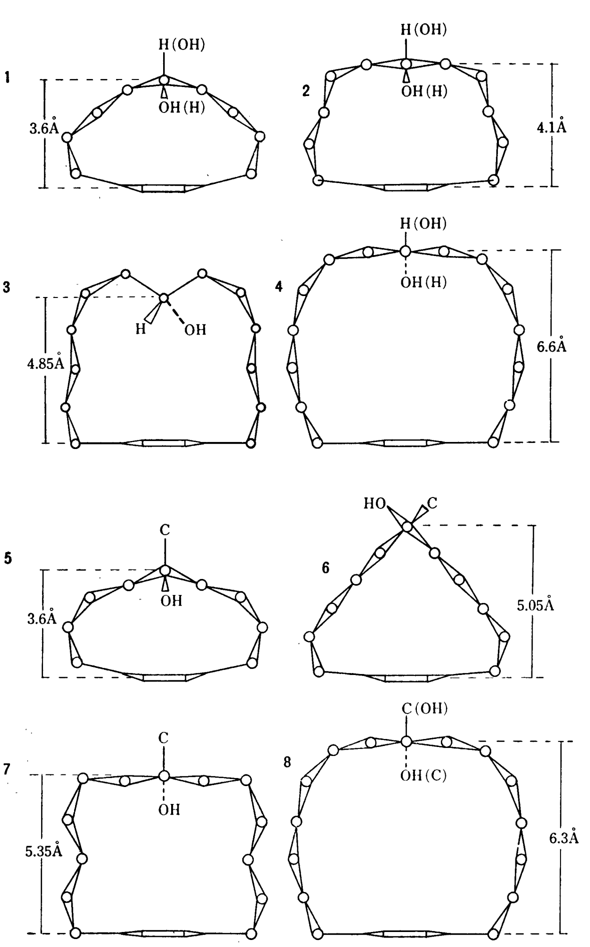


Fig. 4. Projection of the least-crowded conformations of **1**—**8** (shown by means of alkylene-bridge frameworks).

and Bovey method was employed with no modification, because there was no appreciable effect of the ring bending upon the aromatic proton resonance (see Table 6). Furthermore, the three possible rotamers of the OH group around the C–O axis were assumed to be equal in population, but the proportion of the rotamers which would be able to interact with the π-site was taken to be equal to the $A_b/(A_b+A_f)$ ratio, when the paracyclophanol in question was internally bonded. The values thus predicted are summarized in Table 5. They are in fairly good agreement with the observed ones, except for the OH protons of **1**, **2**, and **5**. Figure 4 shows the conformations constructed in the above manner, where **1**, **2**, **4**, and **8** each have two conformers with respect to the positions of OH and H or CH_3, while the others have only one conformer. The conformations of **1** and **2** were used in the calculation of **9** and **11** for comparison.

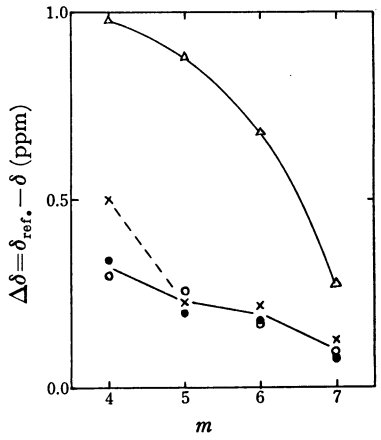
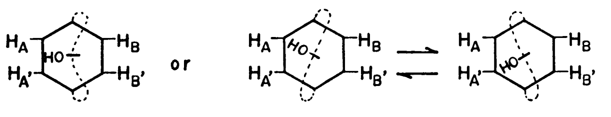


Fig. 5. Plots of m vs. $\Delta\delta$. △: CH; ●: CH_3; ×: OH in Series I; ○: OH in Series II.

Of particular interest in Table 5 are the π-current shieldings ($\Delta\delta=\delta_{ref}-\delta$) for OH, CH, and CH_3 at the central bridge carbons. Figure 5 indicates the plots of $\Delta\delta$ vs. m. In both Series I and II, except for the pair with $m=4$, the $\Delta\delta_{OH}$'s and $\Delta\delta_{CH}$, lie on almost the same curve; therefore, $\Delta\delta_{OH}$ is not related to the population of the π-bonded OH species involved. In other words, a possible deshielding for the OH proton by the π-bonding is not detectable,[25] probably because of the relatively low population of the π-bonded OH species. In the case of $m=4$, however, the $\Delta\delta_{OH}$ for **5** is less by 0.2 ppm than that for **1** (0.5 ppm). The reason for this is not clear, but the much higher population of the π-bonded OH species in **5** might be, at least in part, responsible for it.

In the aromatic region, simple AB-like quartets were observed for the lower paracyclophanols, but not for the higher homologs which showed sharp singlets, as could be confirmed by their five- or ten-fold expanded spectra. The results are listed in Table 6. In order to elucidate the difference, the temperature dependence of the spectra of **1** and **3** was examined in dimethyl-d_6 sulfoxide and acetone-d_6 respectively. On warming, the quartet of **1** changed to a broad triplet and coalesced into a relatively broad singlet at 130 °C (T_C), which thereafter further changed to a sharp singlet. On the other hand, the singlet of **3** changed, in the course of cooling down to −65 °C, to a broad singlet at −47 °C (T_C) and then split into a broad doublet which was further transformed to a broad quartet at −60 °C. These phenomena may be associated with the internal rotation of the benzene ring and/or the alkylene chain, as in substituted paracyclophanes,[26] paracyclophenes,[27] and similar heteraphanes.[28] That is, the signal splitting may be due to the spin-coupling of the aromatic protons rendered distinguishable on the NMR time scale by the slow rotation of the benzene ring and/or the alkylene chain (or by inhibition of the rotation). In the case of **1**, the rotation is slow at room temperature because of the shorter alkylene bridge, but on warming it becomes so fast as to render the protons indistinguishable. Contrary, in **3** the rotation is fast at room temperature because of the longer alkylene bridge, while on cooling it becomes so slow as to render them distinguishable. The internal rotation is expected to be more restricted in II than in I, because the methyl group at the central bridge carbon in II will play a role in restricting the rotation. In fact, **3** shows a singlet, while **7** shows a quartet. The free energy barriers, $\Delta G^{\neq}$, to rotation are 22.4 in **1** and 12.3 kcal/mol in **3**, as can be estimated by putting the observed $\Delta\delta$ (2.6 for **1** and 3 Hz for **3**) and T_C into the Calder and Garratt equation;[29] they are reasonable compared with those in other cyclophanes.[26,28]

The cause of the simple AB-like splitting is the closer approach of the C–O bond to the protons on one side of the benzene ring, as is shown below:



Here, two forms of B interconvert so fast as to render the two pairs of H_A/H_B and $H_{A'}/H_{B'}$ indistinguishable on the NMR time scale. In A and B, if H_A and $H_{A'}$ are immersed in the deshielding cone of the C–O bond, they may be expected to be slightly deshielded compared with H_B and $H_{B'}$. It is, then, safe to assume that the aromatic proton system is an A_2B_2 type, and that the two J_{AB}'s (meta and para) have small, but significant, values. These assumptions may explain the observed resonance pattern, because a rather complicated AA'BB' pattern would otherwise be expected. A computer simulation, performed under these assumptions, gave a good agreement with the observed results. The three typical examples are shown in Fig. 3, and the chemical-shift differences ($\Delta\delta_{A-B}$) and the J values used are listed in Table 6.

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