

## Some Tetraoxacyclotetradecanes and Tetraoxacyclohexadecanes

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The 1,4,7,11- and 1,4,8,11-isomers of tetraoxacyclotetradecane have been synthesized as a mixture, separated by gas chromatography, and their conformations studied by dipole moment determination and by IR and NMR spectroscopy, in particular by using empirical relations between  $\gamma$ -CH<sub>2</sub>...CH<sub>2</sub> and  $\delta$ -CH<sub>2</sub>...O interactions and <sup>13</sup>C chemical shifts. Both have in the liquid state and in CS<sub>2</sub> and CCl<sub>4</sub> solutions the same type of non-diamond-lattice conformation as found by X-ray crystallography for the 1,4,8,11-isomer, but in the polar solvent CHCl<sub>2</sub>F the diamond-lattice conformation becomes increasingly populated by lowering the temperature.

The 1,4,7,12- and 1,4,9,12-isomers of tetraoxacyclohexadecane have been synthesized as a mixture that could not be separated.

Macrocyclic cycloalkanes with an even number of ring atoms have strongly preferred quadrangular conformations of diamond-lattice type (C<sub>14</sub>, C<sub>16</sub>) or non-diamond-lattice type (C<sub>12</sub>).<sup>1</sup> At each of the four corners there are two *gauche* interactions which can both be relieved by fitting a 1,3-dioxa grouping in its favoured  $g^{\pm}g^{\pm}$  conformation (Fig. 1a), or a 1,5-dioxa grouping in its favoured  $ag^{\pm}g^{\pm}a$  conformation (Fig. 1b) across each corner.<sup>2</sup> The repulsive CH...CH interactions are thereby replaced by slightly attractive CH...O interactions, and in fact all known examples (1,3,7,9-tetraoxa-

cyclododecane,<sup>3</sup> 1,3,8,10-tetraoxacyclotetradecane,<sup>4</sup> 1,3,9,11-tetraoxacyclohexadecane,<sup>5,6</sup> and 1,5,9,13-tetraoxacyclohexadecane<sup>7,8</sup>) confirm not only that this feature is present, but also that it is conformationally stabilizing in the sense that IR bands are sharp in solid and solution, and melting points are high. On the other hand, the 1,4-dioxa grouping in its favoured  $ag^{\pm}a$  conformation does not fit across such a corner, and when adapted in the alternative  $ag^{\pm}g^{\pm}$  conformation (Fig. 1c), only one CH...CH interaction becomes replaced by an O...O interaction, which may not even be much better since the ether dipoles are oriented in parallel. In fact, recent X-ray structures reveal that the unchanged cyclododecane-type conformation is observed for 1,4,7,10-tetraoxacyclododecane ("12-crown-4") only in cation complexes;<sup>9-11</sup> the free tetraether, crystallizing with MgCl<sub>2</sub>·6H<sub>2</sub>O<sup>12</sup> or alone,<sup>13</sup> has a different and less polar conformation (see below), is low melting and shows broad IR bands in the solid and the liquid.\*

The present work was undertaken to study the conformational behaviour of the 1,4-dioxa

\* In the earlier publication<sup>14</sup> the diffuse IR spectra were taken to reflect larger librational amplitudes rather than a conformational change.

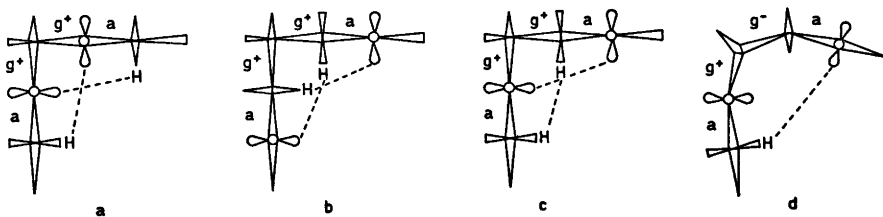
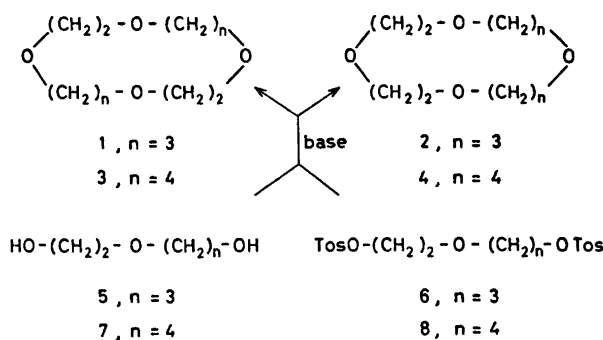


Fig. 1. Observed <sup>2</sup> genuine corners (a—c) and pseudo corner (d) in macrocyclic compounds containing the 1,3-dioxa grouping (a), the 1,5-dioxa grouping (b), and the 1,4-dioxa grouping (c and d).



grouping when two such groupings are present in various relative positions on 14- and 16-membered rings. The simplest cases are the tetraethers *I*–*4* where the remaining two dioxagroupings are also identical.

### SYNTHESIS

The most direct approach to the synthesis of the symmetric compounds *1* and *3* would be a Williamson reaction between one diol and the ditosylate of the other diol, hoping to get by doubling the 14- (or 16-)membered ring along with the 7- (or 8-)membered ring. Although such doubling occurs readily in cyclic formal and ketal syntheses,<sup>4</sup> it failed completely here. Attempts were also made to prepare intermediate monotosylated glycols of the type  $\text{HO}(\text{CH}_2)_2\text{O}(\text{CH}_2)_n\text{OTos}$  ( $n=3$  or  $4$ ), but difficulties were met in all steps, and this route was abandoned.

The synthetic route finally chosen was more easy and safe, but led to a mixture of the two isomers *1* and *2* (or *3* and *4*), which required a final separation step. The dihydroxyalkyl ether *5* (or *7*) was prepared by chain elongation of 1,3-propanediol (or 1,4-butanediol) with ethylene oxide in the presence of base.<sup>15</sup> Equivalent amounts of the diol *5* and the corresponding ditosylate *6* gave with potassium *tert*-butoxide a mixture of the two 14-membered cyclic tetraethers *1* and *2* in 60% yield, while the diol *7* and the corresponding ditosylate *8* gave a mixture of the two 16-membered cyclic tetraethers *3* and *4* in only 22% yield. This difference was not unexpected, since the favoured *ag±g±a* conformation of the 1,5-dioxagrouping creates two sharp bends facilitating the proper folding of the chain in the final cyclization step. The 1,6-dioxagrouping has

only been observed<sup>16</sup> in the elongated chain conformation unsuitable for cyclization.

The separation of the tetraoxacyclotetradecane isomers was achieved by gas chromatography giving the two isomers in about equal amounts. One is crystalline and was found by <sup>13</sup>C NMR spectroscopy to be the 1,4,8,11-isomer *1*; the other is a liquid and was identified as the 1,4,7,11-isomer *2*. Identification was also possible by <sup>1</sup>H NMR spectroscopy in the presence of europium shift reagent.

The tetraoxacyclohexadecane isomers could not be separated by gas chromatography although a series of columns were tried. The analytical determination of the composition of the mixture was also difficult since neither <sup>1</sup>H spectroscopy at 100 MHz nor <sup>13</sup>C spectroscopy at 15 MHz gave fully resolved signals. However, the addition of lithium thiocyanate gave a well-resolved <sup>13</sup>C spectrum which revealed that the 1,4,7,12-isomer *4* constituted about 2/3 and was more strongly complexed by lithium, with signals covering the broadest range. The 1,4,9,12-isomer *3* was also complexed, but less strongly, and constituted about 1/3. Attempts to isolate these two isomers as lithium complexes by crystallization or selective extraction failed.

### CONFORMATIONAL STUDIES OF THE TETRAOXACYCLOTETRADECANES

All known crystal structures<sup>4,17,18</sup> of "saturated" heterocyclic compounds derived from cyclotetradecane have revealed the same diamond-lattice type quadrangular conformation, designated [3434], which has been established for cyclotetradecane itself in the crystal<sup>19</sup> as well in solution.<sup>20</sup> At the outset it was, therefore, reasonable to expect conformation A

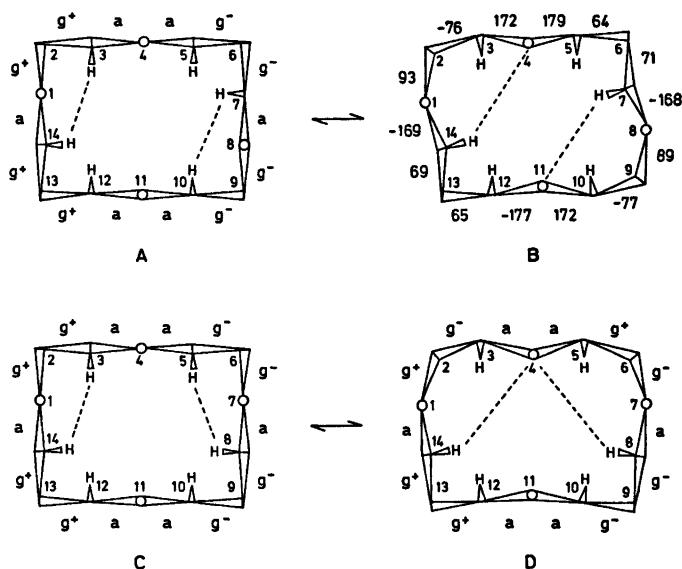


Fig. 2. Diamond-lattice conformation (A) and observed<sup>21</sup> crystal conformation (B) for 1,4,8,11-tetraoxacyclotetradecane **1**, and corresponding conformations (C and D) for 1,4,7,11-tetraoxacyclotetradecane **2**.

for isomer **1** and conformation C for isomer **2** (Fig. 2), with the positions of the ether oxygens defined simply by fitting the 1,5-dioxo groupings across corners in the same way as established<sup>7,8</sup> for 1,5,9,13-tetraoxacyclohexadecane.

The close similarity of the IR-spectra of isomer **1** in the solid, in the liquid and in  $\text{CCl}_4$  solution indicated conformational homogeneity. Furthermore, the dipole moments in benzene solution seemed in satisfactory agreement, being larger for isomer **2** (2.0 D) than for isomer **1** (1.2 D). The NMR-spectra correspond to fast site-exchange even at  $-130^\circ\text{C}$  and therefore provided no direct information about conformational homogeneity or symmetry. Nevertheless, the presence of a single conformer for each of these isomers also in  $\text{CS}_2$  solution was suggested by the fact that the  $^{13}\text{C}$  chemical shifts were remarkably constant over a wide temperature range (Figs. 3 and 4). On the other hand, a very dramatic upfield displacement was observed for some of the signals on cooling solutions in the polar solvent  $\text{CHCl}_2\text{F}$  (Figs. 3 and 4). Since no such displacement was observed for the conformationally homogeneous reference substances 1,4-dioxane and 1,5,9,13-tetraoxacyclohexadecane in the same solvent, this

clearly indicated an equilibrium between at least two conformers for each of the two isomers.

The nature of this conformational equilibrium could not be understood before Groth<sup>21</sup> provided a reference point by determining the crystal structure of isomer **1**. Instead of the expected quadrangular [3434] conformation A this tetraether was found to adopt the biangular [77] conformation B (Fig. 2) having only two "genuine corners" and two "pseudo corners".\* The reason for the preference of B to A is no doubt that the parallel ether dipoles and the repulsive *gauche*  $\text{CH}\cdots\text{CH}$  interactions at the genuine corners of A are avoided at the pseudo corners of B. Also, the 1,5  $\text{CH}\cdots\text{O}$  interactions in B may possibly be slightly attractive, even if in a hydrocarbon this represents a "forbidden" 1,5-interaction.

A very similar torsion-angle pattern had already been observed by Dunitz in the crystal structure of 1,4,7,10,13,16-hexaoxacyclooctadec-

\* A "genuine corner" atom **1** has both substituents pointing out and adjoining ring bonds of the same torsion-angle sign, whereas at "pseudo corner" atoms these angles have opposite signs and particularly large values (Fig. 1).

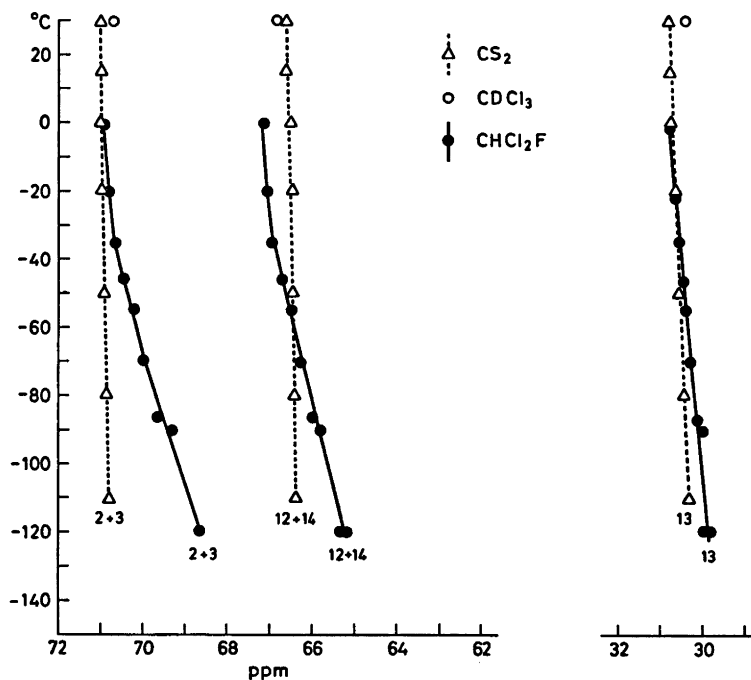


Fig. 3.  $^{13}\text{C}$  NMR chemical shifts for 1,4,8,11-tetraoxacyclotetradecane as a function of temperature. Numbers refer to carbon numbering in Fig. 2, A and B.

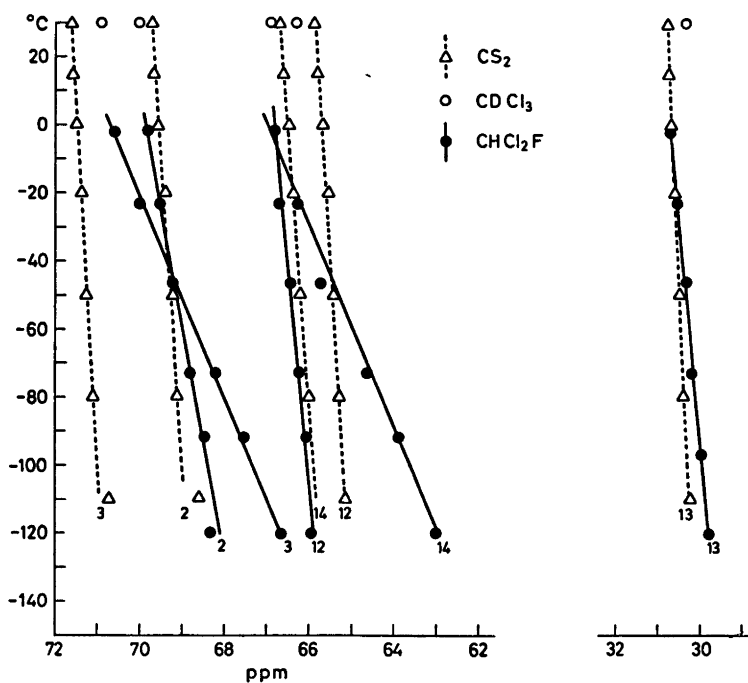


Fig. 4.  $^{13}\text{C}$  NMR chemical shifts for 1,4,7,11-tetraoxacyclotetradecane as a function of temperature. Numbers refer to carbon numbering in Fig. 2, C and D.

Table 1. Observed torsion angle sets ( $^{\circ}$ ) for the  $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$  unit at genuine and pseudo corners in macrocyclic oligoethers.

	CO	OC	CC	CO
Genuine corners				
12-crown-4 <sup>13</sup>	-140	85	75	-174
(12-crown-4) <sub>2</sub> ·NaCl·5H <sub>2</sub> O <sup>9</sup>	-165	81	59	-165
(12-crown-4) <sub>2</sub> ·NaOH·8H <sub>2</sub> O <sup>10</sup>	-163	80	59	-163
12-crown-4·CaCl <sub>2</sub> ·8H <sub>2</sub> O <sup>11</sup>	-167	84	56	-167
dibenzo-30-crown-10·KI <sup>24</sup>	-176	79	62	175
	-169	85	62	-176
	172	62	44	178
Pseudo corners				
12-crown-4 <sup>13</sup>	-174	103	-75	140
1,4,8,11-tetraoxacyclotetradecane <sup>21</sup>	-169	93	-76	172
	-168	89	-77	172
18-crown-6 <sup>22</sup>	-170	80	-75	155
dibenzo-30-crown-10 <sup>24</sup>	-169	95	-67	148

ane ("18-crown-6"); two such bends are present in the uncomplexed ring,<sup>22</sup> whereas a diamond-lattice type conformation is adopted in cation complexes.<sup>23</sup> Furthermore, Bush and Truter had reported<sup>24</sup> two such pseudo corners in uncomplexed dibenzo-30-crown-10 and six genuine corners in its potassium iodide complex. Subsequently, Groth has found<sup>13</sup> that 1,4,7,10-tetraoxacyclododecane ("12-crown-4") has a biangular [66] conformation with similar details at the two pseudo corners when uncomplexed, whereas the expected quadrangular [3333] conformation is used in cation complexes.<sup>9-11</sup> The numerical values for the torsion angles are compared in Table 1.

The remarkable constancy of this conformational unit in four different ring structures suggests that it must also be present in the dominant conformation of the liquid isomer 2. In fact, the well-established conformational requirements of the adjacent 1,5-dioxa groupings<sup>2</sup> fix already nine ring atoms in space, and so the adjacent 1,4-dioxa groupings can link the ends only in the way shown in Fig. 2 to give a biangular [4,10] conformation D. Furthermore, all four conformations A-D are seen to satisfy the general requirement that a maximum number of CO-bonds be *anti* (six out of eight). They seem, therefore, to be the best candidates in a discussion of the conformational equilibria in  $\text{CHCl}_2\text{F}$ . The local dipolar repulsions at the genuine corners of conformers A and C might

be reduced, not only by cation complexing, but also by specific solvation of the ether oxygens from the "acidic" CH of the solvent. Such molecular complex or adduct formation is expected to be most pronounced at low temperature and would thus explain the temperature dependence of the NMR spectra. Crystalline molecular complexes of a similar nature involving interaction between acidic CH and ether oxygen have been reported for 18-crown-6 with dimethyl acetylenedicarboxylate<sup>25</sup> and with malononitrile,<sup>26</sup> and invariably the ring is present in the same conformation as found in cation complexes.

A closer analysis of the observed <sup>13</sup>C chemical shift variation in  $\text{CHCl}_2\text{F}$  supports the hypothesis that isomer 1 changes from mainly conformer B at high temperature to mainly conformer A at low temperature (Fig. 3), and that similarly isomer 2 on cooling changes from conformer D to conformer C (Fig. 4). Among the known intramolecular effects of concern here, leading to upfield or downfield displacements of <sup>13</sup>C signals, the most important is the strong upfield "γ-effect" (often as much as 5 ppm) due to steric compression of a CH<sub>3</sub> or CH<sub>2</sub> group on one side of a *gauche* bond (CO or CC) by a CH<sub>3</sub>, CH<sub>2</sub> or OH group on the other side.<sup>30,27-32</sup> A weaker upfield "vicinal *gauche* effect"<sup>27,32</sup> at carbon atoms participating in *gauche* bonds and the probably related upfield "eclipsing effect"<sup>30,33</sup> may be suitably combined in the

formulation: The smaller the *gauche* angle, the larger the upfield shift.\* Finally, a downfield "δ-effect" is observed when a CH<sub>3</sub> group is sterically compressed by a CH<sub>3</sub>, NH<sub>2</sub> or OH group in 1,5-relationship,<sup>39,35-39</sup> and between similarly compressed CH<sub>3</sub> groups.<sup>40</sup>

The signals in Figs. 3 and 4 can be easily assigned to the numbered carbon atoms of compounds 1 and 2 in Fig. 2 (it is sufficient to consider the left half of each conformer) using the following arguments:

In all conformers of both isomers the γ-effect between C-12 and O-1 and between C-14 and O-11 is present and can be neglected.

In conformer D of isomer 2 one would expect a stronger vicinal *gauche* effect at C-2 than at C-3, and C-2 must therefore be at the higher field at room temperature. The vicinal *gauche* effect increases for both carbons on conversion to the low-temperature conformer C, but is overshadowed by the strong upfield γ-effect felt by C-3 from C-14 in conformer C resulting in cross-over at ~ -40°C. For the other pair of α-carbons, C-14 is at lowest field in the room-temperature conformer D due to the δ-effect from O-4 but feels a strong γ-effect from C-3 in conformer C, whereas C-12 feels no such effects in either conformer, resulting again in cross-over on cooling, now at ~0°C. The insignificant temperature variation not only of C-12 but also of C-13 thus supports the postulated conformational invariance of the 1,5-dioxo grouping during the conversion of D to C.

For isomer 1 exactly the same reasoning applies, but because of the constitutional symmetry, the signals for C-2 and C-3 become averaged, as do the signals for C-12 and C-14. The C-13 signal is unique however, and is, as expected, identical in isomers 1 and 2.

## EXPERIMENTAL

*3-Oxa-1,6-hexanediol* (5) was prepared by a procedure analogous to that of Emerson and coworkers<sup>15</sup> by passing ethylene oxide into 1,3-propanediol containing sodium hydroxide. After working up, redistillation over potassium carbonate gave a fraction, b.p. 120–130°C/8 mmHg, which was used in the next step.

\* In addition, an upfield γ-effect of electronic origin has been observed<sup>34</sup> from a hetero-atom through an *anti* CC-bond, but does not apply here since this conformational feature is absent.

*3-Oxa-hexamethylene bis(p-toluenesulfonate)* (6). To an ice-cooled and stirred solution of 3-oxa-1,6-hexanediol (75 g) in pyridine (500 ml) was added *p*-toluenesulfonyl chloride (251 g) portionwise over 3 h. Cooling and stirring was continued for 1 h, the mixture then left overnight at 5°C, and poured on an ice-water mixture. Precipitated ditosylate was filtered off and washed with water. Recrystallization from ethanol (1 l) gave 6 as white crystals in 66% yield, m.p. 82°C. Anal. C<sub>18</sub>H<sub>24</sub>O<sub>7</sub>S<sub>2</sub>: C, H.

*Tetraoxacyclotetradecanes (1 and 2)*. Potassium (18 g = 0.46 mol) was added to *tert*-butyl alcohol (500 ml). To the resulting *tert*-butoxide solution was first added 3-oxa-1,6-hexanediol (24 g = 0.2 mol) and thereafter a solution of 3-oxa-hexamethylene bis(*p*-toluenesulfonate) (86 g = 0.2 mol) in *tert*-butyl alcohol over 5 min at room temperature. The mixture was stirred at 50°C overnight, and precipitated potassium tosylate was filtered off and washed with chloroform. The combined solutions were evaporated in a rotatory evaporator. The residue was distilled to give a mixture of 1 and 2 as a liquid in 60% yield, b.p. 110–113°C/0.3 mmHg. Preparative gas chromatography (15% Carbowax 4000 on Chrom WAW-DMCS) yielded the two isomers in equal quantities. 1,4,8,11-Tetraoxacyclotetradecane (1) is crystalline, m.p. 34°C, mol.wt. (MS) 204, anal. C<sub>10</sub>H<sub>20</sub>O<sub>4</sub>: C, H. 1,4,7,11-Tetraoxacyclotetradecane (2) is liquid even at -70°C, mol.wt. (MS) 204, anal. C<sub>10</sub>H<sub>20</sub>O<sub>4</sub>: C, H.

*3-Oxa-1,7-heptanediol* (7) was prepared according to Emerson and coworkers.<sup>15</sup> A fraction boiling at 145°C/8 mmHg was used in the next step.

*3-Oxaheptamethylene bis(p-toluenesulfonate)* (8). This compound was prepared as described above for 6. Recrystallization from ethanol gave 8 as white crystals in 64% yield, m.p. 48°C. Anal. C<sub>20</sub>H<sub>28</sub>O<sub>7</sub>S<sub>2</sub>: C, H.

*Tetraoxacyclohexadecanes (3 and 4)*. By a procedure analogous to that described above for 1 and 2, equimolar amounts of 3-oxa-1,7-heptanediol and 3-oxaheptamethylene bis(*p*-toluenesulfonate) gave a mixture of 3 and 4 as a liquid in 22% yield, b.p. 130–140°C/0.5 mmHg, mol.wt. (MS) 232. Separation by gas chromatography was unsuccessful. <sup>13</sup>C NMR spectroscopy of a solution of the tetraether mixture and LiNCS in CDCl<sub>3</sub> showed that 3 and 4 were present in the ratio 1:2.

*General*. IR-spectra were recorded on a Perkin-Elmer 225 instrument with liquids between two pressed KI discs and solutions in 1 mm KBr cells. <sup>13</sup>C NMR spectra were recorded on a Jeol Fourier transform instrument JNM-FX60 operating at 15 MHz using external deuterium lock; ppm is given relative to tetramethylsilane. Dielectric constants were measured at 20°C on a Weilheim Dipolmeter DM 01.

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