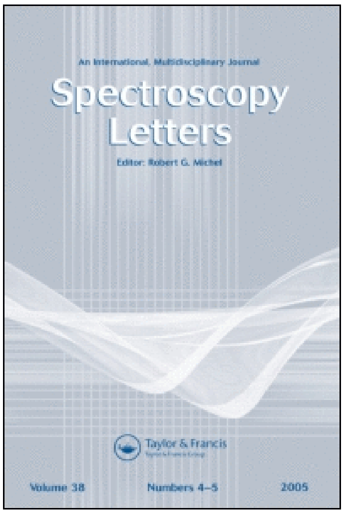

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Conformation of Dioxo-Polyoxa Cycloalkanes by ^{1}H NMR

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CONFORMATION OF DIOXO-POLYOXA CYCLOALKANES BY ^{1}H NMR.

PART.I. Structure of free 2,6-dioxo-1,4,7,10,13,16-hexaoxacyclooctadecane by 500 MHz proton spin-spin simulation.

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INTRODUCTION

The conformation of the macrocyclic polyoxo-oligo ethers and esters of cation binding ability have been known to play important role due to appropriate orientation of moleculer orbitals cousing selective binding on the cationic radii. The oxygen dipoles are enabled to arrange their p orbitals to the direction of delocalised positive charge. The energy transfer -or exchange- between the ion and ligand shell determined the maximum stability and the stoichiometry of the complexation. Accordingly flexibility or the rigidity of the polyoxo-ether-ester ring cousing from the hindered rotation of cyclic lactone mostly determined the degree of association with the cation.(1-3)

On the other hand several methods have been tried for such a large molecule family to search for their conformational-configurational nature However, the DNMR methods have been mostly used as well as the molecular relaxation methods.(4-7)

The conformational studies of cycloalkanes,C_nH_{2n}(n:10-20) have been widely investigated recently.(8-10) Several methods such as IR, microwave

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spectroscopy and NMR have been widely used to dedect the diastereomers. Accordingly, to approach the energy barriers of the pseudorotamers some theoretical ab initio calculation methods like MINDO/2 have been also developed.(11)

In the early of 1970 the conformation of cyclic polyethers become important due to spatial arrangements of ligand sites of particular conformations. Dale et al, have published several reports considering some pioneering discussions on the conformation of the methylene sub units so called torsional sequences of the macrocyclic ethers,(12,13) particularly on 1,4,7,10,13,16-hexaoxocyclooctadecane,(18.Crown.6) which is the six oxygen member analogue of 2,6-dioxo-1,4,7,10,13,16-hexaoxacyclooctadecane of our studied molecule. As a matter of fact our aim to design the above given molecule several years ago was to see the role of hindered rotation due to the carbonyl moieties which resembled the naturally occouring antibiotics. Such a structure also yields a non-equivalent structure as well as different chemical shifts of methylene groups.(14-17) However, most of the reports just published for the 18.Crown.6 concluded the existence of the following equilibria of the torsional sequences depending on ligand-cation-counter ion system.(1,2,18)

1) $$|234234|C_i \rightleftharpoons |234234|C_1 \rightleftharpoons |333333|D_{3d}$$

The X-ray studies on the free or complexed molecules mostly proved the existance of above given structures on different type of host-guest combinations.(19,20) The increasing cation radii usually coused the high order of symmetri although such studies only resemble the complexing solutions in part due to dynamic solute-solvent interactions.

Accordingly we have been also currently investigating the internal -skeletal-motions of the cyclic oligoethers and ether-esters by the aid of ^{13}C dipole-dipole relaxation measurements of free and complexed cyclic ligands.(16,21)

On the other hand the spin coupling analysis of ^{1}H NMR spectra of $-CO-CH_2^{\alpha}-CH_2^{\beta}-O-$ groups of ester methylenes of different chemical shifts and the estimation of the scalar proton spin-spin coupling values could yield some information for a conformational study of such molecules. Nevertheless, AA'BB' approximaton by a simulation program is usually adaquate for a qualitative discussion of homonuclear spin systems. The line assigments are derived by the calculation of test spectrum using one of the relevant programs.(22-24)

Polyoxo-lactones have also been recognized recently as the good cation receptors and several types of such molecules have already been sythesised.(3,14-17)

RESULTS AND DISCUSSION

The conformation of oxyethylene units of cyclic ether-ester backbone is usually excisted as "a,g±,a" unit conformation of the minimum energy barrier energy to pseudorotation.(8) However, for the cyclic oligo ethers of ethyleneoxide the ring enlargement coused high order of symmetry of unit conformation from 12 member to 24 member of cyclic polyether ring as follows, $|g\pm,g\pm,a|_4$ 12.Crown.4... $|a,g\pm,a|_6$ 18.Crown.6 ... $|a,g\pm,a|_8$ 24.Crown.4 .(12,13)

However, the inclusion of carbonyl group naturally coused restricted rotations particularly on the $-CO-CH_2^{\alpha}-CH_2^{\beta}-O-$ bonds which of course give the most practical information for a ring conformation since the rest of the ring chain is expected to be forced to a minimum energy of the torsional sequences, Fig.1.

The dioxo-cyclopolyoxa oligo ether-ester of six oxygen member has been recently reported to exhibit strong cation binding ability with the large variety of cations like Na^+,K^+,Ba^{2+} and Pb^{2+} forming stable solid complexes.(14) Accordingly, the determination of the stability constants by the use of $Eu(fod)_3$ of Lanthanide shift reagent on the ^{13}C NMR spectra strongly proved the distinguished role of rigid oligo ether-ester ring particularly in apolar solvents like $CDCl_3$.(3)

500 MHz proton NMR measurements simply indicated the exsistance of uniform structure of 2,6-dioxo-hexaoxa ring in $CDCl_3$ solutions since the $CO-CH_2^{\alpha}-CH_2^{\beta}-O$ groups were observed only in "gouche" (a,g±,a) form and almost no "trans" unit has appeared. This observed spectra ,however,is an exhibiton of unique conformation of consisting pseudorotamers of the lowest energy content. The process involved in solution is also actually a pseudorotation of a ring which is namely a site exchange of geminal protones. The exchange process considered for hexaoxa ring is involved with the "sign" change and required relatively high barrier but not a complete inversion of the carbon chain. Considering the

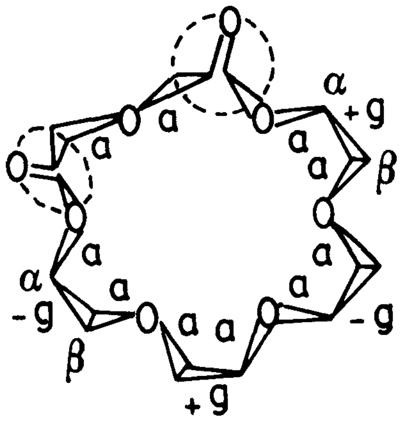
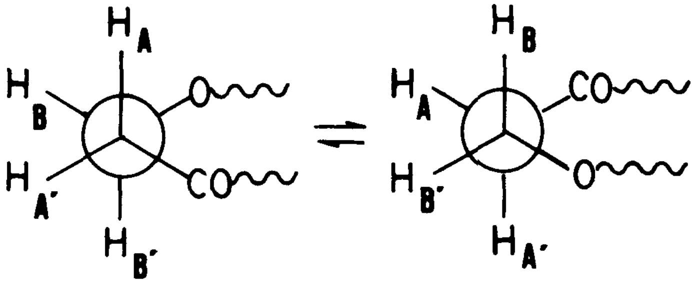


Figure.1. The projection perspective to depict the conformation of 2,6-dioxo-1,4,7,10,13,16-hexaoxacyclooctadecane according to Pitzer "wedge" notation.

"pseudo corners" or "genue corners" which yield high order of symmetry and low barrier hights for the large rings,the movement of a corner by one or two units through a "passage" to other conformational minima which is in most cases considered as an exchange of ring atom sites. Usually, the site exchange is involved as a pseudorotation of "gouche" bounds in anti surroundings along the cyclic backbone (§). The pseudo-rotamers of particular conformations therefore exhibited the vicinal coupling constants of dihedral angles of methylene protons. The observed AA'BB' type of four spin system was analysed by the evaluation of the shift differences $L=J-J'$ and $N=J+J'$ and also the coupling constants of trans and gouche conformers $J=1/2(J_{trans}+J_{gouche})$ and $J'=1/2(J_{gouche}+J_{trans})$ where $\delta_A=\delta_{A'}$ and $\delta_B=\delta_{B'}$ and also $J > J'$ since $N > L$. Above given considerations were intrestingly verified by the computer. compiled spectra of the dioxo-hexaoxa lactone ring,Fig.3a-c.(17,23,24)

(§). Interconversion mechanism is still studied in our laboratory by spin-lattice measurements,see ref.21 and references cited in..



(1) (2)

Figure.2. The exsisting rotamers of $CO-CH_2^{\alpha}-CH_2^{\beta}-O$ groupings of 2,6-dioxo-1,4,7,10,13,16-hexaoxacyclooctadecane ring.

We first of all in our presented study rather discussed estimated sub spectra of AA'BB' structure of $CO-CH_2^{\alpha}-CH_2^{\beta}-O$ groupings of dioxo-hexaoxa lactone ring. This is of course due to the fact that large and relatively elastic ring has broad rotational amplitudes unless the structure is frozen. However, no coalesence was observed down to -90°C in the ^{13}C NMR spectra of this molecule in CD_2Cl_2.

On the other hand the observed coupling values verified the typical simulated spectra and it was understood that the structure is simply consist of two enantiomeric "gouche" type of diastereomers as it is explained on Fig.2 and Table.1. Since the line frequencies and signal intensities obtained even at 500 MHz are only let us to simulate some slightly different spectra of identical shift differences of K,L,M and N values cousing from the slightly different compiled couplings in the experimental limit of observed spectral parameters,Fig.3b-c,4a-c. The iteration was carried out among the 20 theoretical lines of spectra of AA' and BB' parts and the shift difference of line 4 and 7 was considered as the L value which was experimentaly L=3,95+0,05. The shift difference of line 1 to line 10 was N=8,95+0,05 Hz from the observed spectra. This is what we expected due to two exsisting enantiomeric structure so that it was most probably exhibited as a coelesent pattern, Fig.3.b,c. Accordingly, the compiled spectra of structure.I.1 and II.2 are possesed very similar values of rotamers of each other, Table.1.

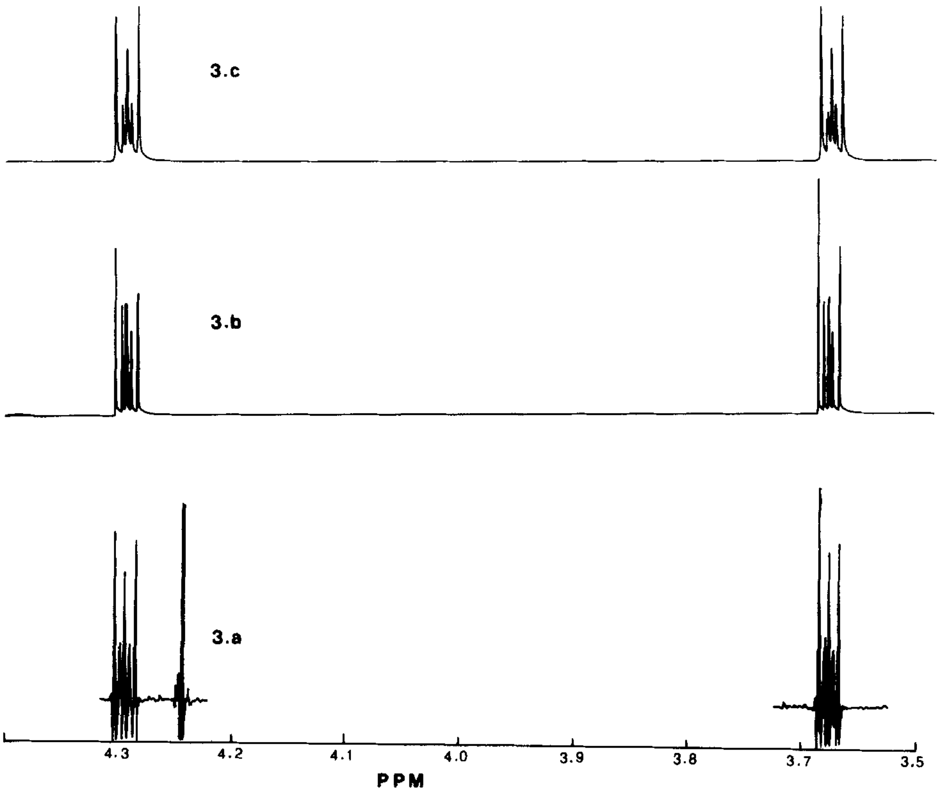


Figure.3.a. The original 500 MHz ^{1}H NMR spectra of 2,6-do-18-crown-6 as it is resolution enhanced-convolution analysed-form in $CDCl_3$, the TMS was incooperated as an internal reference at 333°K.
3.b. The compiled spectra of the structure.III with the estimated parameters of Table.1. The half bandwidth is 2,0-0,2 Hz. Spectral data point 3k. 3.c. The compiled spectra of estimated parameters of structure.I of Table.1.

Table.1. The thoretically calculated vicinal and geminal coupling constants of ($CO-CH_2-CH_2-O$) groups of 2,6-Dioxo-1,4,7,10,13,16-hexaoxacyclooctadecane at 500 MHz in $CDCl_3$ at 333 °K.

J_{av} = 6,44 Hz = $1/2(J_{A'B}+J_{A'B})$ = $1/2(J_{AB'}+J_{AB'})$ N = J + J'

J'_{av} = 2,52 Hz = $1/2(J_{A'B'}+J_{A'B'})$ = $1/2(J_{AB}+J_{AB})$ L = J - J'

Rotamer 1. (Hz)	Rotamer 2. (Hz)	Struct. No.
$J_{AA'}$: 11,30	$J_{AA'}$: 11,30	I.Fig.3.c
J_{AB} : 2,95	J_{AB} : 2,09	
$J_{AB'}$: 5,60	$J_{AB'}$: 7,28	
$J_{A'B}$: 7,90	$J_{A'B}$: 4,98	
$J_{A'B'}$: 3,05	$J_{A'B'}$: 1,99	
$J_{BB'}$: -11,30	$J_{BB'}$: -11,30	
$J_{AA'}$: -11,30	$J_{AA'}$: -11,30	II.Fig.4b,c
J_{AB} : 2,05	J_{AB} : 2,99	
$J_{AB'}$: 4,80 (4,90)	$J_{AB'}$: 8,08 (7,98)	
$J_{A'B}$: 7,75	$J_{A'B}$: 5,13	
$J_{A'B'}$: 2,15	$J_{A'B'}$: 2,89	
$J_{BB'}$: -11,30	$J_{BB'}$: -11,30	
$J_{AA'}$: -11,30	$J_{AA'}$: -11,30	III.Fig.3.b
J_{AB} : 2,95	J_{AB} : 2,09	
$J_{AB'}$: 5,85	$J_{AB'}$: 7,03	
$J_{A'B}$: 7,90 (7,80)	$J_{A'B}$: 4,98 (5,08)	
$J_{A'B'}$: 3,05	$J_{A'B'}$: 1,99	
$J_{BB'}$: -11,30	$J_{BB'}$: -11,30	

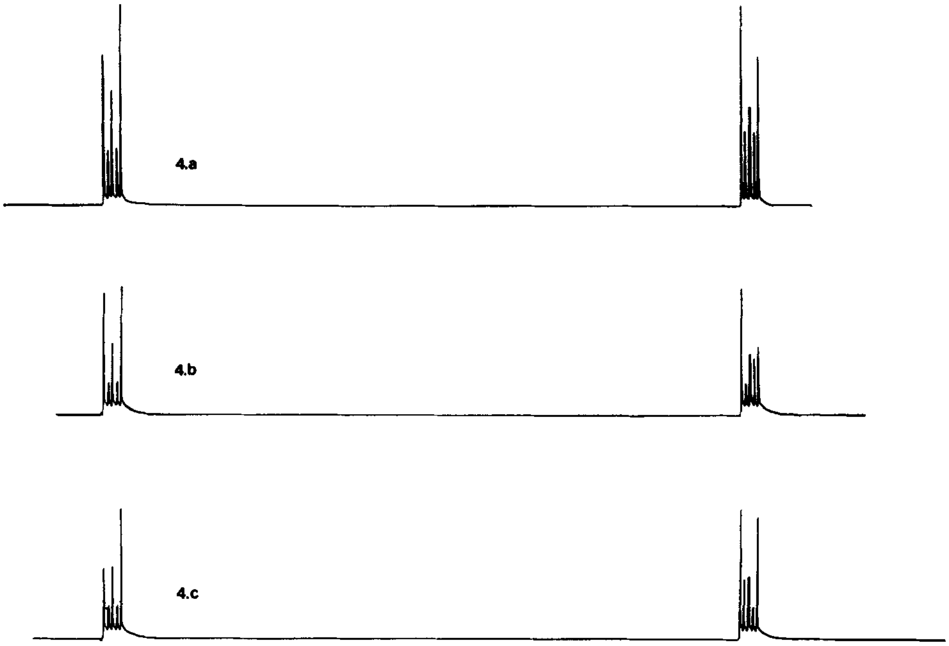


Figure.4.a. The superpositioned spectra of sub spectra of estimated parameters of structure.II at Table.1. Iteration parameters are given at Fig.3. 4.b,c. The sub spectra with the parameters of the structure.II of Table.1.

Likewise, the parameters of structure I.2 and structure II.1 are really close proving our conclusions,Fig.3.c,4.a-c.

This is also interesting to discuss the "trans" couplings are also limited between the 7,75-8,80 Hz indicating the role of carbonyl on the polyoxo-lactone ring,however, the accepted large and negative and also completely identical $J_{AA'} = J_{BB'}$ geminal coupling constants shilded the "trans" effect to realise the structure around the 11.30 Hz.

On the other hand the correlation of J_{AB},$J_{A'B}$ and $J_{A'B'}$ of the "gouche" coupling values are really in agreement with the Karplus relationships since the vicinal dihedral angles were found to be varied within the 40^{o}-60^{o} degrees.

EXPERIMENTAL

The 2,6-dioxo-1,4,7,10,13,16-hexaoxacyclooctadecane was available to us from the earlier studies since we have worked so far for the synthesis of this molecule.[3,14,16,17] However,for the purification it was first crystallised from methanol and then from cold acetone.

The spin-spin simulations were carried out on a JEOL spectrometer, model FX60-Q supplied with a 16k memory.The program was also provided by JEOL used up to six spins. Iterations were tried for Lorentzian line shape analysis and plotings recorded orginally were displayed on the figures of the text.

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