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Conformation of 1, 4, 7, 10-tetraoxacyclododeca-2,3-dion by nmr.

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Conformation of 1, 4, 7, 10-tetraoxacyclododeca-2,3-dion by nmr.

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ABSTRACT

Conformation of the 1, 4, 7, 10-tetraoxacyclododeca-2, 3-dion was analysed by NMR and found out that the "gouch" from of α -diester carbonyls arrange the methylene groups as the "gouch, gouch, anti" (g_{\pm} , g_{\pm} , a) units in equilibrium of pseudorotomers so that oxygens are in non corner positions of "square" conformation.

INTRADUCTION

Structure of medium size of Crown ethers such as 1, 4, 7, 10-tetraoxacyclododecane (12-Crown-4) has been reported that the cyclic ether posses the "square" conformation with the oxygen atoms at side positions both in free and complexed form(1-5), Results were confirmed by low temperature NMR and kinetic studies exhibiting the cation binding effect of the such a medium size ring(3). We now report the conformation of the polyoxo-lactone ring of 1, 4, 7, 10-tetraoxocyclododeca-2, 3-dion of similar size, which was investigated by NMR.

The conformational equilibrium involed in the free state of 12-Crown-4 were explained by Dale(3) and Anet(7) as a stepwise movement of each corner by one position which is applicable for existing conformation of above compound although in the case of tetraoxo-lactone ring consisting of "gouch, gouch, anti" conformer units seem rather rigid because of the fact that practically very low trans conformer of the $\text{COOCH}_2\text{CH}_2\text{O}$ ethylene groups were observed. However if the barrier to pseudo rotation is very low, or in the limit when pseudorotation is free, it is not really justified to consider separate conformations because there is actually only one stable conformation and the psedorotation is simply a molecular vibration(6).

EXPERIMENTAL

Lactone ring gave a typical AA'BB' type of proton spectra at 80 MHz. observed parameters indicate that spectrum of five line is a consequence of ($\nu_A - \nu_B$) and $J_{AA'} - J_{BB'}$ is large compared with $J_{AB} - J_{AB'}$ ($=N$) since the spectrum is deceptively simple. However more spin-spin couplings characterise the spectrum of the slowly re-orientating molecule. Assuming the "trans" (J_t) and "gouch" (J_g) coupling are invariant(8).

$$J_{AB} = n_t J_g - 1/2 n_g (J_t - J_g) \quad (1)$$

$$J_{AB'} = J_{A'B} = n_t J_t - n_g J_g \quad (2)$$

$$\text{therefore } 2 J_{AB} - J_{AB'} = J_t \text{ is obtained} \quad (3)$$

Following coupling values were then obtained and it was shown that $n_t = 0$, $n_g = 1$ therefore $\text{COCH}_2\text{CH}_2\text{O}$ groups are in "gouch" form and practically no "trans" form is existing (Figure-II)

$$J_{AB} = 6,1 \text{ Hz} \quad J_t = 9,4 \text{ Hz} \quad N = 8,9 \text{ Hz}$$

$$J_{AB'} = 2,8 \text{ Hz} \quad J_g = 2,8 \text{ Hz} \quad L = 3,3 \text{ Hz}$$

Geminal values are best found from the iterative spectrum as it is presented at Figure-II. In the other hand "trans" angle was found just in the limit of 180° Where as "gouch" angle $54,9^\circ$ It is important to emphasis that sign of J_{vic} are so that $L > 0$ and "gouch" form of more stability.

DISCUSSION

On the lactone ring C-O bonds are found in "gouch" and "anti" form where as C-C bonds are only "gouch" form therefore one pair of "inner" proton and one pair of "corner" proton are expected to cause different chemical shifts due to anisotropy of the α -dicarbonyls of the lactone. Pseudorotamers are of small effect because of the J_{vic} Values which exhibits rigidity of the ring. of small effect because of the J_{vic} values which exhibits rigidity of the ring. J_{vic} values observed and calculated give the ideal "trans" and "Cis" angles even higher than the Karblus predictions which is actually observed in all other oligomers of the polyoxy-cyclic lactone most probably due to the electron with dra-

wing effect of carboxyl group which also influences the J_{gem} values.

Recently Anet has reported that the keto-cyclododecane consist of "square" conformation with the carbonyl group be in non corner position. However, one could easily suggest a "square" conformation with oxygens on corner positions with the (g^+ , a, g^-) conformer units. In this case on the lactone ring α -carbonyls are expected in "trans" from which theoretically causes a less strained ring.

Regarding the nmr data of tetraoxo lactone ring consist of (g^+ , g^- , a) units of square type conformation (4, 10) which exist in equilibrium of two conformers ($a, g^+, g^- \rightleftharpoons a, g^-, g^+$) as it is described at figure-1.

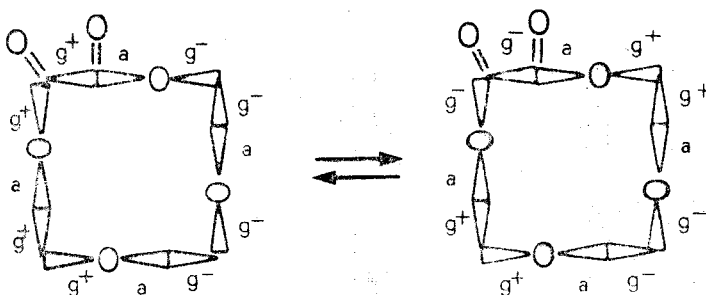


Figure-1. Conformations of 1, 4, 7, 10-tetraoxocyclododeca -2, 3- dione exist in room temperature.

The suggested route for conformational changes by Anet and Dale for tetraoxacyclododecane ring could simply be applicable for similar structures such as above lactone . However, since the practically absence of (g^+ , a, g^-) conformer units it could be concluded that one-cycle conformational interconversion path for low barrier site exchange process is involved.

In order to investigate the structure we run through the pmr spectrum at room temperature and the data obtained was then searched by spin-spin simulation program of a spectrometer.

Results are given in Figure-II with various possibilities due to the broad singals, cousing from the pseudoratamers.

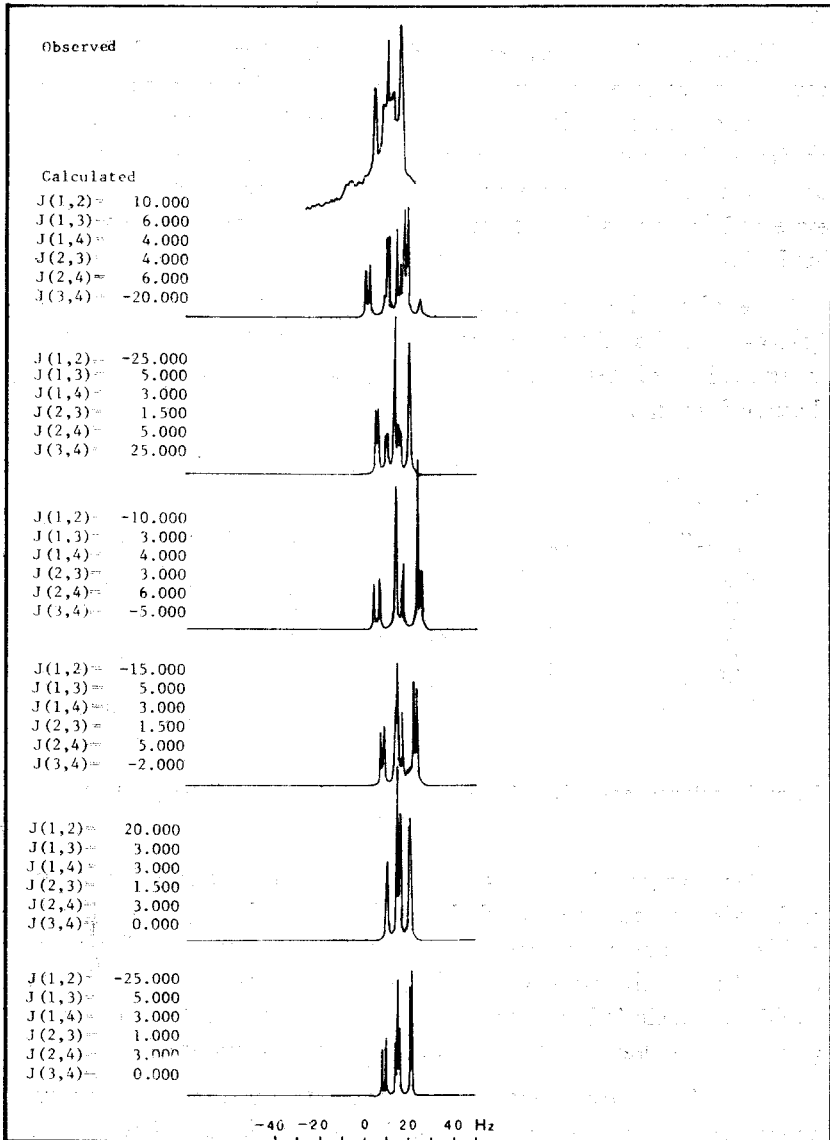


Figure-II Spin-spin Simulation of $-\text{CH}_2-\text{CO}$ methylene of half of the $\text{AA}'\text{BB}'$ type of Spin System. $\delta_{\text{AA}'}$ = 2 Hz and scale is given relative to 1005 Hz.

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ÖZET

Bu çalışmada 1, 4, 7, 10-tetraoksasiklododekan'ın konformasyonu NMR ile incelenmiş ve COCH₂CH₂O gruplarının (gouch, gouch, anti) konformer ünitelerinden oluştuğu saptanmıştır. Sonuçlar ayrıca spin-spin etkileşmesinin teorik yönden incelenmesi ile karşılaştırılmıştır. Buna göre daha önce 12-Crown-4 ile ilgili çalışmalarımız doğrulanmakta ve küçük halkalardaki bu bileşiklere özge davranışlar açıklanmaktadır.

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