Hetera-*p*-carbophanes. IV. The Effect of Rigidity on the Chemical Shifts of Protons in Ansa Chains and Barriers to Rotation of Dioxadioxo[*n*]paracyclophanes[1)]

Kazuhiko SAKAMOTO and Michinori ŌKI*

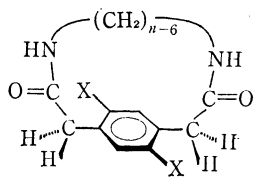
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

(Received June 26, 1974)

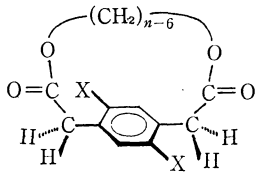
A series of dioxadioxo[*n*]paracyclophanes with or without methyl groups at the benzene ring were prepared and their PMR spectra compared with those of open-chain analogs as well as with those of paracyclophanes. Rigidity of the ansa chain was found to be an important factor in determining the chemical shifts of the ansa chain protons in addition to the ring current effect. Measurement of the PMR spectra at various temperatures revealed that the chemical shifts of the benzylic protons drifted to a small extent according to temperatures and the phenomenon was attributed to the change of solvation. Barriers to rotation of the aromatic rings in $\mathbf{6}_{15}$ and $\mathbf{6}_{16}$ were obtained as 23.3 and 11.0 kcal/mol, respectively. The barrier was discussed from the stand point of rigidity of the ansa chain.

In previous papers, the conformation of amide groups in and the internal rotation of diazadioxo[*n*]paracyclophane derivatives [$\mathbf{1}_n$ (n=12—16), $\mathbf{2}_n$ (n=11—16), $\mathbf{3}_n$ (n=11—16 and 18), and $\mathbf{4}_{18}$ (n=18)] have been reported.[1,2)] The barriers to rotation in these compounds appeared much higher than those in simple polymethylene paracyclophanes. Since these compounds contain rather rigid sp^2-hybridized structures of amide groups, the higher barrier may be attributed to the rigidity of the ansa chain. The barriers to rotation about a single bond of partial double bond characters are considered to be higher in amide groups than in ester groups because for the former it is necessary to raise the temperature to see the coalescence phenomenon of two signals in PMR spectroscopy[3)] (generally barriers are a little less than 20 kcal/mol) whereas it is necessary to cool the solution fairly deeply to observe signals of *s-cis* and *s-trans* forms by PMR spectroscopy for the latter.[4)] Thus it will be interesting to see the barrier height in heteraparacyclophanes containing two ester groups and compare the results with those of other cyclophanes.

In addition to the above point, the selection of the ester derivatives was hoped to give another advantage in studying the barrier to rotation. The amide compounds tend to crystallize out, when the solution is cooled, to give a difficulty in PMR measurements at the low temperature. Thus, although it was possible to obtain upper limits of the barriers for the amides, the precise value was not measured. Esters are known to be more soluble in ordinary solvents and the better solubility may help to see the change in barrier heights by increasing or decreasing the ansa chain length in a more quantitative fashion.



$\mathbf{1}_n$: X=H, n=12—16
$\mathbf{2}_n$: X=CH_3, n=11—16
$\mathbf{3}_n$: X=OCH_3, n=11—16, 18
$\mathbf{4}_n$: X=OC_2H_5, n=18



$\mathbf{5}_n$: X=H, n=11—16
$\mathbf{6}_n$: X=CH_3, n=11—16

This paper describes preparations of dioxadioxo[*n*]-paracyclophane derivatives [$\mathbf{5}_n$ (n=11—16) and $\mathbf{6}_n$ (n=11—16)] and discusses the effect of changing the ansa chain on the barrier to rotation. A part of the results on the internal rotation has been reported briefly.[5)]

Experimental

The syntheses of $\mathbf{5}_n$ and $\mathbf{6}_n$ were accomplished by condensation of α,ω-diols with 1,4-phenylenediacetyl dichlorides[2)] with or without methyl groups under high dilution conditions. The former compounds were of commercial origin except 1,10-decanediol.

1,10-Decanediol. Mp 71.5—72.5 °C (lit,[6)] mp 72—74 °C), was prepared by lithium aluminum hydride reduction of diethyl sebacate in ether in an almost quantitative yield.

Syntheses of Dioxadioxo[n]*paracyclophanes ($\mathbf{5}_n$ and $\mathbf{6}_n$).* The condensation between the chlorides and the diols was carried out in essentially the same method as reported previously.[1)] The crude product was chromatographed on silica gel and fractions eluted with hexane–benzene (v/v 9: 1—1: 1) were collected. Recrystallization from hexane gave the desired products. Melting points, analytical data, and yields for the pure compounds are summarized in Table 1.

Syntheses of Polymethylene Bis(2,5-dimethylphenylacetate)s ($\mathbf{7}_n$). A solution of 10 mmol of 2,5-dimethylphenylacetyl chloride in 10 ml of dry ether was slowly added to a stirred solution of 5 mmol of an appropriate α,ω-diol in tetrahydrofuran. After the addition, the reaction mixture was poured into ice–water. Subsequent work-up of the mixture in a usual manner gave a pale yellow oil. Chromatography of this oil on silica gel, using hexane–benzene mixture as eluent gave a pure compound in an almost quantitative yield. Analytical and some other data are tabulated in Table 2.

Measurement of Spectra. The infrared spectra were recorded on either a Hitachi EPI-G2 infra red spectrometer (4000—400 cm^{-1}) or a Perkin-Elmer 112G grating spectrometer (1750—1700 cm^{-1}). The measurements were run with KBr discs or neat liquids for the former instrument and with solutions in either carbon tetrachloride (*ca.* 0.0005 mol/l) or acetonitrile (*ca.* 0.01 mol/l) for the latter. The PMR spectra were measured on a Hitachi R-20B spectrometer operating at 60 MHz at 34 °C. Samples were dissolved in carbon tetrachloride for conventional measurements and the chemical shifts were recorded using TMS as an internal standard. Lanthanide [$Eu(dpm)_3$ and $Eu(fod)_3$-d_{27}] induced shift measurements were performed in deuteriochloroform solutions analogously to the method as reported previously.[7)] For the

TABLE 1. DIOXADIOXO[*n*]PARACYCLOPHANES (5_n and 6_n)

Compound	Molecular formula	Mp (°C)	Analytical data C(%)	Analytical data H(%)	Mol wt (M^+)	Yield (%)	IR (KBr) $\nu_{C=O}$ (cm^{-1})
5_{11}	$C_{15}H_{18}O_4$	147.0—148.0	68.74	6.82	262[a]	14	1730
			68.69	6.92	262[a]		
5_{12}	$C_{16}H_{20}O_4$	135.5—136.5	69.57	7.32	276	13	1725
			69.54	7.30	276		
5_{13}	$C_{17}H_{22}O_4$	110.0—111.0	70.64	7.86	290	18	1730
			70.32	7.64	290		
5_{14}	$C_{18}H_{24}O_4$	94.0—95.0	71.07	7.78	304	14	1730
			71.03	7.95	304		
5_{15}	$C_{19}H_{26}O_4$	45.0—46.0	71.86	7.95	318	16	1730
			71.68	8.23	318		
5_{16}	$C_{20}H_{28}O_4$	38.0—39.0[b]	72.06	8.32	332	30	1730[c]
			72.26	8.50	332		
6_{11}	$C_{17}H_{22}O_4$	80.0—81.0	70.03	7.85	290	12	1735
			70.32	7.64	290		
6_{12}	$C_{18}H_{24}O_4$	92.5—93.5	71.14	8.08	304	26	1735
			71.03	7.95	304		
6_{13}	$C_{19}H_{26}O_4$	51.5—53.0	71.41	7.97	318	32	1730
			71.68	8.23	318		
6_{14}	$C_{20}H_{28}O_4$	78.0—79.0	72.53	8.69	332	35	1725
			72.26	8.50	332		1740
6_{15}	$C_{21}H_{30}O_4$	87.0—88.0	72.75	8.55	346	18	1725
			72.80	8.73	346		
6_{16}	$C_{22}H_{32}O_4$	89.0—90.0	73.05	9.25	360	26	1725
			73.30	8.95	360		

a) The numerical data in the upper column are those found and those in the lower column are the calculated. b) Recrystallized after short path distillation. c) Neat.

TABLE 2. POLYMETHYLENE BIS(2,5-DIMETHYLPHENYLACETATE)S (7_n)

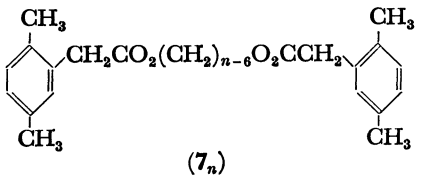
Compound	Molecular formula	Mp (°C)	Analytical data C(%)	Analytical data H(%)	IR (neat) $\nu_{C=O}$ (cm^{-1})
7_{11}	$C_{25}H_{32}O_4$		75.93	7.90[a]	1735
			75.73	8.13[a]	
7_{12}	$C_{26}H_{34}O_4$		76.31	8.12	1735
			76.06	8.35	
7_{13}	$C_{27}H_{36}O_4$		76.49	8.69	1730
			76.38	8.55	
7_{14}	$C_{28}H_{38}O_4$		76.46	8.92	1735
			76.68	8.73	
7_{15}	$C_{29}H_{40}O_4$		77.19	9.10	1740
			76.95	8.91	
7_{16}	$C_{30}H_{42}O_4$	34.5—36.0	77.22	9.12	1740 (1725)[b]
			77.21	9.07	

a) See the footnote of Table 1. b) The numerical datum in parentheses is observed with KBr disc.

DNMR measurements, the solvent system had to be changed in order to meet the requirement of the properties of solvents, as are shown in Table 5. The temperature reading was calibrated by measuring the chemical shift differences between methylene and hydroxy protons of ethylene glycol at the higher temperatures and those between methyl and hydroxy protons of methanol at the lower temperatures. The mass spectra were recorded on a Hitachi RMU-6L spectrometer.

Results and Discussion

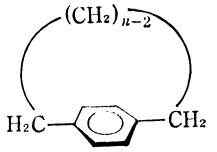
PMR Spectra. PMR spectral data of 5_n and 6_n in carbon tetrachloride solutions at 34 °C are summarized in Table 3 together with those of polymethylene bis(2,5-dimethylphenylacetate)s (7_n). Change in signal shapes of the bridge methylene protons in 5_n and 6_n,



(7_n)

which are remote from the ester moiety, due to the length of the ansa chain is similar with those observed with 2_n and 3_n and reflects rigidity and mobility of the molecules.

The multiplets due to the methylene protons gamma to the oxygen atom of the ester groups in 6_{11} and 6_{12} center at δ 0.45 and 0.80. These chemical shifts are located at the higher magnetic field with respect to those of [*n*]paracyclophanes. Waugh and Fessenden



(8_n)

TABLE 3. NMR DATA OF DIOXADIOXO[n]PARACYCLOPHANES ($\mathbf{5}_n$ and $\mathbf{5}_n$) AND POLYMETHYLENE BIS(2,5-DIMETHYLPHENYLACETATE)S ($\mathbf{7}_n$) IN CARBON TETRACHLORIDE AT 34 °C (δ from internal TMS)[a)]

Compound	Ar–H	CH_2CO	$Ar-CH_3$	OCH_2	β-CH_2[b)]	γ—δ-CH_2[b)]
$\mathbf{5}_{11}$	7.16 (s,4H)	3.49 (s,4H)		3.88 (t,4H)	1.18 (m,4H)	0.40 (m,2H)
$\mathbf{5}_{12}$	7.18 (s,4H)	3.48 (s,4H)		3.93 (t,4H)	1.25 (m,4H)	0.72 (m,4H)
$\mathbf{5}_{13}$	7.21 (s,4H)	3.46 (s,4H)		3.98 (t,4H)	1.34 (m,4H)	0.80 (b,6H)
$\mathbf{5}_{14}$	7.19 (s,4H)	3.47 (s,4H)		4.02 (t,4H)	1.45 (m,4H)	1.03 (b,8H)
$\mathbf{5}_{15}$	7.19 (s,4H)	3.47 (s,4H)		4.04 (t,4H)	1.50 (m,4H)	1.05 (b,10H)
$\mathbf{5}_{16}$	7.19 (s,4H)	3.51 (s,4H)		4.07 (t,4H)	1.54 (m,4H)	1.16 (b,12H)
$\mathbf{6}_{11}$	6.90 (s,2H)	3.47(AB-q, J=13.7, $\Delta\delta$=17.6 Hz,4H)	2.27 (s,6H)	3.86 (t,4H)	1.18 (m,4H)	0.45 (m,2H)
$\mathbf{6}_{12}$	6.92 (s,2H)	3.48(AB-q, J=13.8, $\Delta\delta$=16.0 Hz,4H)	2.28 (s,6H)	3.93 (t,4H)	1.26 (m,4H)	0.80 (m,4H)
$\mathbf{6}_{13}$	6.97 (s,2H)	3.45(AB-q, J=13.2, $\Delta\delta$=15.9 Hz,4H)	2.32 (s,6H)	3.98 (t,4H)	1.32 (m,4H)	0.83 (b,6H)
$\mathbf{6}_{14}$	6.93 (s,2H)	3.43(AB-q, J=13.7, $\Delta\delta$=14.7 Hz,4H)	2.27 (s,6H)	4.01 (t,4H)	1.46 (m,4H)	1.05 (b,8H)
$\mathbf{6}_{15}$	6.96 (s,2H)	3.45(AB-q, J=13.6, $\Delta\delta$=14.8 Hz,4H)	2.30 (s,6H)	4.03 (t,4H)	1.50 (m,4H)	1.08 (b,10H)
$\mathbf{6}_{16}$	6.95 (s,2H)	3.43 (s,4H)	2.29 (s,6H)	4.04 (t,4H)	1.50 (m,4H)	1.13 (b,12H)
$\mathbf{7}_{11}$	6.90 (s,6H)	3.44 (s,4H)	2.27, 2.23 (s,s,12H)	3.94 (t,4H)	1.49 (m)[c)]	1.37(m)(6H)[c)]
$\mathbf{7}_{12}$	6.90 (s,6H)	3.44 (s,4H)	2.26, 2.23 (s,s,12H)	3.95 (t,4H)	1.45 (m)	1.30(m)(8H)
$\mathbf{7}_{13}$	6.90 (s,6H)	3.44 (s,4H)	2.27, 2.23 (s,s,12H)	3.96 (t,4H)	1.50 (m)	1.26(b)(10H)
$\mathbf{7}_{14}$	6.90 (s,6H)	3.45 (s,4H)	2.27, 2.24 (s,s,12H)	3.98 (t,4H)	1.50 (m)	1.23(b)(12H)
$\mathbf{7}_{15}$	6.90 (s,6H)	3.45 (s,4H)	2.27, 2.24 (s,s,12H)	3.99 (t,4H)	1.50 (m)	1.24(b)(14H)
$\mathbf{7}_{16}$	6.90 (s,6H)	3.46 (s,4H)	2.28, 2.26 (s,s,12H)	3.99 (t,4H)	1.50 (m)	1.25(b)(16H)

a) s=singlet, q=quartet, m=multiplet, and b=broad signal b) relative to O-atom c) Since there were so significant overlapping with the integrals of β—δ-methylene protons in $\mathbf{7}_n$ that it was difficult to estimate the intensities of β- and γ—δ-methylene protons respectively, the intensity of β—δ-methylene protons was shown.

have reported that the central bridge methylene protons in [10]- and [12]-paracyclophanes ($\mathbf{8}_n$) give signals at δ 0.80 and 1.0, respectively, and sustain the ring current effect induced by π-electron delocalization.[8)] The difference in chemical shifts in these hetera- and homo-cyclophanes could be attributed to the anisotropy effect of atoms or groups in the most-populated conformation.

It has been well known that the shielding of a nucleus can be expressed as the sum of several terms.[9,10)] However, in the comparison of the shielding of bridge methylene protons (σ_{CH_2}) in similar molecules such as $\mathbf{6}_n$ and $\mathbf{7}_n$, the difference in the shielding exerted by atoms or groups other than the aromatic ring may be negligible at the first approximation if the conformations of ester groups are the same with each other. The ester group is known to take the *s-trans*[11)] conformation in usual cases, but it takes the *s-cis* in some cases.[4,7,12)] Lanthanide induced shift in PMR spectra is reported to be a convenient method for diagnosis of the ester conformation. If the ester is the *s-trans*, the ratio of the lanthanide induced shift *versus* [lanthanide]/[substrate] for the ether methylene is almost the same with that of carbonyl methylene, whereas it is about half when the conformation is *s-cis*.[7)] Indeed $\mathbf{6}_n$ has been reported to be *s-trans* by this method.[7)] Lanthanide induced shifts of $\mathbf{5}_n$ and $\mathbf{7}_n$ were measured and almost the same lanthanide induced shifts were obtained for CH_2O and CH_2CO in all the cases. Infrared spectra of the $\mathbf{5}_n$ and $\mathbf{6}_n$ gave only one band ($\sim$1730 cm^{-1}) for the carbonyl stretching both in carbon tetrachloride and in acetonitrile.[12)] It may be concluded from these data that the ester groups in the dioxadioxo[n]paracyclophanes examined here take *s-trans* conformations. Thus an approximation that the difference, $\Delta\sigma_{CH_2}$, in shielding of the bridge methylene is determined by the ring current effect becomes valid. Contribution of the aromatic rings to σ_{CH_2} in $\mathbf{7}_n$ will be much smaller than that in $\mathbf{6}_n$ because the distance (r) between the aromatic ring and the central methylene protons in question in an extended molecule like $\mathbf{7}_n$ is much larger than that in a folded molecule such as $\mathbf{6}_n$ and the effect is propotional to $1/r^3$.

TABLE 4. HIGH FIELD SHIFT OF THE CENTRAL BRIDGE METHYLENE PROTONS INDUCED BY DIAMAGNETIC RING CURRENT IN $\mathbf{6}_n$ (ppm)

Number of ansa chain atoms	n=11	12	13	14	15	16
σ_{CH_2} of $\mathbf{7}_n$ $-\sigma_{CH_2}$ of $\mathbf{6}_n$	0.92	0.50	0.43	0.18	0.16	0.12

Increase of the number of ansa chain atoms causes decrease in $\Delta\sigma_{CH_2}$, as is seen in Table 4. The results are close to the values which are expected from the calculation by the Johnson and Bovey method[13)] and indicate that the ansa chain conformation of the smaller chain length are fairly fixed to have the bridge-center just above the benzene ring. In such a conformation, the central part of the ansa chain will never come to the shielding cones of the C–O and/or the C=O bonds of the ester group, of which conformation has been deduced to be *s-trans*. Thus, from the stand point of

anisotropy of the ester group, the chemical shift of the bridge-center methylenes of $\mathbf{6}_n$ should be at the lower magnetic field than those of $\mathbf{8}_n$. The fact that, contrary to the simple discussion, the chemical shifts of the central methylene protons of $\mathbf{8}_n$ is at lower magnetic field than those of $\mathbf{6}_n$ may reflect the more flexibility of the methylene chain in $\mathbf{8}_n$ than that in $\mathbf{6}_n$, if the chain lengths are the same, due to the absence of sp^2 hybridized groups and, on an average, the shielding by the ring current effect in $\mathbf{8}_n$ is the less. The barriers to rotation of the aromatic rings reflect this situation also (see the later discussion).

The benzylic protons of $\mathbf{6}_{11}$—$\mathbf{6}_{15}$ give signals of the AB type at δ 3.4—3.5, whereas those of $\mathbf{5}_{11}$—$\mathbf{5}_{16}$ and $\mathbf{6}_{16}$ do signals of the A_2 type at almost the same magnetic field. The AB type signals for $\mathbf{6}_n$ are expected if the aromatic ring rotates slowly on the NMR time scale because, in these cases, the molecules exhibit chirality due to the plane asymmetry. Thus it appears that the rotation of the aromatic ring in $\mathbf{6}_{11}$—$\mathbf{6}_{15}$ is slow whereas that in $\mathbf{6}_{16}$ is fast at room temperature.

Temperature Dependence of the PMR Spectra. The PMR spectra of $\mathbf{6}_n$ were measured at various temperatures to obtain barriers to rotation of the aromatic ring. However, during the course of the study, an unexpected phenomenon appeared. That is, the differences between the chemical shifts of benzylic methylene protons showed small but definite changes within the range of 1.5—3.0 Hz at the temperatures of 34—190 °C, while the coupling constants remained intact. The changes in the chemical shift differences are linearly correlated with temperatures as shown in Fig. 1. The cause for the change cannot be the change in degrees of association of the solute, since the chemical shift differences observed at different concentrations of $\mathbf{6}_{12}$ in dimethyl-d_6 sulfoxide give the same inclinations of straight lines within experimental errors, as are shown in Fig. 2, although the absolute values of the chemical shifts change to some extent.

Such a temperature dependence may be attributed to either the solvation effect or the population effect: the latter concerns with the change in populations of conformers at various temperatures. Ifthe phenomenon were caused by the population effect, the following consideration would apply. Since the principal group which affects the chemical shifts of the benzylic protons is the aromatic ring, conformations made by rotation about the C_{Ar}–C_{CH_2} bonds may be considered: three possible conformations are shown in Fig. 3. The less stable conformers like **9** and **11** should increase in their populations when the temperature is raised. Interestingly, however, the coupling constants of the gem-hydrogens in conformations in **9** and **11** are expected to be larger than that of conformation **10** from the theory by Pople and Bothner-By.[14] This consideration leads to a conclusion that, if it were the population effect that caused the change in chemical shift differences, the coupling constants should have increased as well at higher temperatures. Since the coupling constants were almost the same at various temperatures, the situation discussed above will not apply to the present case. Thus the solvent effect becomes the reason of choice.

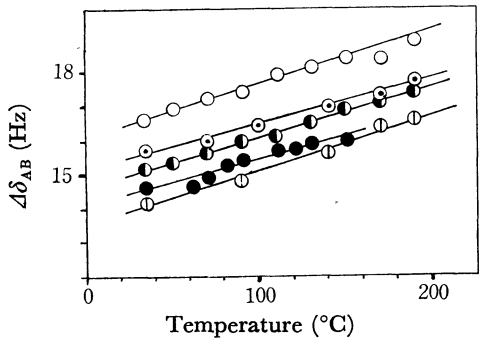


Fig. 1. Temperature dependence of the chemical shift difference between the benzylic methylene protons in $\mathbf{6}_{11}$—$\mathbf{6}_{15}$.
-○-; $\mathbf{6}_{11}$, -⊙-; $\mathbf{6}_{12}$, -◐-; $\mathbf{6}_{13}$, -◑-; $\mathbf{6}_{14}$, -●-; $\mathbf{6}_{15}$.

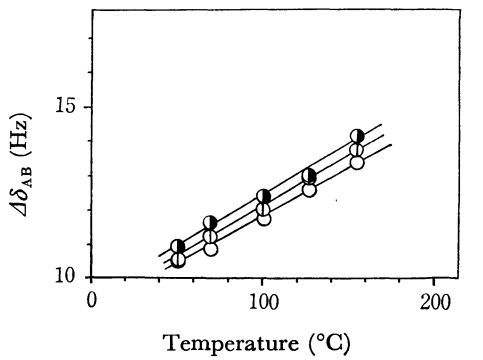
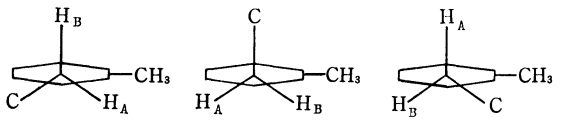


Fig. 2. Temperature dependence of the chemical shift difference between the benzylic methylene protons in $\mathbf{6}_{12}$ in DMSO-d_6.
-○-; 0.052 mol/l, -◑-; 0.25 mol/l, -◑-; 1.0 mol/l.



9 **10** **11**

Fig. 3. Rotational isomerism about C_{Ar}–C_{CH_2} bond.

The line shape of the AB quartet of $\mathbf{6}_n$ with n of 14 or less do not show any essential change on raising the

TABLE 5. FREE ENERGIES OF ACTIVATION FOR INTERNAL ROTATION OF THE AROMATIC RING[a]

Compound	$\Delta\delta_{AB}$ (Hz)	J_{AB} (Hz)	T_c (°C)	$\Delta G_c^{\ddagger}$ (kcal/mol)	Solvent
$\mathbf{2}_{15}$[2]	14.1	15.9	>170	>22.3	$CHCl_2CHCl_2$
$\mathbf{2}_{16}$[2]	(14.1)	(15.9)	<−50	<10.8	$CDCl_3$
$\mathbf{6}_{11}$	18.1	13.9			
$\mathbf{6}_{12}$	17.8	14.3	>190	>23.4	HCB[b]
$\mathbf{6}_{13}$	17.3	13.3			
$\mathbf{6}_{14}$	16.6	14.3			
$\mathbf{6}_{15}$	16.7	13.6	189	23.3	HCB[b]
$\mathbf{6}_{16}$	12.1	14.3	−50	11.0	$CDCl_3$–CS_2 (v/v 1:3)

a) The figures in parentheses are the assumed values.
b) HCB: hexachlorobutadiene.

temperature. Thus the barriers to rotation of the aromatic ring in these compounds must be very high. The minimum free energies of activation (see Table 5) are obtained by putting the NMR parameters into the following Eq. (2),[15] where $\Delta\delta_{AB}$'s were obtained by extrapolation of the straight lines shown in Fig. 1 to the coalescence temperature, when applicable.

$$\Delta G_c^* = 4.57T_c\{9.97+\log_{10}(T_c/\sqrt{\Delta\delta_{AB}^2+6J_{AB}^2})\} \quad (2)$$

As the temperature of a solution of $\mathbf{6}_{15}$ in hexachlorobutadiene was raised, the AB quartet signal gradually broadened accompanied by apparent increase in the chemical shift difference. On further warming, the chemical shift difference decreased and finally merged into a single broad peak. The temperature at which this line shape was attained was regarded as the coalescence temperature (Fig. 4).

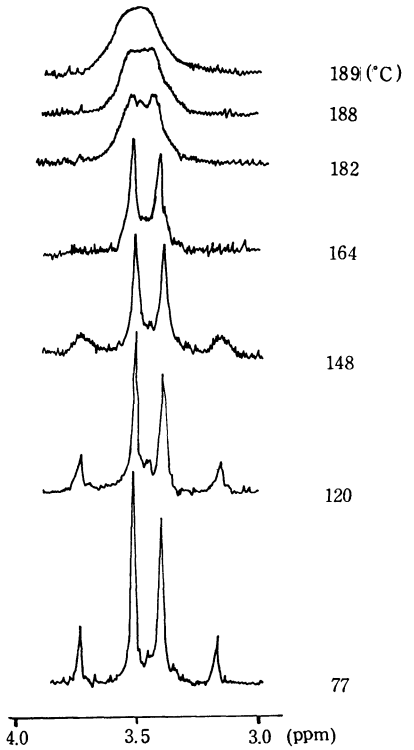


Fig. 4. Temperature dependence of PMR spectrum of $\mathbf{6}_{15}$ in hexachlorobutadiene.

In contrast, a solution of $\mathbf{6}_{16}$ in deuteriochloroform–carbon disulfide had to be cooled to find the coalescence. A chemical shift difference of 12.1 Hz and a coupling constant of 14.3 Hz were obtained at −70 °C. The free energy of activation for rotation in $\mathbf{6}_{16}$ was obtained as 11.0 kcal/mol.

The difference in the free energies of activation for internal rotation between $\mathbf{6}_{15}$ and $\mathbf{6}_{16}$ of the dioxa[n]-paracyclophane series is apparently as large as that between $\mathbf{2}_{15}$ and $\mathbf{2}_{16}$ of the diaza[n]paracyclophane series. This large difference in the height of barriers is caused by changing the number of methylene groups but one.

Comparison of the barriers and seeking a relation with the rigidity of the ansa chain will be interesting. Unfortunately, however, it is not possible to compare directly the barriers of the $\mathbf{2}_n$ series with those of the $\mathbf{6}_n$ series since the exact values of the former are not known. It might be said that, by and large, the barriers are about the same in both amide chains and ester chains, if the chain lengths are the same (see Table 5).

Rotational barriers for the aromatic rings in 14-substituted [12]paracyclophanes[16] and 1,12-disubstituted [12]paracyclophanes[17] have been reported to be 11—13 kcal/mol and *ca.* 13 kcal/mol, respectively. In contrast, 14,17-disubstituted 1,12-dioxa[12]paracyclophanes have been resolved into optical isomers at room temperature to indicate that the barrier will be more than 25—26 kcal/mol.[18] Apparently, the substitution pattern of the cyclophane must be taken into consideration in discussion of the barrier. Since the compounds discussed here have two methyl groups bonded to aromatic rings, the barrier may best be compared with those compounds resolved by Lüttringhaus and co-workers. Since the compounds of the largest ansa chain which have been resolved into enantiomers are 12 and it has not been possible to resolve a compound with an ansa chain of 14 atoms, it will be natural to assume that the compound of this type having an ansa chain of 14 atoms possesses a barrier lower than 25—26 kcal/mol. Then, since the barrier is lowered by *ca.* 10 kcal/mol by changing the chain length by one at the very critical length, the barrier for a compound having an ansa chain of 15 atoms may be assumed to have *ca.* 15 kcal/mol or less. Now comparison of the estimated barrier with those of the compounds having the ester or the amide groups in the ansa chain clearly indicate that the barrier is heightened by the introduction of these groups. Apparently the flexibility of the ansa chain is reflected to the barrier to rotation of the aromatic ring. Further study is necessary to estimate the effect of the rigidity on the barrier more quantitatively.

We wish to thank Prof. T. Shimanouchi of the University of Tokyo for permission of the use of the Perkin-Elmer 112G spectrometer. Thanks are also due to Dr. H. Nakanishi of National Chemical Laboratory for Industry who gave technical assistance in measurement of the spectra.

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