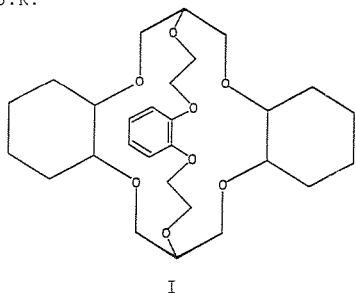


09.2-37 SYNTHESIS AND CRYSTAL STRUCTURES OF THREE ISOMERIC MACROBICYCLIC POLYETHERS HAVING THE SAME MELTING POINT AND DIFFERENT COMPLEXING POWER FOR ALKALI METAL CATIONS. By Judith A. Bandy, D.G. Parsons and Mary R. Truter, Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Herts. AL5 2JQ, U.K.



I

Three isomers of I have the same melting point, 155°, and diagnostically different, but not interpretable, infrared spectra. Stability constants for formation of complexes with potassium bromide in methanol are 1.5×10^8 , 3.2×10^6 and $4.5 \times 10^4 \text{ l mol}^{-1}$. The third isomer also yields from methanol crystals of a 1:1 solvate with an infrared spectrum indicating no hydrogen bonding by the OH group. The configuration of each of the three isomers has been determined by X-ray diffraction. Intensities were measured on a CAD4 diffractometer with Mo-K α radiation; the phase problem was solved by direct methods and final parameters obtained by full matrix refinement.

Hydrogen atoms were located unequivocally. There is a *cis* substitution at the cyclohexane bridges, at each of which the hydrogen atoms may be on the same or the opposite side as the $\text{OCH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{O}$ link. The configurations provide a basis for understanding their behaviour as ligands.

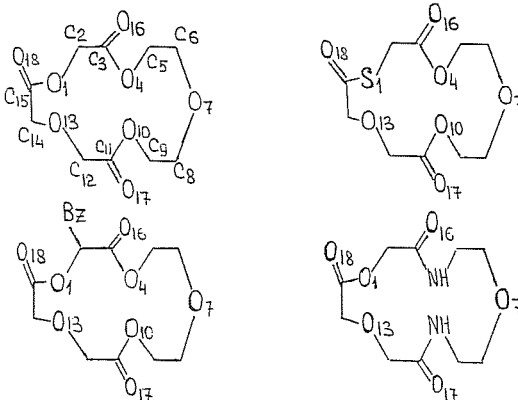
- Ia Monoclinic, $\underline{a} = 15.613(2)$, $\underline{b} = 21.492(4)$,
 $\underline{c} = 8.021(1) \text{ \AA}$, $\beta = 96.99^\circ$, $\underline{Z} = 4$ in $P2_1/a$.
 $R = 0.078$ for 2163 reflections.
- Ib Triclinic, $\underline{a} = 8.842(2)$, $\underline{b} = 16.702(6)$,
 $\underline{c} = 10.050(5)$, $\alpha = 114.10(5)$, $\beta = 98.97(2)$,
 $\underline{c} = 91.22(2)^\circ$, $\underline{Z} = 2$ in $P\bar{1}$. $R = 0.060$ for
 2666 observed reflections.
- Ic, CH_3OH Monoclinic, $\underline{a} = 14.520(2)$, $\underline{b} = 15.391(5)$,
 $\underline{c} = 12.754(2)$, $\beta = 95.02(2)^\circ$, $\underline{Z} = 4$ in $P2_1/n$.
 $R = 0.062$ for 2071 observed reflections. The
 shortest (hydroxy) $\text{H}\dots\text{O}$ (ligand) distances
 are 2.37 and 2.51(10) Å .

Crystal structures of complexes with alkali metal salts are being investigated.

09.2-38 THE STRUCTURE OF 15-MEMBERED POLY-FUNCTIONAL MACROHETEROCYCLES. By Yu. Simonov, T. Malinowsky, Yu. Ganin, A. Dvorkin, Institute of Applied Physics, Academy of Sciences of Mold. SSR, Kishinev, USSR and A. Bogatsky, N. Lukyanenko, Yu. Popkov, Physico-Chemical Institute, Academy of Sciences of Ukr.SSR, Odessa, USSR.

The structures of 15-membered macroheterocycles (I-IV) were determined on an automatic diffractometer. The crystal data and aspects of the molecular geometry are given below:

	a, Å	b, Å	c, Å	γ , °	Sp. gr.	R
I	16.865	18.323	7.759	90	Pcab	0.056
II	15.508	9.252	9.016	76.26	$P2_1/b$	0.083
III	10.798	9.057	17.585	93.02	$P2_1/b$	0.047
IV	14.056	11.218	8.184	68.08	$P2_1/n$	0.075



The geometric and conformational parameters of the rings depend on the character of the functional groups as well as of the substituents. The substitution of O(I) by S(II) leads to the fragment changing its configuration X-C(15)-C(14)-O(13); X=O(I), S(II). The torsion angle is 179° in (I) and 9° in (II). The other parts of molecules (I) and (II) remain identical from the geometric and conformational point of view. The typical bond lengths are C(sp³)-C(sp³) 1.49-1.52; C(sp³)-O 1.43-1.45; C(sp²)-O 1.33-1.35; C(sp³)-N 1.42-1.45; C(sp²)-N 1.32-1.35; C=O 1.18-1.22 Å and the bond angles are C(sp³) 109-114°; C(sp²) 118-122°; O 112-115°; N 120-125°. In the ester and amide groups there is π -delocalisation of electron systems. The interatomic distance S(1)-O(13) 1.906 Å (II) can be considered as non-bonded. The carbonyl groups in (I)-(IV) are eclipsed to methylene groups of ester or ether fragments. The conformation of cycle (III) changes because of the C(2)-benzyl group. The O(18) atom of carbonyl in (I), (II) and (IV) is directed towards the inside of the cavity of the ring, in (III) a similar position is occupied by O(18) and O(17). This is probably due to a peculiarity of the packing of the rings. (The conformation of (IV) does not differ from that of (I)). The amide-hydrogen atoms form intra- (N(10)-H 0.86; N(10)...O(18) 3.087; H...O(18) 2.30 Å ; O...H-N 152°) and intermolecular (N(4)-H 0.77; N(4)...O(17) 3.094; H...O(17) 2.36 Å ; O...H-N 161°) hydrogen bonds. The structures (I)-(III) are molecular ones.