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Conformation of some Pentaoxacyclopentadecandiones

by

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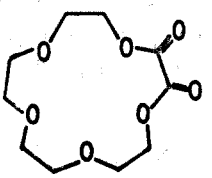
ABSTRACT

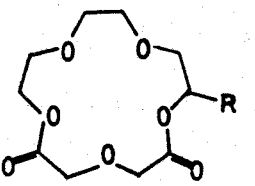
The conformation of some pentaoxacyclopentadecanediones were investigated by ^{1}H–^{13}C NMR and conformations were found as regular anti, gouch, anti (a, $g^{\pm}$,a) units. However the role of a side group was observed that the rate of interconvertion was strongly influenced so that the polyoxa-lactone ring could excist as diastereomers of in equilibrium.

INTRODUCTION

The conformation of cyclopentadecane has been concluded by Dale(1) as an entyalpy - preffered, highly symmetric and regular quinquangular conformations of | 33333 |, five times monomers of unity. However little is known experimentally about odd membered cycloalkane conformations(2). Regarding the cyclic pentamer of ethyleneoxide, 15–Crown–5 with 1,4-dioxa groupings we found the IR spectrum too complex for un am biquous interpretation(3). Therefore in order to investigate the conformational behavior of cyclic pentadecanes we run through the NMR spectrum of the compounds of close structural similarity. Those are of the lactones of polyethyleneglcoles given at figure-1.



I.A



II.A R : H

II.B R : CH_2Cl

Figure–1. Structures of pentaoxacyclopentadecanediones.

It is very interesting to note that three of the compounds given above exhibit cristalinity and all gave sharp melting points(3). Where as the 15–Crown–5 did not show such a behavior(4). Their NMR spectrums clearly perform the conformations of the rings with side groups are in equilibrium even at the room temperature

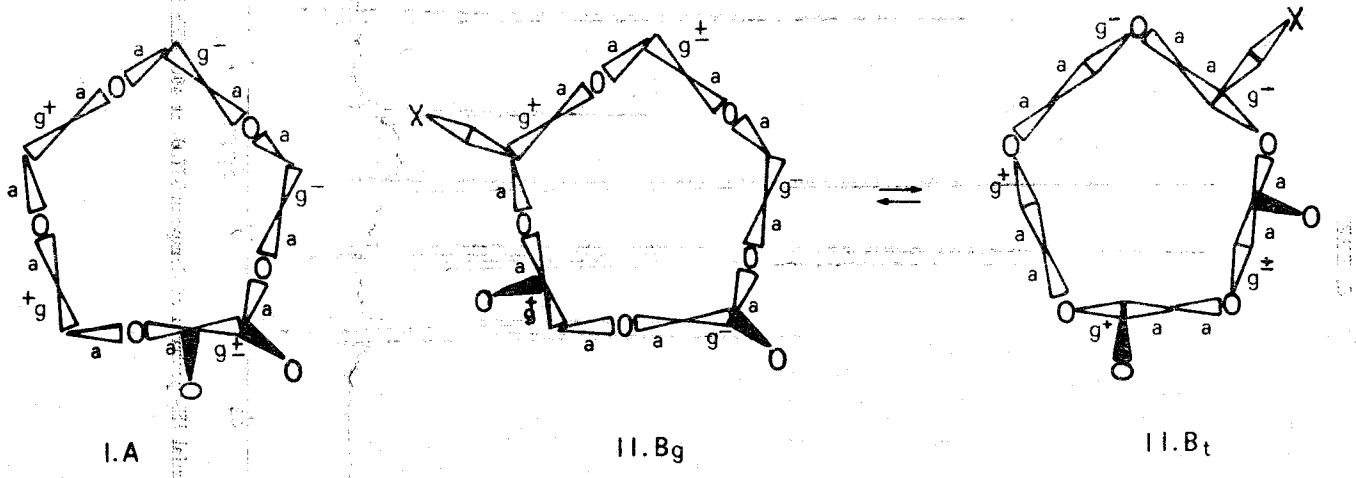
RESULTS AND DISCUSSIONS

Structures of the polyoxa-lactones discribed at Figure-II obtained from the first order analyses of ^{1}H-spectrum of $COCH_2$ CH_2O groups which simply indicates the preferred conformations of the polyoxa-lactones. As they are exhibited on table-1. The COC_2H CH_2O units consist of (a, g^+ , a) series with the most presumably symmetri of C_2. It was also observed that the convertion rates of lactones fast enough so that they gave simple ^{13}C spectra although the compound-II.B,, due to the side groupings, possess two of the diastereomers in equilibrium. 400 MHz ^{1}H spectrum indicated the presence of two sets of AA' part of AA'XX'type of methylene spectra of anisotopic protones. Figure–III clearly exhibits the effect of (a, g^+ , a, $\rightleftarrows g^-$, a, g^+) equilibrium with slow rate of psedorotation.

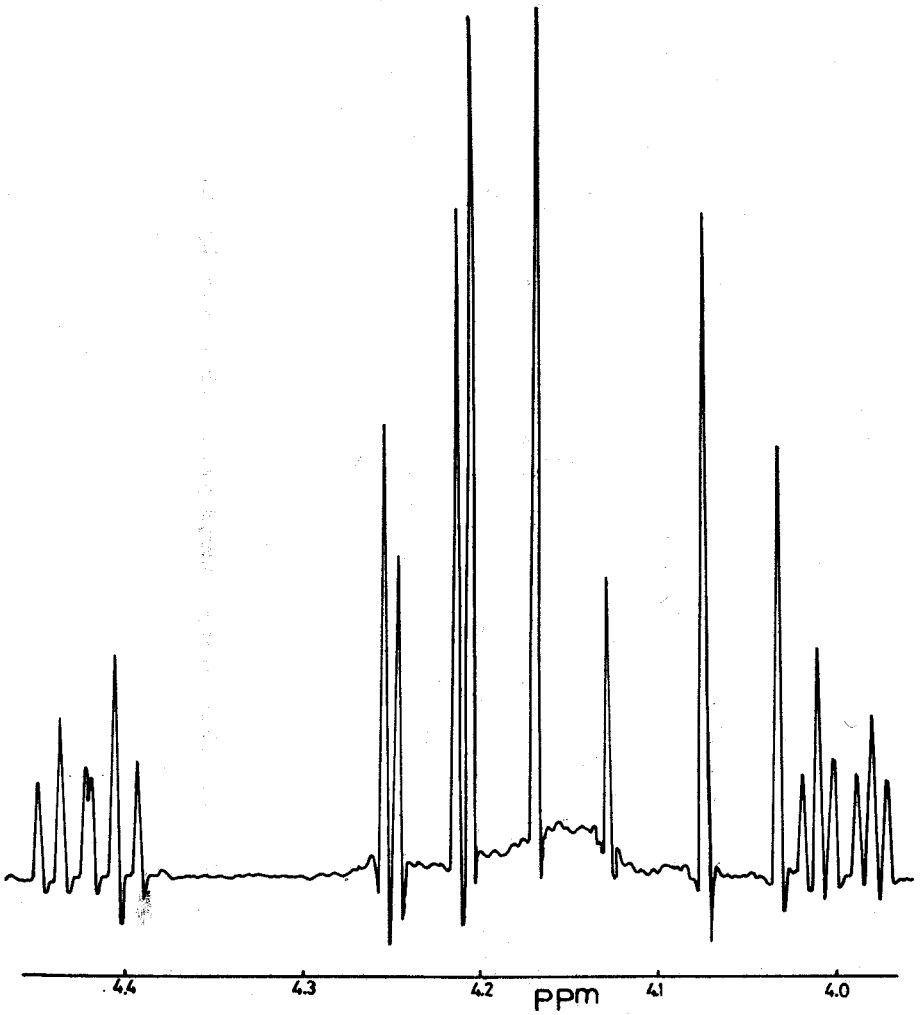
On the other hand, coupling values observed also very well in concistensy with the torsional angles expected for the polyoxa-lactones.

ACKNOWLEDGEMENTS

We are indepted to Bruker-Physik A.G., Karlsruhe for the ^{1}H spectra. It was obtained by Dr. William E.Hull with a WH-400 spectrometer. 80 MHz ^{1}H and 20 MHz ^{13}C spectrums were run at Organic Chemistry institut of Ankara University with Varian, model CFT-20 spectrometer.



Figure–II. Conformations of some pentaoxacyclopentadecanediones proved by NMR.



Figure–III. Partial ^{1}H-spectrum of Compound-II.B. at 400 MHz in $CDCl_3$

Table–I. ^{1}H-data of $COCH_2$ CH_2 O group of pentaoxacyclopentadecanediones given at figure–I. Coupling values are given in Hz at 80 MHz. $CDCI_3$ was taken as a solvent relative to TMS.

COMPOUND	J_{AX}	J_{AX}	J_t	J_g	ν_A
(IA) 1,4,7,10,13-pentaoxacyclopentacane–1,3–dione.	6.40	2.40	10.10	2.00	355.0
(IIA) 1,4,7,10,13-pentaoxacyclopentade cane–2,6–dione.	6.45	2.35	10.10	2.50	347.6
(IIB) 1,4,7,10,13-pentaoxa-8-chlormethyl cyclopentadecane-2,6-dione(t)	3.78	8.42	8.42	3.78	319.2
(IIB). 1,4,7,10,13-pentaoxa-8-chlormet hylcyclopentadecane-2,6-dione(g)	6.36	4.85	7.87	4.86	358.8

(t). Indicating the trans isomer, (g) gouch isomer.

Table–II. ^{13}C Chemical shifts of some pentaoxacyclopentadecanediones. At 20 MHz in $CDCl_3$ relative to TMS.

COMPOUND	Chem Shift (ppm)	Rel. Int.
Compound-I.A.	157.00	11
	71.11	82
	70.12	140
	68.08	102
	65.64	92
Compound-II.A.	169.58	20
	69.97	94
	68.60	90
	68.12	100
	63.58	97
Compound-II.B.	169.73	18
	168.89	18
	72.40	62
	70.46	99
	70.06	87
	69.82	96
	68.69	86
	68.03	79
	67.87	100
	63.81	79
	41.93	75

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ÖZET

Bazı pentaoksasiklopentadekandionların konformasyonları ^1H-^{13}C spektroskopisi ile incelenmiştir. Yapının "anti, gouche, antı' (a, g, a) ünitelerinden oluştuğu saptanmıştır. Ancak yapıda bulunan yan grupların halkanın dönüşüm hızını kuvvetle etkiledikleri ve bunun sonucu olarak diastereomerlerin oda sıcaklığında dengede bulundukları ortaya konmuştur.

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