Hetera-*p*-carbophane. VIII. The Change in Binding Sites of NMR Shift Reagents in Polyoxadioxo[*n*]paracyclophanes and Their Open-chain Analogs[1)]

Kazuhiko SAKAMOTO and Michinori ŌKI*

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received May 7, 1976)

A series of polyoxadioxo[*n*]paracyclophanes were prepared by condensation of polyethylene glycols with the corresponding 2,5-disubstituted *p*-phenylenediacetyl dichlorides under high dilution conditions. ^{1}H NMR spectra of these compounds were recorded in the presence and absence of lanthanoid shift reagents and the results are compared with those of the open-chain analogs. The change in binding sites of the shift reagents is observed as the number of ethylenedioxy units increases, and the result is discussed from the standpoint of electronic and steric effects.

The usefulness of NMR shift reagents for the determination of the ester conformations, *s-cis* and *s-trans*, has been reported from this laboratory.[2)] As a combined extension of this and other studies on hetera-*p*-carbophanes, it was of interest to investigate the binding sites of the shift reagent for polyoxadioxo[*n*]paracyclophanes.

A literature search revealed that, although ether oxygen is usually a very weak binding site for the shift reagent,[3)] polyglyme does form a complex at the end of the chain[4)] and several aromatic compounds which possess two ether groups *ortho* to each other bind more strongly to the shift reagent at the ethers than to the ester groups.[5)] Therefore, if an ansa chain contains ethylenedioxy units there is a possibility that competition takes place among the binding sites including the ethylenedioxy and the ester groups.

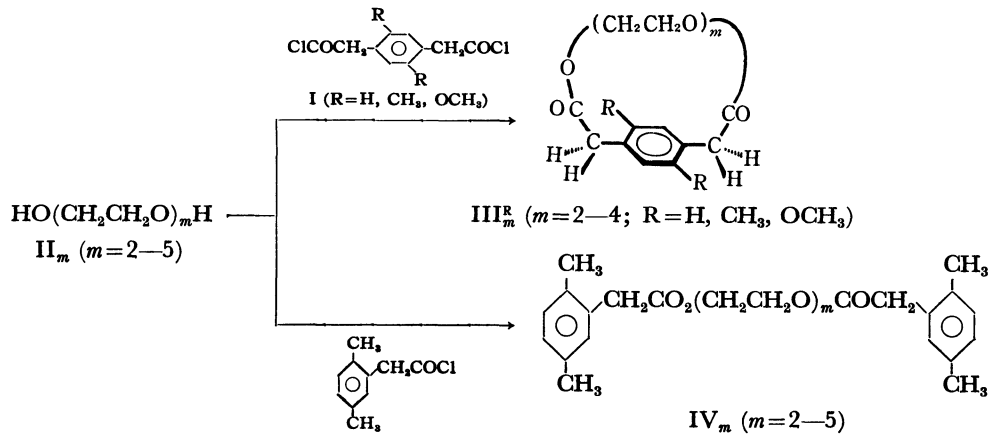
Therefore, a series of polyoxadioxo[*n*]paracyclophanes and open-chain analogs were prepared and their ^{1}H NMR spectra were observed in the presence of the shift reagents. This paper describes an interesting result which suggests that a change in the binding sites occurs according to the chain length of the polyoxyethylene compounds.

Experimental

The syntheses of a series of disubstituted polyoxadioxo[*n*]-paracyclophanes (III^R_m, where *m* is the number of oxyethylene units and R the substituent) and open-chain analogs (IV_m, where *m* is the number of oxyethylene units) were accomplished by the condensation of polyoxaalkane-α,ω-diols (polyethylene glycols) with the corresponding acyl chlorides (Scheme 1). The polyoxaalkane-α,ω-diols were of commercial origin except for 3,6,9,12-tetraoxatetradecane-1,14-diol (II_5) which was prepared according to a method described in the literature.[6)] The acid chlorides were synthesized in a manner reported previously.[7)]

Syntheses of Polyoxadioxo[n]*paracyclophanes (III^R_m) and Bis(2,5-dimethylphenylacetate)s (IV_m) of Polyoxaalkane-α,ω-diols.* The condensation between the chlorides (I) and the diols (II_m) was carried out in essentially the same manner as that reported previously,[8)] except for the omission of the base. A chromatograph of the crude products on silica gel using a hexane–ether mixture as the eluent gave pure compounds. Esterification of II with 2,5-dimethylphenylacetyl chloride proceeded normally. Analytical and other pertinent data are summarized in Table 1.

Measurement of Spectra. The infrared spectra were recorded on a Hitachi EPI-G2 infrared spectrometer with KBr discs for III^R_m and with a neat liquid for IV_m. The ^{1}H NMR spectra were measured at 34 °C on a Hitachi R-20B spectrometer operating at 60 MHz. Samples were dissolved in deuteriochloroform for conventional measurements and the chemical shifts were recorded relative to an internal TMS. Lanthanoid [Eu(dpm)$_3$ and Eu(fod)$_3$-d_{27}] induced shifts were measured with deuteriochloroform solutions in a manner analogous to that reported previously.[2)] The mass spectra were recorded on a Hitachi RMU-6L spectrometer.



Scheme 1.

TABLE 1. POLYOXADIOXO[*n*]PARACYCLOPHANES (III^R_m) AND BIS(2,5-DIMETHYLPHENYLACETATE)S (IV_m) OF POLYOXAALKANE-α,ω-DIOLS[a]

Compound	*m*	R	Molecular formula	Mp (°C)	Analytical data C(%)	Analytical data H(%)	Mol wt	Recrystallization solvent	IR ν_{CO} (cm^{-1})
III^R_m	2	H	$C_{14}H_{16}O_5$	158.5—159.5	64.11	6.21	264	CH_2Cl_2	1725
					63.62	6.10	264.3		
	2	Me	$C_{16}H_{20}O_5$	96.0— 97.0	66.09	7.26	292	ether–hexane	1725
					65.74	6.90	292.3		
	3	H	$C_{16}H_{20}O_6$	39.0— 40.0	62.37	6.30	308	ether–hexane	1720[b]
					62.33	6.54	308.3		
	3	Me	$C_{18}H_{24}O_6$	70.5— 71.0	64.51	7.11	336	ether–hexane	1730[b]
					64.27	7.19	336.4		
	4	H	$C_{18}H_{24}O_7$	95.5— 96.5	61.37	6.83	352	CH_2Cl_2	1735
					61.35	6.87	352.4		
	4	Me	$C_{20}H_{28}O_7$	85.5— 86.5	63.23	7.53	380	ether	1720
					63.14	7.42	380.4		
	4	OMe	$C_{20}H_{28}O_9$	94.5— 95.0	58.23	6.64	412	ether	1725
					58.24	6.84	412.4		
IV_m	2		$C_{24}H_{30}O_5$	oil	72.12	7.50			1740
					72.34	7.59			
	3		$C_{26}H_{34}O_6$	oil	70.77	7.61			1725
					70.56	7.74			
	4		$C_{28}H_{38}O_7$	oil	69.30	7.64			1745
					69.11	7.87			
	5		$C_{30}H_{32}O_8$	oil	68.06	8.09			1730
					67.90	7.99			

a) The numerical values in the upper column are those found experimentally and those in the lower column are calculated values. b) A broad or bifurcated absorption.

TABLE 2. ^1H NMR DATA FOR POLYOXADIOXO[*n*]PARACYCLOPHANES (III^R_m) AND BIS(2,5-DIMETHYLPHENYLACETATE)S (IV_m) OF POLYOXAALKANE-α,ω-DIOLS IN DEUTERIOCHLOROFORM AT 34 °C (δ)[a]

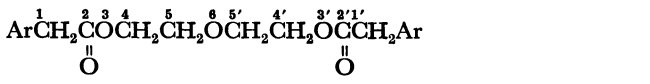
Protons	Compounds										
	III^H_2	III^{Me}_2	IV_2	III^H_3	III^{Me}_3	IV_3	III^H_4	III^{Me}_4	III^{OMe}_4	IV_4	IV_5
1-CH_2	3.52	3.60	3.61	3.60	3.58	3.61	3.63	3.59	3.65	3.61	3.63
	s	AB-q[b]	s	s	AB-q[c]	s	s	s	s	s	s
	4H	4H	8H*	8H*	8H*	12H*	16H*	8H*	8H*	16H*	16H*
4-CH_2	4.07	4.03	4.20	4.21	4.19	4.24	4.29	4.24	4.27	4.25	4.26
	AA′	AA′	AA′	AA′	AA′	AA′	AA′	AA′	AA′	AA′	AA′
	4H	4H	4H	4H	4H	4H	4H	4H	4H	4H	4H
5-CH_2	3.21	3.21	3.58	3.53	3.54	3.63	3.63	3.62	3.65	3.66	3.68
	BB′	BB′	BB′	BB′	BB′	BB′	BB′	BB′	BB′	BB′	BB′
	4H	4H	8H*	8H*	8H*	12H*	16H*	8H*	8H*	16H*	16H*
7-CH_2				3.15	3.14	3.54					
				s	s	s					
				4H	4H	12H*	3.50	3.41	3.44	3.59	3.60
8-CH_2							m	m	m	s	s
							16H*	8H*	8H*	16H*	16H*
10-CH_2											
Ar–H	7.20	6.94	7.00	7.25	7.02	7.00	7.30	7.02	6.78	7.00	7.02
	s	s	s	s	s	s	s	s	s	s	s
	4H	2H	6H	4H	2H	6H	4H	2H	2H	6H	6H
Ar–CH_3		2.26	2.27		2.28	2.27		2.28	(3.80)	2.27	2.28
(or–OCH_3)		s	bs		s	bs		s	bs	bs	bs
		6H	12H		6H	12H		6H	6H	12H	12H

a) s=singlet, AB-q=AB-quartet, m=multiplet, AA′=AA′ part of AA′BB′ type signal, BB′=BB′ part of AA′BB′ type signal, and bs=broad signal. b) J_{AB}=14.0 Hz, $\Delta\delta_{AB}$=16.8 Hz. c) J_{AB}=14.5 Hz, $\Delta\delta_{AB}$=14.5 Hz. *) Since there was so much overlapping of the methylene protons at δ 3.4—3.7 in III^R_m and IV_m that it was difficult to estimate the intensities separately, the intensity of all protons contributing to the overlapped signals was shown.

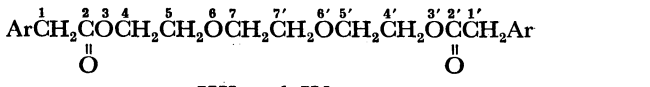
Results and Discussion

Peak Assignments of Bridge Methylene Protons. The ^1H NMR spectral data of polyoxadioxo[n]paracyclophanes (III^R_m) and bis(2,5-dimethylphenylacetate)s (IV_m) of polyoxaalkane-α,ω-diols are summarized in Table 2.

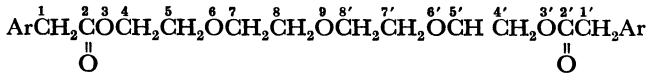
The benzylic protons of III^{Me}_2 and III^{Me}_3 give signals of the AB type at δ *ca.* 3.60, suggesting a slow internal rotation of the aromatic ring on the NMR time scale, whereas those of III^R_m other than III^{Me}_2 and III^{Me}_3 and IV_m give signals of the A_2 type at δ 3.52—3.65. AA'BB' signals appearing at δ 4.0—4.3 and 3.2—3.7 for III^R_m and IV_m are assigned to 4- and 5-methylene protons,



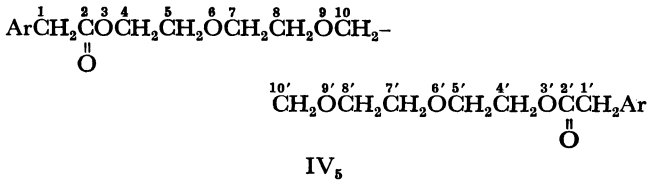
III^R_2 and IV_2



III^R_3 and IV_3



III^R_4 and IV_4



IV_5

respectively, from a comparison of the chemical shifts with those for α-methylene protons of the corresponding dioxadioxo[n]paracyclophanes (V_n, where n is the number of atoms in the ansa chain) and open-chain analogs,[8] and by taking advantage of a known chemical shift rule.[9] The singlets observed at δ *ca.* 3.15 for III^R_3 and at δ 3.54 for IV_3 were then assigned to 7-methylene protons. Similarly, the multiplets centered at δ *ca.* 3.5 for III^R_4 and the broad singlet at δ *ca.* 3.6 for IV_4 were attributed to 7- and 8-methylene protons. IV_5 has a singlet signal for 7-, 8-, and 10-methylene protons.

Table 3. High-field shift induced by a diamagnetic ring current[a]

m	Position of bridge methylenes			
	4	5	7	8
2	0.17	0.37		
3	0.05	0.09	0.40	
4	0.01	0.04		0.18

a) For the numbering of the bridge methylene, see text.

On the basis of the above assignments, the difference in chemical shifts of the corresponding methylene protons can be calculated, as $\Delta\delta_{CH_2}=\delta_{CH_2}(IV_m)-\delta_{CH_2}(III^{Me}_m)$, and the results are shown in Table 3. The results are believed to be a reflection of the ring current effect of the benzene ring and, indeed, are in close agreement with the expected values from a calculation using the Johnson-Bovey method.[10] An increase in the number of oxyethylene units causes a decrease in $\Delta\delta_{CH_2}$ indicating that the mobility of the ansa chain is increased and the ring current effect is increasingly cancelled out.

Lanthanoid-induced Shifts [LIS] and Assignment of the Binding Site. The shift reagents, Eu(dpm)$_3$ and Eu(fod)$_3$-d_{27}, were added to solutions containing the substrate and the molar ratios were changed from 0 to 0.5. The LIS was plotted against [L]/[S], where [L] and [S] have their usual meanings,[3] indicating proper linearity. Relative slopes of the straight lines were obtained by taking the slope of the straight line due to methylene protons in the α-position of the carbonyl group as a reference and are shown in Table 4.

The assignment of straight lines obtained by plotting

Table 4. Relative slopes of LIS vs. [L]/[S] lines obtained for polyoxadioxo[n]paracyclophanes (III^R_m) and bis(2,5-dimethylphenylacetate)s (IV_m) of polyoxaalkane-α,ω-diols[a]

Protons	Compounds										
	III^H_2	III^{Me}_2	IV_2	III^H_3	III^{Me}_3	IV_3	III^H_4	III^{Me}_4	III^{OMe}_4	IV_4	IV_5
1-CH_2	1.0	1.0	1.0	1.0	1.0	1.0 (1.0)	1.0	1.0	1.0	1.0 (1.0)	1.0 (1.0)
4-CH_2	1.0_4	1.0_3	1.1_7	0.1_9	0.1_8	1.0_9 (1.4_1)	0.6_8	0.6_4	0.5_9	1.0_9 (1.4_6)	1.1_6 (1.7_9)
5-CH_2	0.5_7	0.5_3	0.7_5	2.0_8	1.8_9	2.1_5 (3.8_6)	1.9_8	2.0_1	2.0_0	1.8_3 (3.9_2)	1.8_3 (3.9_2)
7-CH_2				8.1_0	7.9_5	5.7_9 (8.8_2)	5.0_4	5.1_0	5.1_0	4.3_2 (6.4_6)	4.2_3 (6.3_9)
8-CH_2							6.6_6	6.6_7	6.5_0	5.5_5 (7.9_4)	4.9_2 (9.0_6)
10-CH_2											5.1_2 (9.6_0)
Ar–H	0.5_0	0.5_3		1.1_9	1.1_8		1.3_3	1.3_0	1.3_8		
Ar–Me (or–OMe)		0.4_2	0.3_8		0.9_1	0.5_3 (0.6_6)		1.0_9	0.8_0	0.5_5 (0.6_4)	0.5_6 (0.7_3)
			0.0_9			0.3_1 (0.5_3)				0.3_2 (0.5_2)	0.2_9 (0.5_0)

a) Values in parentheses are those obtained using Eu(fod)$_3$-d_{27} while the others were obtained using Eu(dpm)$_3$.

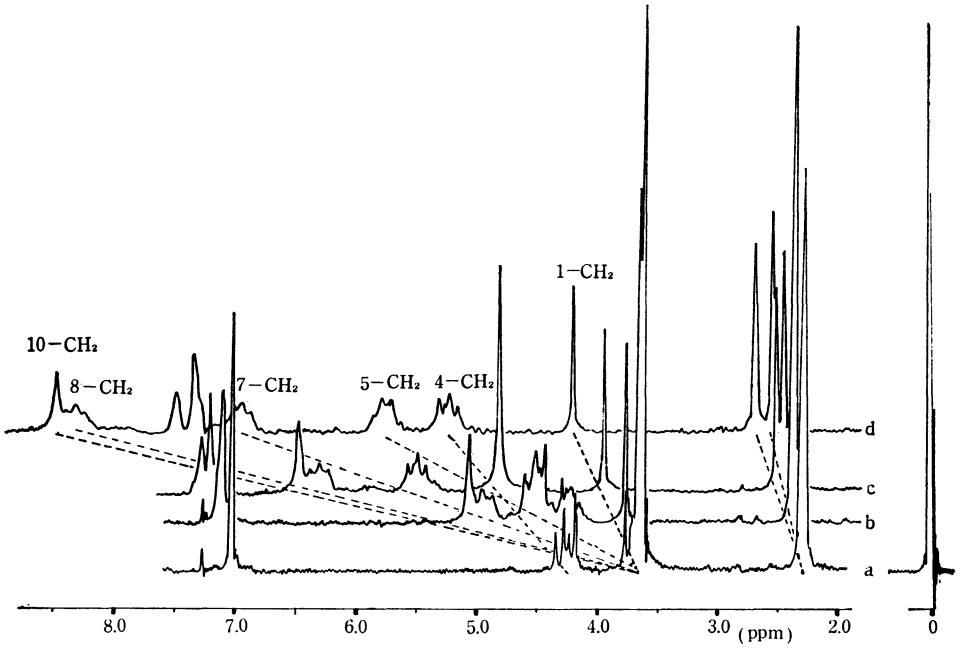


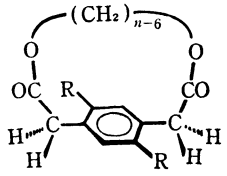
Fig. 1. ^{1}H NMR spectra of IV_5 with various amounts of Eu(fod)$_3$-d_{27} in $CDCl_3$ at 34 °C. Curves a, b, c, and d correspond to [L]/[S] of 0, 0.17, 0.29, and 0.52, respectively.

LIS *vs.* [L]/[S] is straightforward when the number of oxyethylene groups is 2 or 3, because they result in a set of independent signals for each pair of protons. However, it is necessary to carefully assign those signals which appear separately after the addition of the shift reagent, but which overlap in the absence of the reagent.

The ^{1}H NMR spectra of IV_5 for varying amounts of Eu(fod)$_3$-d_{27} in deuteriochloroform at 34 °C are shown in Fig. 1. The apparent singlet at δ 3.60 in the absence of the reagent separates into a singlet and two multiplets with an increase in the value of [L]/[S]. The singlet at the lowest field is necessarily assigned to 10-methylene protons because the neighboring methylene group is equivalent and no coupling with other protons is expected. From the 7- and 8-methylene protons, the latter produces the lower field signal because the 10-methylene protons give the signal at the lowest field and the shift reagent must be coordinated closer to the 8-methylene than to the 7-methylene protons.

The assignments of signals due to III_2^R and IV_4 were carried out analogously. The chemical shifts of 4- and 5-methylene protons are known even in the absence of the shift reagent. For the 7- and 8-protons, it must be the 8-protons that result in the lower field signals for the addition of the shift reagent, because if a complex is formed using the 6'- and 9-oxygens, the 8-protons are closer to the shift reagent than the 7-protons. Although the binding site may change as discussed later, the situation still holds because if the binding sites are 6- and 9-oxygens, the effect should be equal for the 7- and 8-protons.

The relative slopes of 1-methylene protons in III_2^R are in good agreement with the data for 13,16-dimethyl-3,9-dioxa-2,10-dioxo[11]paracyclophane (V_{11})[5] which has an ansa chain with the same number of atoms and is known to form a complex with the shift reagent at the oxygen of the ester carbonyl. IV_2 showed a similar tendency. Thus, it may be concluded that the reagent binds to the ester carbonyl in III_2^R and IV_2.



V_{11}: n=11, R=CH_3
V_{14}: n=14, R=CH_3

In contrast, the relative slopes of 1-methylene protons in III_3^R are different from those of V_{14} to a great extent, although similar values are expected if III_3^R binds at the carbonyl oxygen, as does V_{14}.[8] IV_3 behaves similarly to III_3^R. Therefore, the results must be attributed to the presence of (a) binding site(s) other than the carbonyl.

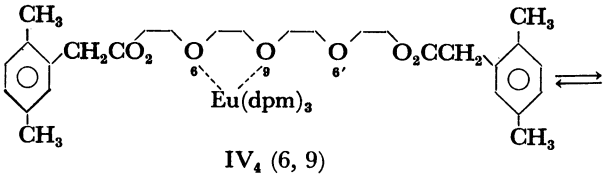
Although lactarorufin is known to bind preferentially to the shift reagent at an ether oxygen rather than at an ester carbonyl,[11] this anomaly is caused because of steric blocking of the carbonyl oxygen and such a steric factor is not expected in these compounds (III_m^R). Rather, it is reasonably assumed that the ethylenedioxy unit is a preferred binding site for the shift reagent, because two ether oxygens *ortho* to each other in the aromatic system are known to bind as a bidentate ligand to the shift reagent more readily than the ester group,[5] and because polyglyme binds to the shift reagent.[4]

Judging from the failure of complex formation at the ethylenedioxy units in III_2^R and IV_2, it is concluded that the ethylenedioxy unit, one oxygen of which is a part of the ester moiety, is inferior to the ester carbonyl for complexation. Thus the order of binding ease is $ROCH_2CH_2OR > RCOOR > ROCH_2CH_2OCOR$.

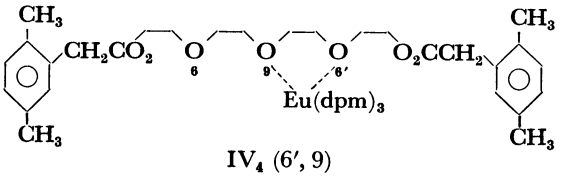
Since the slopes of LIS *vs.* [L]/[S] for the methylenes

in III_3^R and IV_3 become steeper as the methylene becomes closer to the center of the chain, it is reasonable to assume that the shift reagent forms a complex at the 6,6′-positions. Indeed, it is generally accepted that in ^1H NMR an LIS results by complexation to an oxygen function of an organic compound predominantly from the pseudocontact interaction.[3]

The data for III_4^R may be interpreted as the result of rapid equilibrium between the two equivalent complexes as has been pointed out for polyglyme,[4] because there are two equally good binding sites. The LIS values observed for a compound with only one strong binding site may be taken to represent "intrinsic" shifts for protons of such complexes. Then the observed shifts in a molecule with two or more good complexing sites can be taken as weighted means of the "intrinsic" shifts, and are determined by the populations of the complexes. Since IV_4 has two equivalent binding sites, it may be assumed that two complexes exist in equal populations and exchange rapidly on the NMR time scale. By analogy to the cases of III_3^R and IV_3, these two complexes are shown by IV_4(6,9) and IV_4(6′,9).

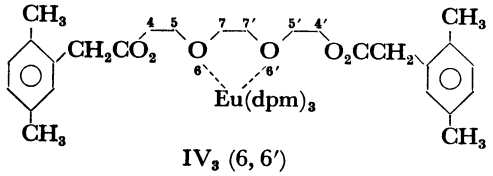


IV_4 (6, 9)



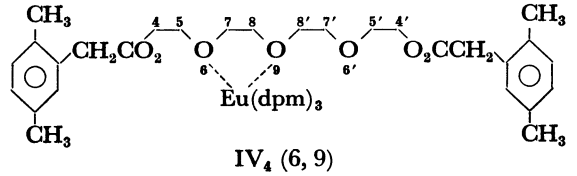
IV_4 (6′, 9)

According to the above assumption, the relative slopes of the LIS *vs.* [L]/[S] lines for IV_4(6,9) and IV_4(6′,9) can be taken as almost the same as those in the IV_3–lathanoid complex IV_3(6,6′); the 7- and 8-methylenes in IV_4(6,9) give a slope of 5.8, since these are equivalent to the 7- and 7′-methylenes in IV_3(6,6′). Then 5- and 8′-methylenes in IV_4(6,9) will give a slope of 2.2, since these are equivalent to the 5- and 5′-methylenes in IV_3(6,6′), *etc.* Using the above assumption, we can calculate the relative slopes as shown in Fig. 2. The calculated values are in good agreement with those observed.



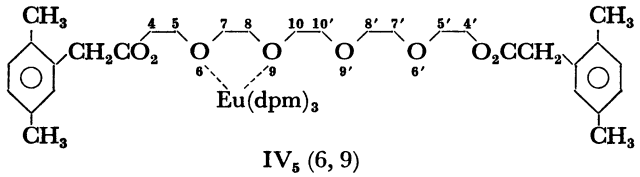
IV_3 (6, 6′)

Similarly, the observed values of IV_5 are reasonably well reproduced by the assumption of equal populations of complexes IV_5(6,9), IV_5(9,9′), and IV_5(6′,9′) (see Fig. 2). Since, if we assume that there is only one complex IV_5(9,9′) or only two complexes, IV_5(6,9) and IV_5(6′,9′), we obtain much less satisfactorily calculated values, it may be assumed that the three complexing



IV_4 (6, 9)

	4	5	7	8	8′	7′	5′	4′
IV_4(6, 9)	(1.1	2.2	5.8	5.8	2.2	1.1	∼1	∼1)×1/2
IV_4(6′, 9)	+(∼1	∼1	1.1	2.2	5.8	5.8	2.2	1.1)×1/2
	(2.1	2.3	6.9	8.0	8.0	6.9	2.3	2.1)×1/2
Ratio of relative slopes Calcd			1.0	0.86	0.40	0.26		
Ratio of relative slopes Obsd			1.0	0.77	0.32	0.20		



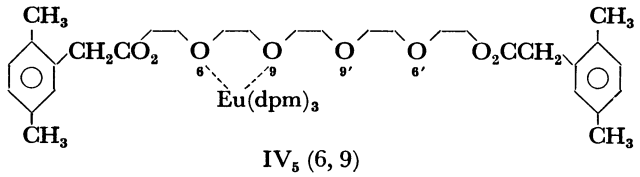
IV_5 (6, 9)

	4	5	7	8	10	10′	8′	7′	5′	4′
IV_5(6, 9)	(1.1	2.2	5.8	5.8	2.2	1.1	∼1	∼1	∼1	∼1)×1/3
IV_5(9, 9′)	(∼1	∼1	1.1	2.2	5.8	5.8	2.2	1.1	∼1	∼1)×1/3
IV_5(9′, 6′)	+(∼1	∼1	∼1	∼1	1.1	2.2	5.8	5.8	2.2	1.1)×1/3
	(3.1	4.2	7.9	9.0	9.1	9.1	9.0	7.9	4.2	3.1)×1/3

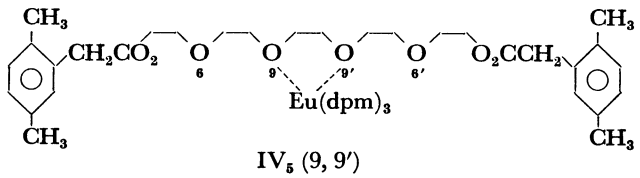
	10′	8′	7′	5′	4′
Ratio of relative slopes Calcd	1.0	0.99	0.87	0.46	0.37
Ratio of relative slopes Obsd	1.0	0.96	0.82	0.35	0.24

Fig. 2. Calculations of the relative slopes of straight lines, LIS *vs.* [L]/[S], on an assumption of "intrinsic" slopes.

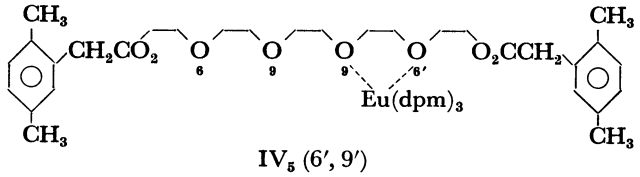
sites contribute almost equally.*



IV_5 (6, 9)



IV_5 (9, 9′)



IV_5 (6′, 9′)

IV_5 (9, 9′)

IV_5 (6, 9) ⟷ IV_5 (6′, 9′)

It is concluded, by taking advantage of the results with open-chain analogs, that the polyoxadioxo[n]-paracyclophanes with long ansa chains behave similarly

* Although the above simple calculation gives satisfactory results for flexible molecule, it appears that the method is not applicable to less mobile molecules. Thus, application of the method to the cyclophanes (III_m^R) gives results far from satisfactory.

toward the shift reagent. The binding sites in these compounds are changing rapidly among the favored ethylenedioxy units. The chemical shifts of the methylene protons and the slopes of LIS *vs.* [L]/[S] lines are in agreement with this conclusion.

Origin for the Change in Binding Sites. It is clear from the above discussion that the ester carbonyl is an inferior binding site for the shift reagent with respect to the ethylenedioxy unit, unless one of the oxygens in the latter is a part of the ester moiety. The inferiority of the $ROCH_2CH_2O_2CR$ moiety can be attributed to the low electron density of the ether oxygen in the ester group.

Among the ethylenedioxy units referred to in this paper, the binding ability appears to be invariant irrespective of the position of the unit. This is in sharp contrast to the fact that polyglymes bind to the shift reagent at the terminal ethylenedioxy units. It is proposed that this difference be ascribed to steric and electronic effects for the following reasons. Firstly, the methyl group is known to be smaller than the ethyl group and other long chain alkyls, the most noted example being the reactivity of the carbonyl group in ketones toward hydrogen sulfite.[12] In complex formation also, the heat of formation and the entropy term will be unfavorable when the chain becomes longer. Secondly, the oxygen in position 2 of polyoxaalkanes will have the highest basicity, since the oxygens in the inner positions are substituted by an "ethyl" group which carries an oxygen atom in the β-position. In fact, 3-methoxypropionic acid is known to be a stronger acid than acetic acid by an order of magnitude, indicating that the $CH_3OCH_2CH_2$ group is electron-withdrawing relative to the CH_3.[13]

References

1) Part VII of this series; K. Sakamoto and M. Ōki, *Chem. Lett.*, **1976**, 257.
2) K. Sakamoto and M. Ōki, *Bull. Chem. Soc. Jpn.*, **47**, 2623 (1974).
3) A. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, **73**, 553 (1973).
4) A. M. Grotens, C. W. Hilbers, E. de Boer, and J. Smid, *Tetrahedron Lett.*, **1972**, 2067.
5) G. E. Wright and T. Y. Tang Wei, *Tetrahedron*, **29**, 3775 (1973).
6) C. J. Pederson, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
7) K. Sakamoto and M. Ōki, *Bull. Chem. Soc. Jpn.*, **46**, 270 (1973); **48**, 497 (1975).
8) K. Sakamoto and M. Ōki, *Bull. Chem. Soc. Jpn.*, **47**, 2739 (1974).
9) K. Nukada, O. Yamamoto, T. Suzuki, M. Takeuchi, and M. Ohnishi, *Anal. Chem.*, **35**, 1892 (1963).
10) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).
11) R. Caple and S. C. Kuo, *Tetrahedron Lett.*, **1971**, 4413.
12) M. A. Gubareva, *Zh. Obshch. Khim.*, **17**, 2259 (1947); *Chem. Abstr.*, **42**, 4820a (1948).
13) H. S. Harned and B. B. Owen, *J. Am. Chem. Soc.*, **52**, 5091 (1930).