

# Self-Complexation of Macrocyclic Polyethers Studied by Carbon-13 NMR Longitudinal Relaxation Time Measurements and Molecular Mechanics<sup>1</sup>

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**Abstract:** Carbon-13 spin-lattice relaxation time measurements on three series of macrocyclic polyethers with ring sizes varying from 15 to 33 ring atoms reveal that 2,6-pyrido (**1**) and benzo (**3**) crown ethers with at least 24 ring atoms can adopt conformations in which the aromatic moiety is encapsulated by the polyether ring of the ligand. This type of intramolecular *self-complexation* is not observed in the case of 1,3-xylylene crown ethers (**2**). A number of possible structures of self-complexed crown ethers could be generated and studied by molecular mechanics. The calculations indicate that the nature of the driving force for self-complexation of 2,6-pyrido crown ethers is mainly electrostatic whereas van der Waals forces favor self-complexation of benzo crown ethers.

The capability of many biological systems (hosts) to recognize and selectively bind substrates (guests) is related to the existence of molecular cavities which may preferably be filled by (parts of) molecules that possess a complementary binding relationship to the receptor site. Synthetic macrocyclic polyethers have been widely used as mimics for biological receptor systems because of their capability to form complexes both with charged<sup>2</sup> and with neutral molecules.<sup>3</sup> Cram has stated that two principles seem to determine host-guest interactions and complexation, viz., complementarity of the binding sites and preorganization of the host.<sup>4</sup> Application of the latter principle has led Cram et al. to design and synthesize the highly structured (hemi)spherands in which at least half of the binding sites are preorganized.<sup>5</sup> The spherands represent the most selective and powerful ligands for small centrosymmetrical cations (Li<sup>+</sup>, Na<sup>+</sup>). For the complexation of larger and polyfunctional guests both principles can be used to serve as guidelines for the design of hosts. The principle of complementarity inspired the design of large flexible (polytopic) macrocycles with binding sites that can occupy positions in which maximum complementary binding is accomplished. We have used this principle in our work on the complexation of guanidinium cations.<sup>6</sup> The principle of preorganization has resulted in the construction of cavitands and cyclophanes, i.e., compounds with enforced cavities, in which the guest should occupy the energetically most favorable position.<sup>7</sup>

As part of our efforts to design and synthesize receptor molecules that selectively complex urea, we have concentrated our work on macrocycles with more than 24 ring atoms, a virtually unexplored area in crown ether chemistry.<sup>8</sup> During this work we found from an X-ray study that the cavity of uncomplexed 2,6-pyrido-24-crown-8 was filled by the pyrido moiety.<sup>6b</sup> It is known from numerous crystallographic studies that host molecules tend to fill their cavities by adopting conformations in which atoms or groups point into the cavity.<sup>4</sup> We propose to call this phenomenon *self-complexation*. Host molecules in which in the solid state hydrogen atoms,<sup>9</sup> intraannular groups,<sup>10</sup> or even substantial parts of the ligand,<sup>11</sup> e.g., (ter)pyridin or phenanthrene moieties, (partly) fill the cavity have been described.

Obviously during the process of complexation the cavity must become available for the guest species, and consequently the contribution of the self-complexation to the overall free energy change will offset part of the energy gained in the complexation process. The differences in orientation of the pyrido moiety in the free 2,6-pyrido-24-crown-8<sup>6b</sup> and the 2:1 water complex of the protonated macrocycle<sup>9b</sup> may illustrate the rather large conformational reorganizations that may be involved. However, we

realized that solid-state phenomena may only partly be responsible for this self-complexation as the role of crystal packing effects is unknown in most cases.

Few papers are devoted to the dynamics of molecular cavities, and no systematic study on self-complexation phenomena of macrocyclic polyethers in solution has been performed so far. NMR *T*<sub>1</sub> relaxation time determinations of various nuclei were performed to study the conformational changes upon complexation of podands,<sup>12</sup> tetraazamacrocycles,<sup>13</sup> crown<sup>14</sup> and lariat ethers,<sup>15</sup>

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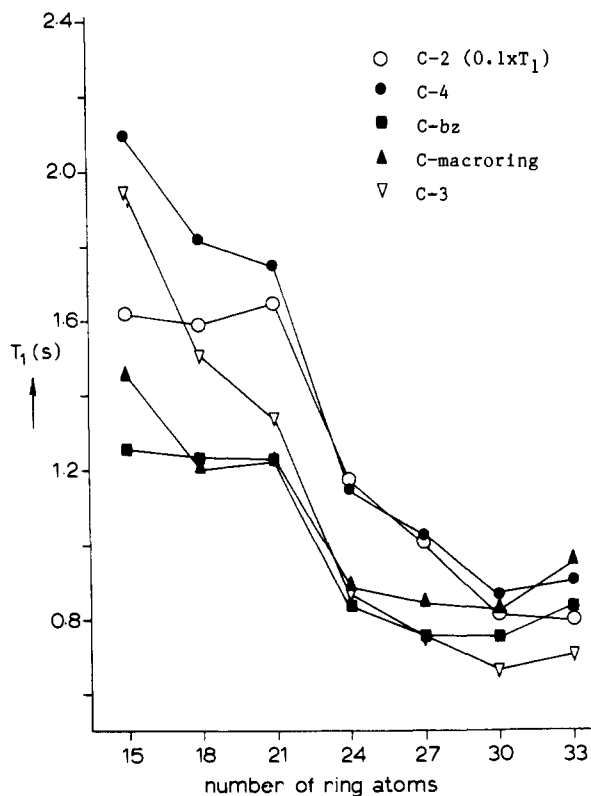
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**Figure 1.**  $T_1$  values (s) of 2,6-pyrido crown ethers (**1**,  $n = 0-6$ ) in  $\text{CDCl}_3$  at 293 K. In order to facilitate visual comparison, for the quaternary C-2 carbons the values given are  $0.1 \times T_1$ . The averaged  $T_1$  value is given for the macroring carbons.

and cryptands.<sup>16</sup> Using similar methods we have studied conformational effects such as the role of preorganization in the complexation of neutral molecules by hemispherands.<sup>17</sup> Recently, we published a method yielding qualitative information on intramolecular interactions within free macrocycles in solution.<sup>18</sup> It is based on the comparison of thermodynamical data of the complexation of a neutral probe molecule (malononitrile) by a series of crown ethers. Conformational analyses of host-guest complexes using (dynamic) NMR spectroscopy were recently reviewed by Sutherland.<sup>19</sup> IR spectroscopy was used by Dale et al. to compare the conformations of free and complexed crown ethers.<sup>20</sup>

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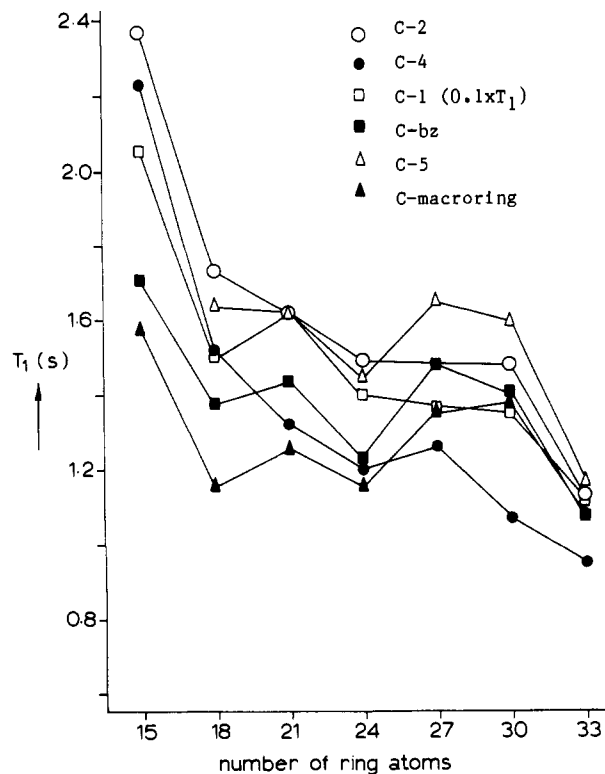
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**Figure 2.**  $T_1$  values (s) of 1,3-xylyleno crown ethers (**2**,  $n = 0-6$ ) in  $\text{CDCl}_3$  at 293 K. In order to facilitate visual comparison, for the quaternary C-1 carbons the values given are  $0.1 \times T_1$ . The averaged  $T_1$  value is given for the macroring carbons.

**Table I.**  $^{13}\text{C}$   $T_1$  Data (s) of 2,6-Pyrido Crown Ethers (**1**,  $n = 0-6$ ) in  $\text{CDCl}_3$  at 293 K

ring atoms	C-2	C-3	C-4	C-bz	C(rest)
15	16.17	1.95	2.10	1.26	1.46
18	15.87	1.51	1.82	1.23	1.21
21	16.45	1.34	1.75	1.23	1.23
24	11.74	0.87	1.15	0.84	0.89
27	10.22	0.76	1.03	0.76	0.85
30	8.23	0.67	0.87	0.76	0.83
33	8.05	0.71	0.91	0.84	0.96

**Table II.**  $^{13}\text{C}$   $T_1$  Data (s) of 1,3-Xylyleno Crown Ethers (**2**,  $n = 0-6$ ) in  $\text{CDCl}_3$  at 293 K

ring atoms	C-1	C-2	C-4	C-5	C-bz	C(rest)
15	20.67	2.37	2.23	nd	1.71	1.58
18	15.06	1.73	1.52	1.64	1.38	1.16
21	16.16	1.62	1.32	1.61	1.44	1.26
24	14.02	1.49	1.20	1.45	1.23	1.16
27	13.71	nd	1.26	1.65	1.48	1.36
30	13.51	1.48	1.07	1.60	1.41	1.38
33	11.65	1.13	0.95	1.17	1.08	1.08

**Table III.**  $^{13}\text{C}$   $T_1$  Data (s) of Benzo Crown Ethers (**3**,  $n = 0-6$ ) in  $\text{CDCl}_3$  at 293 K

ring atoms	C-1	C-3	C-4	C-a	C-b	C-c	C-d	C(rest)
15	32.95	1.82	1.65	1.17	1.17	1.34	1.35	
18	24.64	1.37	1.25	0.96	1.05	1.10	1.15	1.07
21	27.19	1.32	1.23	0.98	1.00	1.09	1.23	1.17
24	17.09	0.73	0.73	0.73	0.77	0.90	nd	0.96
27	14.33	0.67	0.72	0.74	0.77	0.93	nd	0.93
30	20.86	0.92	0.95	0.90	0.95	1.29	1.21	1.17
33	20.67	0.91	0.94	0.85	0.94	nd	nd	1.15

The conformational properties of macrocyclic ligands have also been studied with the molecular mechanics method.<sup>21</sup> Several

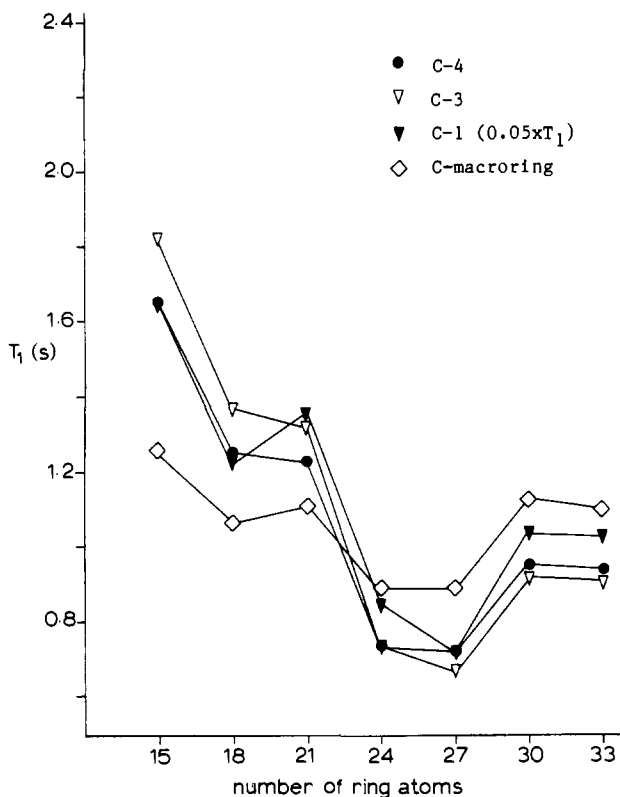


Figure 3.  $T_1$  values (s) of benzo crown ethers ( $3$ ,  $n = 0-6$ ) in  $\text{CDCl}_3$  at 293 K. In order to facilitate visual comparison, for the quaternary C-1 carbons the values given are  $0.05 \times T_1$ . The averaged  $T_1$  value is given for the macroicing carbons.

studies deal with the structural flexibility of simple crown ethers.<sup>22</sup> Conformational aspects of the complexation of metal ions have been studied for 18-crown-6,<sup>22a,23</sup> tetraaza macrocycles,<sup>24</sup> cryptands,<sup>25</sup> and spherands.<sup>26</sup> The complexation of neutral entities by macrocycles has received less attention in molecular mechanics calculations until now; only results for the complexes of 18-crown-6 with urea and formamide are reported.<sup>22e</sup> Molecular mechanics calculations and NMR experiments have been combined to study the passage of aryl-tipped alkyl groups through cyclophane cavities<sup>27a</sup> and to determine the most stable conformation of a 14-membered macrocycle.<sup>27b</sup>

In this paper we report a systematical study of the effect of incorporating rigid moieties in macrocyclic polyethers on the dynamics of the molecular cavities. Three series of crown ethers with ring sizes varying from 15 to 33 ring atoms, modified with 2,6-pyrido, 1,3-xylyleno, and benzo units, were synthesized and investigated. The combination of carbon-13 NMR  $T_1$  data with

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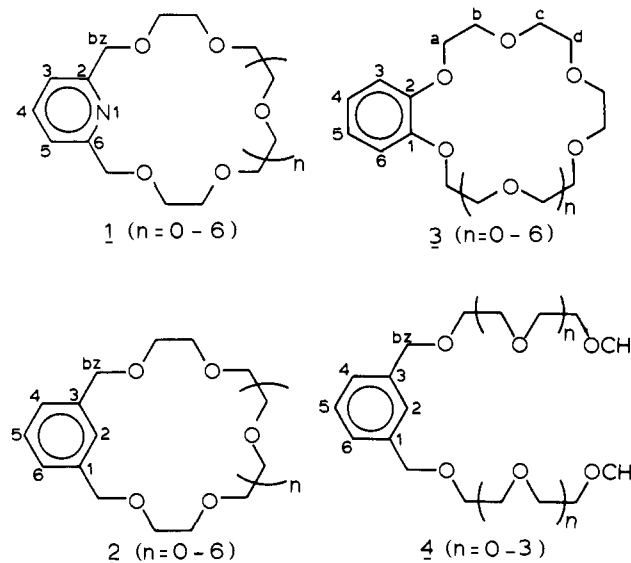
Table IV.  $^{13}\text{C}$   $T_1$  Data (s) of Open-Chain Model Compounds **4** in  $\text{CDCl}_3$  at 293 K

$n$	C-1	C-2	C-4	C-5	C-bz	C(rest)	$\text{OCH}_3$
0	20.94	2.17	1.68	2.18	2.01	2.85	5.96
1	15.73	1.55	1.20	1.55	1.40	2.16	6.10
2	13.73	1.21	0.97	1.24	1.20	1.80	6.02
3	11.92	1.02	0.93	1.17	1.10	1.76	6.44

molecular mechanics calculations has been used to gain insight into self-complexation phenomena in these ligand systems.

## Results

**Relaxation Time Measurements.**  $^{13}\text{C}$   $T_1$  relaxation time values<sup>28</sup> of the 2,6-pyrido (**1**), 1,3-xylyleno (**2**), and benzo crown ethers (**3**) were measured by the inversion recovery method, and they are depicted as a function of the ring sizes in Figures 1, 2, and 3, respectively. The corresponding data are included in Tables I, II, and III, respectively. For the evaluation of the macrocyclic effects we also studied the open-chain model compounds **4** (Table IV). Nuclear Overhauser enhancement (NOE) factors,  $\eta$ , of all



protonated carbons were between 1.7 and 2, indicating that the dipole-dipole (DD) relaxation mechanism is dominating (eq 1).

$$T_1^{\text{DD}} = T_1^{\text{obsd}} \cdot 1.988 / \eta \quad (1)$$

In that case the  $T_1$  values can be expressed by eq 2, where  $N$  is the number of covalently bonded protons,  $\hbar = h/2\pi$ ,  $\gamma_C$  and  $\gamma_H$  are the gyromagnetic ratios for C and H nuclei,  $r$  is the C-H internuclear distance, and  $\tau_C$  is the correlation time. Since the

$$1/T_1 = N\hbar^2\gamma_C^2\gamma_H^2r^{-6}\tau_C \quad (2)$$

correlation times are related to the mobilities of the nuclei, the  $T_1$  data yield information on the mobilities of the various carbon-13 nuclei in the ligands. A more rapid motion of a carbon-13 will result in an increased  $T_1$  value, assuming that extreme narrowing conditions are fulfilled.<sup>28</sup>

The  $T_1$  values and the mobilities for all atoms of the three different ligands and model systems generally decrease when the ring size and chain length increase. This is in agreement with what one should expect for a homologous series of compounds in which the molecular weight increases and is consistent with

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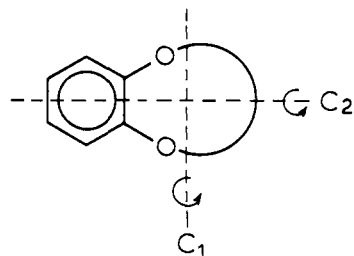


Figure 4. Principal rotation axes of benzo crown ethers.

observations from Gokel and co-workers<sup>15</sup> on 15-crown-5 and 18-crown-6.

However, for the 2,6-pyrido and benzo crown ethers an abrupt decrease of the  $T_1$  values is observed between 21 and 24 ring atoms. On the basis of Corey–Pauling–Koltun (CPK) model studies and molecular mechanics calculations (vide infra) we interpreted this change in terms of the self-complexation of the aromatic moiety by the crown ether. The loss of degrees of freedom in the intramolecular complex, probably combined with a change in solvation, is expressed in the decreased mobilities of both the aromatic and polyether chain <sup>13</sup>C nuclei. A minimum ring size of 24 ring atoms is needed for the encapsulation of the aromatic moiety by the polyether ring.

The 1,3-xylyleno crown ether series does not show such a clear discontinuity in the  $T_1$  values. Apparently self-complexation is not important in these ligands.

From the literature<sup>12–17</sup> it is known that intermolecular complexation of a host molecule with a guest generally lowers the mobilities of the binding sites and has the same effect on the  $T_1$  values as observed in the case of self-complexation. Previously<sup>1</sup> we have reported the changes in  $T_1$  values of the macro ring carbons when guanidinium cations were complexed by several large 2,6-pyrido crown ethers.

A second indication for a conformational reorganization of the benzo crown ethers with at least 24 ring atoms comes from a comparison of the  $T_1$  values of C-3 and C-4. From 15 to 21 ring atoms the  $T_1$  of C-3 is larger than that for C-4. This was also reported for structurally related compounds, i.e., benzocycloalkenes,<sup>29</sup> and explained in terms of preferential rotations around the  $C_2$  axis. However for the benzo crown ethers with a ring size of 24 atoms the  $T_1$  values of C-3 and C-4 become equal, and for larger macrocycles the  $T_1$  values of C-4 are larger than the corresponding  $T_1$  values of C-3. A switch of the axis of preferential rotation of the  $C_2$  toward the  $C_1$  axis (see Figure 4) can be rationalized by assuming a conformational reorientation to a more circular structure, which is characteristic for a self-complexed ligand.

For all members of the pyrido crown ether series the  $T_1$  values of the C-3 atoms are somewhat smaller than the  $T_1$  values observed for the C-4 atoms. This indicates the presence of anisotropic motion. The molecule preferentially rotates around an axis perpendicular to the  $C_2$  axis.<sup>30</sup> In systems where the pyridine nitrogen is hydrogen-bonded to methanol the  $C_2$  axis is the preferential axis of rotation.<sup>31</sup>

**Molecular Mechanics.** Various conformations of the 2,6-pyrido, 1,3-xylyleno, and benzo crown ethers were studied with the molecular mechanics method. Selected results are displayed in Figures 5 and 6 and Table V. Details of all conformations studied are in the supplementary material.

For the 1,3-xylyleno crown ethers the rotational freedom of the xylyleno moiety of the 18-membered macrocycle was studied with the “dihedral driver” option of MM2. Starting point was the conformation, observed in the solid state in a complex with *tert*-butylammonium perchlorate,<sup>32</sup> which has approximate  $D_{3d}$

Table V. Steric Energies of Selected Conformations of 1,3-Xylyleno ( $2, n = 1-4$ ), 2,6-Pyrido ( $1, n = 3$ ), and Benzo ( $3, n = 4$ ) Crown Ethers: Total Energies and the Bonded and Nonbonded Contributions (kcal mol<sup>-1</sup>)

ligand	conf.	$E_{st,tot}$	$E_{st,bond}$	$E_{st,nonbond}$	
				van der Waals	electrostatic
1,3-xylyleno-18-crown-5	I	17.3	-6.7	19.1	4.8
	II	24.5	3.4	19.1	1.9
1,3-xylyleno-21-crown-6	I	24.4	-4.2	23.4	5.1
	II	29.0	3.2	21.7	4.1
1,3-xylyleno-24-crown-7	I	27.0	-4.7	25.8	5.9
	II	30.2	1.7	23.3	5.3
2,6-pyrido-24-crown-8	I	24.1	-7.3	25.7	5.8
	II	23.9	-1.6	23.2	2.4
1,3-xylyleno-27-crown-8	I	36.2	1.6	29.2	5.5
	II	36.4	5.4	25.1	5.8
benzo-27-crown-9	I	42.4	2.0	32.9	7.4
	II	41.5	11.1	25.7	4.8

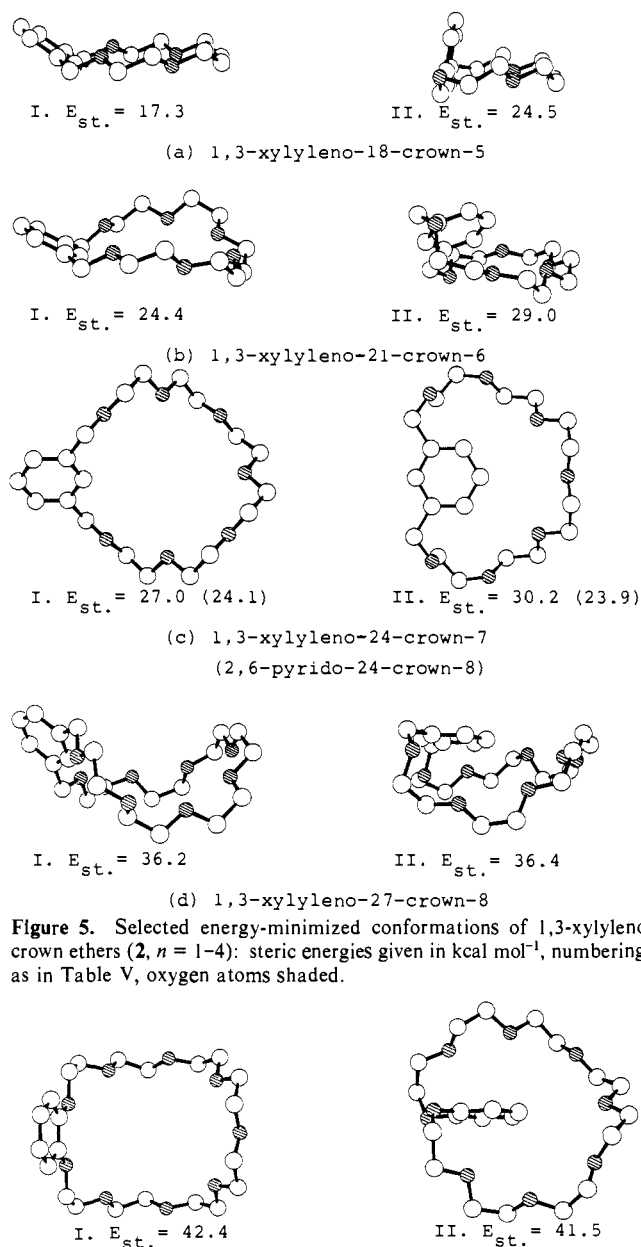


Figure 5. Selected energy-minimized conformations of 1,3-xylyleno crown ethers ( $2, n = 1-4$ ): steric energies given in kcal mol<sup>-1</sup>, numbering as in Table V, oxygen atoms shaded.

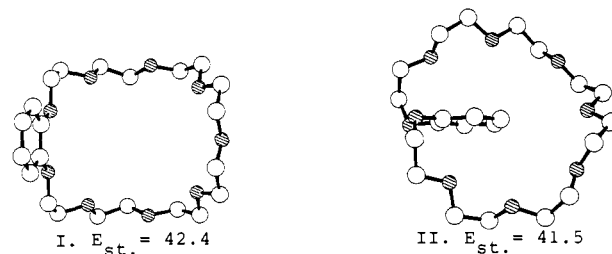


Figure 6. Two energy-minimized conformations of benzo-27-crown-9 ( $3, n = 4$ ): steric energies given in kcal mol<sup>-1</sup>, numbering as in Table V, oxygen atoms shaded.

symmetry (torsion code  $ag^+a ag^-a ag^+a ag^-a ag^+a ag^-a$ ) when neglecting the aromatic part. The xylyleno moiety was forced to rotate into the cavity of the macrocycle, which resulted in a

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(30) In the preliminary communication,<sup>1</sup> this effect was interpreted incorrectly.

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drastic increase of the steric energy. A local minimum, 7.2 kcal mol<sup>-1</sup> higher in energy, was found in which the xylyleno moiety is almost perpendicular to the mean plane of the macrocycle (Figure 5a). Further rotation was prevented by strong van der Waals repulsion.

Several conformations of 1,3-xylyleno-21-crown-6 were studied: five were derived starting from the crystal structures of a 21-crown-7<sup>33</sup> and a 2,6-pyrido-21-crown-7<sup>9b</sup> compound. They were all of comparable energy and had the xylyleno moiety in a position outside the cavity. The conformation with lowest energy had the torsion code  $ag^+a\ ag^-a\ ag^+a\ ag^-a\ ag^+a\ ag^-a\ ag^+a\ ag^-a$ . Another three conformations were generated with molecular graphics, starting from an inward orientation of the xylyleno moiety, which was to some extent retained upon minimization. They were 1.1–4.6 kcal mol<sup>-1</sup> higher in energy than the 21-membered cycles with an outward orientation of the xylyleno moiety (Figure 5b).

Two conformations of 1,3-xylyleno-24-crown-7 were studied, both derived from the X-ray coordinates<sup>6b,9b</sup> of the corresponding *pyrido crown ether*: one with the xylyleno moiety pointing away from the cavity, having approximate  $D_{2d}$  symmetry, neglecting the substituent (torsion code  $ag^+a\ ag^-a\ ag^+a\ ag^-a\ ag^+a\ ag^-a\ ag^+a\ ag^-a$ ), and one with the xylyleno moiety lying completely inside the cavity (Figure 5c). The " $D_{2d}$ " conformation was 3.2 kcal mol<sup>-1</sup> lower in energy. For 2,6-pyrido-24-crown-8 the same conformations, with the pyrido moiety replacing the xylyleno moiety, were studied. The minimized structures resembled those of the corresponding conformations of 1,3-xylyleno-24-crown-7, but in this case the two conformations with the outward respective inward orientation of the pyrido moiety had approximately equal steric energies (Figure 5c).

Five conformations of 1,3-xylyleno-27-crown-8 were obtained from X-ray coordinates of the ligand or the corresponding pyrido crown ether,<sup>6b,8c</sup> with different orientations of the xylyleno moiety relative to the macrocycle. Steric energies differed by as much as 4.2 kcal mol<sup>-1</sup>. The two conformations with lowest energy are shown in Figure 5d.

Five conformations obtained from X-ray coordinates of benzo-27-crown-9 or similar benzo macrocycles<sup>6a,34</sup> and six conformations generated with molecular graphics were studied. The steric energies were in a range of 12.6 kcal mol<sup>-1</sup>. The two lowest energy conformations are shown in Figure 6.

## Discussion

As pointed out in the Experimental Section, no decisive conclusions can be drawn from the molecular mechanics calculations, because of the limited scans of the conformational space and the inability to determine the global minimum for the ligands studied. Another problem is posed by the fact that the calculations relate to "gas-phase" molecules while the spin-lattice relaxation time measurements are performed in solution. However, we feel that some effects can be understood more quantitatively by combining the results from the experimental and computational studies.

**Xylyleno vs. Pyrido Crown Ethers.** Although there is much structural resemblance, the conformational properties of the xylyleno and pyrido crown ethers are significantly different. The  $T_1$  data indicate that the pyrido ligands show a rather abrupt change in conformation at a ring size of 24 ring atoms. On the contrary the  $T_1$  data of the xylyleno crown ethers show no distinct shifts which point to important conformational reorganization. The calculations indicate that the self-complexation process, which is possible for both type of ligands, is more favorable for the pyrido crown ethers, the difference in energy between the "inward" and "outward" conformations amounting to approximately 3.4 kcal mol<sup>-1</sup> for the 24-membered macrocycle. This is mainly due to electrostatic effects: the C–N bond of the pyrido moiety provides a strong dipole, which is repelled from the electronegative cavity, caused by the oxygen atoms. The van der Waals forces of course

favor the filling of the cavity, if it is large enough. This is illustrated by the calculations on the series of xylyleno crown ethers. The conformations with an inward-oriented substituent are favored by the nonbonded interactions with 3–4 kcal mol<sup>-1</sup>, whereas the bonded interactions favor an outward orientation of the substituent. The difference in internal (bonded) strain between the conformations with an inward respective outward-orientated substituent decreases with ring size, resulting in equal total steric energies for the 27-membered macrocycle, which suggests the possibility of self-complexation in the case of 1,3-xylyleno-27-crown-8.<sup>35</sup>

**Benzo vs. Pyrido (Xylyleno) Crown Ethers.** An interesting difference between pyrido (xylyleno) crown ethers and benzo crown ethers regarding possible inward-orientated substituents is observed. The pyrido (and xylyleno) crown ethers have the substituent parallel to the mean plane of the macrocycle, whereas the benzo moiety is perpendicular to the mean macrocyclic plane (Figure 6). This inward orientation of the benzo moiety is strongly favored by the van der Waals interactions, the difference between the two lowest energy conformations of benzo-27-crown-9 with inward and outward orientation of the benzo moiety being 7.2 kcal mol<sup>-1</sup>. There may be a relation to the different behavior with regard to the preferential rotation axes as was observed in the  $T_1$  studies.

**Comparison with Model Compounds.** The  $T_1$  values of the xylyleno moiety of the open-chain compounds **4** ( $n = 0, 1, 2, 3$ ) are almost the same as the corresponding values of the xylyleno crown ethers **2** ( $n = 0, 2, 4, 6$ ). Discontinuities in the  $T_1$  values are not observed, showing that no significant conformational effects are present in the model compounds.

The relatively high  $T_1$  values of the chain <sup>13</sup>C atoms clearly indicate the large flexibility of acyclic chains in comparison to cyclic chains. The  $C_2$  axis serves as the preferential rotation axis for the symmetrical 1,3-substituted benzenes, as is concluded from the  $T_1$  values of the C-4 and C-5 atoms.

## Conclusions

Spin-lattice relaxation time studies combined with molecular mechanics calculations yield a more detailed picture of the conformational properties of macrocyclic polyethers.

From the experimentally obtained results in this paper it may be concluded that crown ethers with at least 24 ring atoms, functionalized with pyrido or benzo moieties, fill up their own cavities by adopting conformations in which the aromatic unit is encapsulated by the macroring. This intramolecular self-complexation hinders the complexation of guest molecules because energetically unfavorable conformational reorganizations have to take place before guests can be encapsulated.

The functionalization of the aromatic moiety using sterically bulky groups might be a method for avoiding self-complexation. This approach is investigated currently in our laboratory.

## Experimental Section

**Materials.** The crown ethers **1** and **3** were prepared and purified according to literature procedures.<sup>6b,34b</sup> The xylyleno crown ethers **2** were synthesized by using the method described for 1,3-xylyleno-27-crown-8 by Uiterwijk et al.<sup>6b</sup> The yields for the isolated 15-, 18-, and 21-membered macrocycles were 35%, 50%, and 35%, respectively, which means a considerable improvement in comparison with the original synthetic procedure for the 15–21-membered macrocycles.<sup>36</sup> The open-chain model compounds **4** were synthesized in high yields (85–95%) by reacting 1,3-bis(bromomethyl)benzene with the monomethyl ethers of the poly(ethylene glycols) (commercially available) under the same conditions as described for the synthesis of the xylyleno crown ethers.

**NMR Measurements.** <sup>13</sup>C spin-lattice relaxation times were obtained on a Nicolet NT200 spectrometer at 50.31 MHz by using the inver-

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(35) With regard to this, it must be noted that the calculations do not completely reproduce the geometry of 2,6-pyrido-24-crown-8 in its crystal structure with the inward orientation of the pyrido moiety. This is partly due to the inability of MM2 to deal with the short nonbonded contacts in the cavity, without explicit treatment of the potential (weak) hydrogen-bonding that occurs.<sup>22c</sup> It means that the steric energies of conformations with an inward-orientated substituent can be overestimated.

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sion-recovery technique (T1 IR) under proton-noise-decoupling conditions. A waiting time of 140 s was maintained. Every run consisted of at least 48 accumulations at 10 different pulse intervals. The samples were stored in 12-mm tubes, degassed by at least two freeze-pump-thaw cycles, and sealed under a nitrogen atmosphere. All measurements were carried out in duplicate at  $293 \pm 2$  K. Finally, the  $T_1$  values were obtained by using a fitting program.<sup>37</sup> The standard deviation is approximately 10%.

Nuclear Overhauser enhancement factors were measured for all crown ethers by using the standard ALNOE pulse sequence. Whenever it was necessary for the assignment of the resonances, 2D (<sup>13</sup>C, <sup>1</sup>H) correlated spectra were recorded.

**Molecular Mechanics.** The molecular mechanics method determines the steric energy of conformations of a molecule as a measure of their relative stabilities. The steric energy is a sum of bonded (stretch, bend, stretch-bend, and torsion) and nonbonded (van der Waals and electrostatic) contributions.

Steric energies of conformations of the macrocyclic polyethers were minimized with the MM2 force field.<sup>21</sup> Parameters for the energy functions were standard ones, except for the aromatic moieties. Following a communication by Allinger,<sup>38</sup> the parameters involving aromatic carbon atoms were modified.<sup>39</sup> In one instance calculations were also carried out with MMP2,<sup>40</sup> the MM2 program for conjugated systems: the relative energies agreed within 0.1 kcal mol<sup>-1</sup>. The parameters for the xylylene and benzo moieties therefore are assumed to give reliable results. For the pyrido moiety, however, parameters involving the aromatic nitrogen atom were not available and had to be estimated,<sup>39,41</sup> and they are thus less reliable. In all cases the error in the results is assumed to be less than 1 kcal mol<sup>-1</sup>.

Starting conformations for the energy minimization of the macrocycles investigated were obtained from X-ray coordinates or were generated by

molecular graphics methods with the aid of CPK models. In this way local minima are found for the steric energy in conformational space. Macrocycles with ring sizes of 18 atoms or larger, however, have hundreds of local minima,<sup>42</sup> and the substituents even enlarge this number. A systematic search for the global minimum is therefore not feasible, and at most it can be rationalized that certain conformations are of low energy, e.g., conformations that have all macrocyclic C-C dihedrals gauche ( $g^+ = 60^\circ$  or  $g^- = -60^\circ$ ) and all C-O dihedrals anti ( $a = 180^\circ$ ),<sup>42</sup> which means that their torsion code consists of  $ag^+a$  and  $ag^-a$  units.

**$T_1$  Data.** The spin-lattice relaxation times are collected in Tables I-IV. Abbreviations used are nd, not determined; bz benzylic; rest, the average of the remaining macro ring carbons.

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**Registry No.** **1** ( $n = 0$ ), 77877-86-2; **1** ( $n = 1$ ), 53914-89-9; **1** ( $n = 2$ ), 86309-73-1; **1** ( $n = 3$ ), 86309-74-2; **1** ( $n = 4$ ), 95216-11-8; **1** ( $n = 5$ ), 95216-12-9; **1** ( $n = 6$ ), 95216-13-0; **2** ( $n = 0$ ), 57624-50-7; **2** ( $n = 1$ ), 53914-83-3; **2** ( $n = 2$ ), 57624-51-8; **2** ( $n = 3$ ), 57624-52-9; **2** ( $n = 4$ ), 57659-55-9; **2** ( $n = 5$ ), 57624-53-0; **2** ( $n = 6$ ), 108744-27-0; **3** ( $n = 0$ ), 14098-44-3; **3** ( $n = 1$ ), 14098-24-9; **3** ( $n = 2$ ), 67950-78-1; **3** ( $n = 3$ ), 72216-45-6; **3** ( $n = 4$ ), 63144-76-3; **3** ( $n = 5$ ), 77963-50-9; **3** ( $n = 6$ ), 104946-62-5.

**Supplementary Material Available:** Tables of all nonstandard MM2 parameters used in the calculations and coordinates, torsion angles, and steric energies of all energy-minimized conformations (21 pages). Ordering information is given on any current masthead page.

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## An XPS Study of Rhodium Carbonyls Adsorbed on Planar Aluminas: Formation of Geminal Dicarboxyl Species

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**Abstract:** The rhodium geminal dicarbonyl species has been observed to form from the evaporation of Rh<sub>4</sub>(CO)<sub>12</sub> onto cooled planar aluminas under ultrahigh vacuum (UHV) conditions. The Rh 3d core level binding energies, Rh:(CO) stoichiometric ratio, and CO bonding site of the geminal dicarbonyl have been determined with X-ray photoelectron spectroscopy (XPS, ESCA). Comparisons are made with Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub>, Rh<sub>4</sub>(CO)<sub>12</sub>, and Rh<sub>6</sub>(CO)<sub>16</sub> evaporated on amorphous and crystalline carbon supports at low temperatures. The instability of these rhodium carbonyls under UHV at room temperature is demonstrated; therefore, our low-temperature data permit us to correct previously reported values for Rh 3d binding energies of rhodium complexes impregnated on powder catalysts and recommend, in some cases, the species responsible for the previously reported binding energies. We identify the Rh 3d<sub>5/2</sub> binding energy of the geminal dicarbonyl as 310.2 eV, indicating that the electron density on the rhodium atom is comparable to Rh<sup>3+</sup> compounds despite its assigned formal charge of Rh<sup>1+</sup>. Reversible changes in Rh core level binding energies following repetitive treatments of vacuum and 1 atm CO exposure at room temperature indicate dispersive effects of rhodium and further demonstrate that the planar aluminas behave similarly to conventional powder alumina catalyst systems.

### I. Introduction

Transition-metal carbonyl clusters supported in a variety of ways have provided a wealth of information concerning interactions among support, metal, and ligands.<sup>1-3</sup> Analogies have also been

made that discrete molecular metal clusters may model metal surfaces in processes of chemisorption and bonding.<sup>4</sup> Decomposition of supported organometallic compounds has provided a

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