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Hetera-*p*-carbophanes. IX. Effect of the Chain-Length of Alkoxyl Groups on the Barrier to Internal Rotation of Dialkoxybenzene Rings in Dialkoxydioxodioxa[*n*]paracyclophanes[1]

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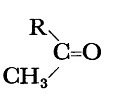
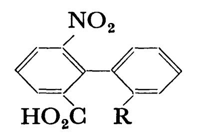
Dioxodioxa[*n*]paracyclophanes which carry two methoxyl, ethoxyl, or propoxyl groups at the aromatic rings were prepared by condensation of α,ω-diols with corresponding 2,5-dialkoxy-1,4-phenylenediacetyl dichlorides under high dilution conditions. Dynamic ^{1}H NMR spectra of these compounds show that barriers to internal rotation of the dialkoxybenzene rings are affected by the chain-length of the alkoxyl groups; the longer the chain length, the higher the barrier.

It has been well documented that the steric hindrance of the alkyl group toward reactivities of organic compounds increases as the chain-length of the alkyl group increases. A typical example is the reactivity of carbonyl groups in alkyl methyl ketones (**1**) toward sodium hydrogen sulfite:[2] the reactivity decreases as the chain-length increases. Likewise, the chain-length of alkyl groups is known to play some role in the internal rotation of molecules. The rates of racemization of $2'$-alkoxy-6-nitrobiphenyl-2-carboxylic acids (**2**) are affected by the chain-length of the alkyl group and the half-lives of **2** are 1 : 5 : 9 at *ca.* 18 °C for methyl, ethyl, and propyl compounds, respectively.[3] An apparently reverse phenomenon is observed in the internal rotation about the C_{sp^2}–R bond of dimethyl 1-methoxyalkylidenemalonates (**3**): the barrier lowers when R changes from methyl to ethyl.[4] This anomaly is, however, attributed to the steric effect which stabilizes the ground state to a greater extent than the transition state for rotation.



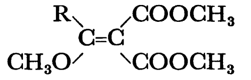
(**1**)

R = CH_3, CH_3CH_2, or $CH_3CH_2CH_2$



(**2**)

R = CH_3, CH_2CH_2, or $CH_3CH_2CH_2$



(**3**)

R = CH_3 or CH_3CH_2

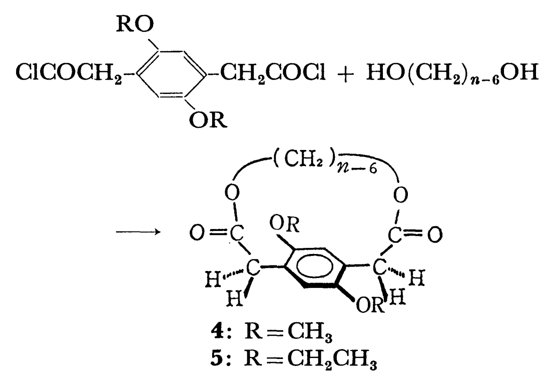
In any event, the change in barriers for internal rotation discussed above is 1 kcal/mol at the most. This small increase may be interpreted as such that the alkyl group takes a conformation, in which the steric effect is given by a first atom or group of the chain and the rest is located far from the site of direct interaction. Evidence for this consideration is found in ultraviolet spectral data which show that 2-alkylbiphenyls, where the alkyl is a straight chain, give absorption at almost the same wavelength.[5] This restriction of conformation, of course, causes the decrease in entropy in the transition state. Indeed, Hall and Harris found that the difference in the free energies of activation for rotation of compounds **2** is attributable to the difference in entropies of activation.[6]

We have briefly reported in a recent paper[7] that the barrier to internal rotation of cyclophanes is greatly influenced by the chain length of the alkoxyl groups which are attached to the benzene ring. The phenomenon was attributed to the fact that the steric hindrance is given not only by an atom or a group which is directly attached to the benzene ring in question but by the group as a whole. The group itself must pass a space provided by the ansa chain and the benzene ring for racemization of the compounds. Then a large difference in barriers is expected on elongating the chain length in contrast to the cases cited above. Our data presented before[7] give only the smallest limit ($>$1.0 kcal/mol) of difference and more work is needed to find the change in energies by lengthening the alkoxyl chain.

In this paper, we wish to describe the syntheses of dialkoxydioxodioxa[*n*]paracyclophanes, of which the alkoxyl groups are either methoxyl, ethoxyl, or propoxyl, and finding a large change in barriers due to the change in the alkoxyl group, as obtained by the ^{1}H DNMR method.

Experimental

The syntheses of dialkoxydioxodioxa[*n*]paracyclophanes ($\mathbf{4}_n$, $\mathbf{5}_n$, and $\mathbf{6}_n$) were accomplished by condensation of α,ω-diols with 2,5-dialkoxy-1,4-phenylenediacetyl dichlorides under high dilution conditions as reported previously.[8]



4: R = CH_3
5: R = CH_2CH_3
6: R = $CH_2CH_2CH_3$

The diols were of commercial origin except for 1,11-undecanediol which was prepared by lengthening the chain of 1,9-nonanediol. 1,9-Nonanediol was treated with hydrogen bromide followed by sodium cyanide in dimethyl sulfoxide to give undecanedinitrile which was hydrolyzed and esterified to give the corresponding diester. Lithium aluminium hydride reduction of the ester gave 1,11-undecanediol, mp 57—60 °C (lit,[9] mp 62.0—62.5 °C). IR (KBr) 3300 cm^{-1} (ν_{OH}). Overall yield was *ca.* 50%.

2,5-Dialkoxy-1,4-phenylenediacetyl dichlorides were known compounds[7] except for the 2,5-dipropoxy compound of which synthesis is described below.

1,4-Dipropoxybenzene. To a solution of hydroquinone (11 g, 0.1 mol) and sodium hydroxide (8.8 g, 0.22 mol) in 200 ml of water was added 43 g of propyl tosylate, which was prepared from 1-propanol and *p*-toluenesulfonyl chloride,[10] in small portions. The mixture was heated under reflux for 20 h with stirring. The reaction mixture was extracted with ether and the extract was washed with 6 M hydrochloric acid and then with cold water. After drying over magnesium sulfate, the extract was evaporated to give a pale yellow residue. Recrystallization from CH_2Cl_2–CCl_4 gave 7.0 g (36%) of the desired material, mp 48.0—49.5 °C. IR (KBr) ν_{C-O} 1220, 1025 cm^{-1}. NMR ($CDCl_3$) δ=6.82 (s, 4H), 3.85 (t, J=6.5 Hz, 4H), 1.75 (sestet, J=*ca.* 6.5 Hz, 4H), 1.02 (t, J=*ca.* 6.5 Hz, 6H).

α^1,α^4-Dichloro-2,5-dipropoxy-1,4-xylene. A mixture of 1,4-dipropoxybenzene (7.0 g, 0.035 mol), 37% formalin (6.6 g), concentrated hydrochloric acid (40 ml), and glacial acetic acid (35 ml) was warmed at 50—60 °C for 1.5 h with stirring and introducing dry hydrogen chloride. The resulting solid was collected by filtration and was washed with water. Recrystallization from CH_2Cl_2–CCl_4 gave 8.0 g (78%) of the pure material, mp 79.5—81.0 °C. IR (KBr) ν_{C-O} 1230, 1030 or 1050 cm^{-1}. NMR ($CDCl_3$) δ=6.92 (s, 2H), 4.63 (s, 4H), 3.96 (t, J=6.5 Hz, 4H), 1.84 (sestet, J=*ca.* 6.5 Hz, 4H), 1.08 (t, J=*ca.* 6.5 Hz, 6H).

α^1,α^4-Dicyano-2,5-dipropoxy-1,4-xylene, mp 107.0—108.0 °C (recrystallized from ether–hexane), was prepared from the above dichloride by treatment with sodium cyanide[7] in *ca.* 90% yield. IR (KBr) $\nu_{C\equiv N}$ 2250, ν_{C-O} 1240 and 1030 cm^{-1}. NMR ($CDCl_3$) δ=6.92 (s, 2H), 3.95 (t, J=6.5 Hz, 4H), 3.70 (s, 4H), 1.84 (sestet, J=*ca.* 6.5 Hz, 4H), 1.06 (t, J=*ca.* 6.5 Hz, 6H). Found: C, 70.76; H, 7.52; N, 10.45%. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29%.

2,5-Dipropoxy-1,4-phenylenediacetic Acid. A mixture of the dicyanide (6.5 g, 0.24 mol), ethylene glycol monomethyl ether (50 ml), and sodium hydroxide (5.0 g) in 20 ml of water was refluxed until a homogeneous solution resulted. The reaction mixture was then diluted with 50 ml of cold water, cooled, and poured with stirring into 50 ml of concentrated hydrochloric acid to yield 5.0 g (67%) of a crude product. After purification, the product melted at 200.0—203.0 °C with decomposition. IR (KBr) $\nu_{C=O}$ 1710, ν_{C-O} 1240 and 1030 cm^{-1}.

2,5-Dipropoxy-1,4-phenylenediacetyl dichloride was obtained by a reaction of thionyl chloride with the diacid in dry ether. The yield was 70%. Mp 106.0—107.0 °C (recrystallized from ether). IR (KBr) $\nu_{C=O}$ 1810, ν_{C-O} 1230 and 1000 cm^{-1}. NMR ($CDCl_3$) δ=6.72 (s, 2H), 4.10 (s, 4H), 3.89 (t, J=6.5 Hz, 4H), 1.79 (sestet, J=*ca.* 6.5 Hz, 4H), 1.13 (t, J=*ca.* 6.5 Hz, 6H).

Syntheses of Dialkoxydioxodioxa[n]*paracyclophanes* (**4_n**, **5_n**, *and* **6_n**). The method of syntheses of the paracyclophanes was essentially the same as reported previously.[3] The products were purified by column chromatography on silica gel. Either hexane–benzene or hexane–ether was used for both chromatography and recrystallization. Melting points, analytical data, and solvents of recrystallyzation are summarized in Table 1.

Measurement of Spectra. The infrared spectra were recorded on a Hitachi EPI-G2 spectrometer as KBr discs or neat liquid. The ^1H NMR spectra were measured on a Hitachi R-20B spectrometer with a variable temperature accessory, operating at 60 MHz. The chemical shifts at lower temperatures than 34 °C were recorded with the use of TMS as an internal standard, whereas those at higher temperatures were recorded relative to internal $Cl_2CHCHCl_2$ and converted to the usual δ scale. The temperature reading was calibrated by measuring the chemical shift difference between methyl and hydroxyl protons of methanol at the lower temperatures, whereas the chemical shift difference between methylene and hydroxyl protons of ethylene glycol was used for the higher temperatures. The mass spectra were observed on a Hitachi RMU-6L spectrometer.

Table 1. Dialkoxydioxodioxa[*n*]paracyclophanes

Compound	Molecular formula	Mp(°C)	Analytical data[a)] C(%)	Analytical data[a)] H(%)	Mol wt[a)] (M+)	Solvent of recrystallization	Yield (%)
4_{15}	$C_{21}H_{30}O_6$	61.5—62.5	66.56	8.08	378	hexane	17
			66.64	7.99	378.5		
4_{16}	$C_{22}H_{32}O_6$	63.0—64.0	67.26	8.50	392	hexane	20
			67.32	8.22	392.5		
4_{17}	$C_{23}H_{34}O_6$	74.5—75.0	67.92	8.33	406	hexane–ether	
			67.96	8.43	406.5		
5_{16}	$C_{24}H_{36}O_6$	oil	68.31	8.82	420		
			68.55	8.63	420.5		
5_{17}	$C_{25}H_{38}O_6$	50.0—51.0	68.80	8.81	434	hexane–ether	
			69.10	8.81	434.6		
5_{18}	$C_{26}H_{40}O_6$	oil	69.91	9.25	448		
			69.61	8.99	448.3		
6_{17}	$C_{27}H_{42}O_6$	oil	69.82	9.39	462		
			70.09	9.15	462.3		
6_{18}	$C_{28}H_{44}O_6$	oil	70.86	9.60	476		
			70.56	9.30	476.3		

a) The upper numerical values are those found experimentally and the lower are the calculated.

Results and Discussion

For the convenience of discussion, compounds are denoted by bold face numbers with suffixes. The suffix corresponds to the length of the ansa chain.

Due to wide variety of coalescence temperatures and solubility, it was not possible to obtain spectra at appropriate temperatures with the use of a single solvent. Although this could cause, in principle, change in barriers, the barrier to rotation is known to be affected by solvent to a small extent expect special cases such as hydrogen bond formation.11) Thus we discuss the barrier neglecting the solvent effect. Large differences shown below will allow such an approximation.

Heavy overlap of the signals handicapped the total line shape analysis and data so obtained are not expected to be highly reliable. Therefore we limited the investigation to obtaining the free energies. The discussion given below does have drawbacks due to comparison of free energies at different temperatures, yet it is valid because the difference in free energies are large enough to make the contribution of the entropy factor minor.

DNMR Spectra and Rotational Barriers. ^{1}H NMR spectral data of dialkoxydioxodioxa[*n*]paracyclophanes (**4**$_n$, **5**$_n$, and **6**$_n$) at 34 °C are summarized in Table 2. Geminal benzylic protons of **4**$_{15}$, **4**$_{16}$, **5**$_{16}$, **5**$_{17}$, **6**$_{17}$, and **6**$_{18}$ give AB type signals which suggest that the internal rotation of the dialkoxybenzene ring is slow on the NMR time scale. In contrast, those which carry longer ansa chains in the series of **4** and **5** give singlets for benzylic protons to indicate that the internal rotation in these compounds is fast. Thus the temperatures of measurement were varied to see possible coalescence phenomena. By observing coalescence temperature (T_C), difference ($\Delta\delta_{AB}$) in chemical shifts of the AB protons, and the coupling constant (J_{AB}), the barrier to rotation should be obtained by applying the following equation.12)

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

The line shape of the AB quartets due to benzylic protons of **4**$_{15}$, **5**$_{16}$, and **6**$_{17}$ does not show any essential change on raising the temperature up to 190 °C. The barriers to rotation in these compounds are estimated to be over 23 kcal/mol. In contrast, the AB quartets due to benzylic protons of **4**$_{16}$, **5**$_{17}$, and **6**$_{18}$ coalesce on raising the temperature, as is illustrated in Fig. 1. taking **5**$_{17}$ as an example.

The sharp singlet due to benzylic protons of **4**$_{17}$ broadened considerably on lowering the temperature and finally split into an AB quartet, although the downfield part of the quartet was masked by the signals due to CH$_2$'s alpha to ether oxygens and by that of methoxyl groups. The coalescence temperature of the benzylic methylene signals of **4**$_{17}$ in CS$_2$–CDCl$_3$ (v/v 3: 1) was −52 °C. Likewise the coalescence temperature of signals due to benzylic protons in **5**$_{18}$ was found to be −69 °C.

The AB signals due to benzylic protons of **4**$_{17}$ and **5**$_{18}$ were still dull at the lowest temperature attainable with the instrument. Thus exact values of $\Delta\delta_{AB}$ for both com-

Table 2. Spectral data of dialkoxydioxodioxa[*n*]paracyclophanes

	^{1}H NMR (δ)										IR(cm^{-1})	
Compound	Ar–H	OCH$_3$ or OCH$_2$ or OCH$_2$	CH$_3$ or CH$_2$	CH$_3$	COOCH$_2$	CH$_2$CO a)	β-CH$_2$ b)	Other CH$_2$'s	Solvent	State	$\nu_{C=O}$	ν_{C-O}
4$_{15}$	6.69	3.79			4.03	3.48 (J=15.0, $\Delta\delta$=41.2)	1.50	1.11 c)	CDCl$_3$	KBr	1730	1220 1055
4$_{16}$	6.69	3.78			4.09	3.48 (J=14.7, $\Delta\delta$=39.9)	1.50	1.15 c)	CCl$_4$	KBr	1725	1220 1055
4$_{17}$	6.62	3.72			4.00	3.42 (singlet)	1.52	1.18 c)	CS$_2$	KBr	1730	1225 1050
5$_{16}$	6.68	3.97	1.41		4.04	3.48 (J=14.8, $\Delta\delta$=41.7)	1.8—1.0 d)		CCl$_4$	neat	1735	1210 1050
5$_{17}$	6.69	3.96	1.39		4.05	3.49 (J=14.9, $\Delta\delta$=39.0)	1.9—0.9 d)		CCl$_4$	KBr	1720 1740	1220 1060
5$_{18}$	6.58	3.87	1.33		3.97	3.42 (singlet)	1.8—0.9 d)		CS$_2$	neat	1735	1215 1055
6$_{17}$	6.67	3.87	1.8	1.07	4.09	3.49 (J=15.0, $\Delta\delta$=39.7)	1.9—1.0 d)		CCl$_4$	neat	1735	1215 1070
6$_{18}$	6.66	3.85	1.7	1.04	4.05	3.48 (J=15.1, $\Delta\delta$=39.9)	1.8—0.9 d)		CCl$_4$	neat	1735	1210 1070

a) These signals are of AB type unless otherwise stated. Center of the chemical shifts, coupling constant, and difference in chemical shifts of two protons (in Hz) are shown. b) Relative to ether oxygen of the ester. c) Broad singlets. d) The signals are not resolved enough for identification.

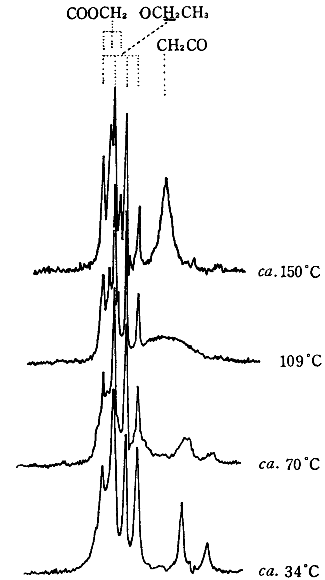
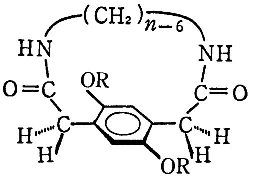


Fig. 1. DNMR Spectra of $\mathbf{5}_{17}$ in HCB.

pounds and that of J_{AB} for $\mathbf{5}_{18}$ could not be obtained. Then $\Delta\delta_{AB}$ and J_{AB} of $\mathbf{6}_{17}$ in CS_2 at 34 °C must be diverted to $\mathbf{4}_{17}$ and $\mathbf{5}_{18}$: this operation should not cause serious errors in barriers since the structures of these compounds are alike. The results are summarized in Tables 3 and 4. Data[7] of dialkoxydioxodiaza[*n*]-paracyclophanes (**7** and **8**) and dimethyldioxodioxa[*n*]-paracyclophanes (**9**) are also included for comparison.



7: $R=CH_3$
8: $R=CH_2CH_3$

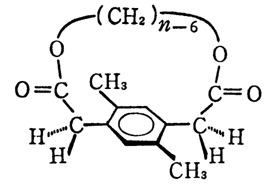


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Table 3. ^{1}H NMR Data of geminal benzyl protons of substituted hetera-*p*-carbophanes[a)]

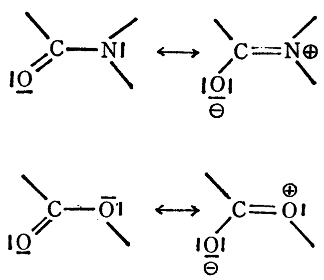
Compound	$\Delta\delta_{AB}$(Hz)	J_{AB}(Hz)	T_C(°C)	Solvent[b)]
$\mathbf{4}_{15}$	41.3	14.6	>190	HCB
$\mathbf{4}_{16}$	40.9	14.3	164	HCB
$\mathbf{4}_{17}$	(40.0)	15.0	−52	CS_2-$CDCl_3$(v/v 3: 1)
$\mathbf{5}_{16}$	42.9	14.5	>190	HCB
$\mathbf{5}_{17}$	39.2	14.8	109	HCB
$\mathbf{5}_{18}$	(40.0)	(15.0)	−69	CS_2
$\mathbf{6}_{17}$	39.7	14.7	>190	HCB
$\mathbf{6}_{18}$	37.8	15.1	102	HCB
$\mathbf{7}_{16}$	36.8	14.4	>174	$CHCl_2CHCl_2$
$\mathbf{7}_{18}$	(39.8)	(14.4)	<−50	$CDCl_3$
$\mathbf{8}_{18}$	(39.8)	(14.4)	−30	$CDCl_3$
$\mathbf{9}_{15}$	16.7	13.6	189	HCB
$\mathbf{9}_{16}$	12.1	14.3	−50	CS_2-$CDCl_3$(v/v 3: 1)

a) The values in parentheses are assumed ones. See the text and Ref. 7. b) HCB=hexachloro-1,3-butadiene.

Table 4. Free energies of activation for rotation of substituted benzene rings at coalescence temperatures (kcal/mol)

Diaza series				
Substituents at the aromatic ring		CH_3O (**7**)	CH_3CH_2O (**8**)	
Ansa-chain length	16	>22.2		
	18	<10.9	11.9	
Dioxa series				
Substituents at the aromatic ring		CH_3O (**4**)	CH_3CH_2O (**5**)	$CH_3CH_2CH_2O$ (**6**)
Ansa-chain length	15	>23.1		
	16	21.7	>23.0	
	17	10.7	18.9	>23.1
	18		9.8	18.5
Dioxa series				
Substituents at the aromatic ring		CH_3 (**9**)		
Ansa-chain length	15	23.3		
	16	11.0		

Effect of Rigidity of the Ansa Chain on the Rotational Barriers. It is well known that formal single bonds (C–N and C–O) of amides and ester groups often have considerable double bond character due to delocalization of the lone pair electrons as is visualized by the canonical forms:



Contribution of these canonical forms with a double bond between C and N or between C and O raises the barrier to rotation about the bond in question by lowering the ground state and/or raising the transition state for rotation. Since contribution of the dipolar structure of amides is larger than that of esters, the barriers to internal rotation of amides[13)] are usually higher than those of esters.[14)] In other words, a chain containing amide groups is considered to be more rigid than that containing ester groups. The cyclophanes dealt with here and elsewhere[7)] consitute a series to be compared from the stand point of the rigidity of the chain.

Inspection of Table 4 reveals that an amide with two ethoxyl groups ($\mathbf{8}_{18}$) has a higher barrier to rotation of the diethoxybenzene ring than an ester having the same groups ($\mathbf{5}_{18}$) by 2.1 kcal/mol. Since the coalescence temperature of $\mathbf{8}_{18}$ is higher than that of $\mathbf{5}_{18}$, the difference in enthalpies of activation may be still larger. Similar comparison is made between $\mathbf{7}_{16}$ and $\mathbf{4}_{16}$ to show that the amide gives a higher barrier by at least 0.5 kcal/mol. Thus if we compare the barriers to rotation of the dialkoxybenzene ring in diamides with that in diesters with the same ansa-chain length, the barriers are always higher in amides. This must be a reflection of the fact that the higher mobility makes it easier for the ansa chain to take a suitable conformation to rotation of the substituted benzene ring.

Effect of the Chain Lengths of Alkoxyl Groups on Rotational Barriers. A recent report from this laboratory has revealed that $\mathbf{4}_{16}$ with two methoxyl groups at the aromatic ring possesses a higher barrier to rotation of the aromatic ring than $\mathbf{9}_{16}$ with two methyl groups by 10.7 kcal/mol.[15] This result was attributed to the steric hindrance of the methoxyl group, given not only by the oxygen atom but by the group as a whole: the methoxyl group must be bulkier than the methyl if the whole group is considered. The phenomenon makes a sharp contrast to the fact that the methoxyl group is generally considered to be of less effective bulkiness than the methyl as is shown by a typical example of barriers to rotation of 2′-substituted 5′-methyl-6-nitrobiphenyl-2-carboxylic acids.[16]

By finding an example of a methoxyl group giving its steric hindrance as a whole, comparison of the steric effect given by a series of straight chain alkyl groups becomes of interest. This is a reason why various dialkoxydioxodioxa[*n*]paracyclophanes were prepared to examine the barriers. Comparison of the data in Table 4 indicates that changing the alkoxyl group from methoxyl to ethoxyl causes the increase in the barrier to rotation by 8.2 kcal/mol in the series of 17-membered ansa chain. Similarly the barrier increases by at least 4.2 kcal/mol on going from ethoxyl to propoxyl in the same series. The same change in the series of 18-membered ansa chain causes the increase of 8.7 kcal/mol. The dramatic change in rotational barriers reflects a fact that the whole substituent must pass through a space, probably as a folded form, provided by the ansa-chain and the benzene ring. In sharp contrast to the fact that the chain-lengthening of the alkyl group usually affects the barriers to rotation to a small extent (1 kcal/mol or less), the steric effect presented here increases by 8—9 kcal/mol by lengthening the chain by but one carbon. This finding is a support for an assumption that the steric effect is often given by the first atom or group in the chain and gives a measure for the bulkiness of the alkoxyl group as a whole.

Effect of the Ansa-Chain Length on the Rotational Barriers. The difference ($\Delta\Delta G^{\neq}$) in free energies of activation for rotation of the aromatic rings in $\mathbf{9}_{15}$ and $\mathbf{9}_{16}$ with two methyl groups has been reported to be 12.3 kcal/mol.[8] $\Delta\Delta G^{\neq}$ between $\mathbf{4}_{16}$ and $\mathbf{4}_{17}$ of the dimethoxy series and that between $\mathbf{5}_{17}$ and $\mathbf{5}_{18}$ of the diethoxy series are 10.0 and 9.1 kcal/mol, respectively.

Although it is not possible to compare the whole series to investigate the effect of lengthening the ansa-chain on barriers to rotation, the effect of lengthening the ansa-chain by one on the barriers should become small, in principle, if the ansa-chain length is long enough. The present series represents a part of such tendency. Namely $\Delta\Delta G^{\neq}$ decreases as follows: $\Delta\Delta G^{\neq}$ ($\mathbf{9}_{15}$ and $\mathbf{9}_{16}$)$>\Delta\Delta G^{\neq}$ ($\mathbf{6}_{16}$ and $\mathbf{6}_{17}$)$>\Delta\Delta G^{\neq}$ ($\mathbf{7}_{17}$ and $\mathbf{7}_{18}$). Extending the chain of the alkoxyl group should provide a method of study on the effect of the ansa-chain length on the rotational barriers.

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