

from 3 or 4 occurs between the nematic and isotropic phases.

Conclusions. The constraints imposed by the crystalline and mesophase matrices of BCCN on 1,4-biradicals from ketones 1-4 are very different. Whereas both the crystalline and smectic phases restrict solute breadth and length, the consequences of the specific interactions are vastly different due to the differing solute shapes and mobilities in the two phases. In the smectic and nematic mesophases, the difference between strong and weak (or no) solvent control over solute length and breadth has a marked influence on the fate of the initially formed BRs as they equilibrate with their environment before yielding either elimination or cyclization products.

The governing factors—mobility of solutes during their reactive lifetimes and solvent control over their shapes—should be operative in many other reactive solutes. Indeed, we have found that some lyotropic phases exhibit control over solute reactivity which is remarkably sensitive to solute-solvent shape matches.¹⁸ Although the specific manner in which all of the ordered solvent-solute interactions express themselves is not understood, it is clear that they influence both structural and dynamic aspects of the reactions.

Our results indicate that liquid-crystalline order may play an even more important role in biological reactivity (and structure)

than that which has been recognized.⁵⁴

In future work we intend to investigate how modifications of other structural features of aromatic ketones influence the ways in which BCCN and related ordered solvents control solute reactivity.

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Supplementary Material Available: Five tables of data for E/C and cyclobutanol ratios from irradiations of 1-4 in BCCN (3 pages). Ordering information is given on any current masthead page.

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Complexation of Crown Ethers with Neutral Molecules. 2. Comparison of Free Macrocycles and Their Complexes with Malononitrile in Solution

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Abstract: Thermodynamic parameters for the complexation of a neutral guest (malononitrile) with crown ethers having ring sizes of 15 to 33 ring atoms and various functionalities were obtained. The results give useful information about the conformations of the free crown ethers and their interactions with solvent molecules. 18-Membered macrocycles form the most stable complexes with malononitrile. Crown ethers in which the uncomplexed form strong intraannular interactions are present form weaker complexes while macrocycles in which additional binding sites (e.g., C=O) are available for complexation form more stable complexes with malononitrile than expected. A compensating effect of $T\Delta S^\circ$ and ΔH° of complexation was found for all complexes. The crystal structure of 2,6-pyrido-18-crown-6- $\text{CH}_2(\text{CN})_2$ (1:2) was determined; it shows a hydrogen bond to the pyridyl nitrogen atom.

Although most of the work on crown ethers has been focussed on their complexation with metal ions,¹ more recently also the complexation of neutral polar guest molecules has been studied.² The complexation of CH-acidic neutral molecules was first reported by Cram et al.,³ who suggested the complexation of 18-crown-6 and acetonitrile as a method for the purification of 18-crown-6. Up to now, several complexes of crown ethers and CH-acidic polar neutral molecules⁴⁻¹⁵ (e.g., $\text{CH}_2(\text{CN})_2$,⁴⁻⁸ CH_3CN ,^{3,7,9-12} and CH_3NO_2 ,^{4,7,10-12}) have been reported. X-ray data^{5-8,13,15} show that the nature of the host-guest binding in the solid state seems to be dominated by hydrogen bonds between the acidic hydrogen atoms of the guest and the crown ether oxygen atoms. Hydrogen bonding in solution was confirmed by ¹H NMR^{4,7-9} and IR^{8,9} measurements.

Only in a few cases, the thermodynamic stabilities of complexes of crown ethers and neutral molecules have been determined. We have reported thermodynamic constants for complexes of 18-crown-6 with CH_3NO_2 , CH_3CN , and $\text{CH}_2(\text{CN})_2$ and of 1,3-xy-

lyl-18-crown-5 with CH_3NO_2 in C_6D_6 .⁷ Besides, association constants of the complexes of 18-crown-6 with CH_3CN (in CCl_4),⁹

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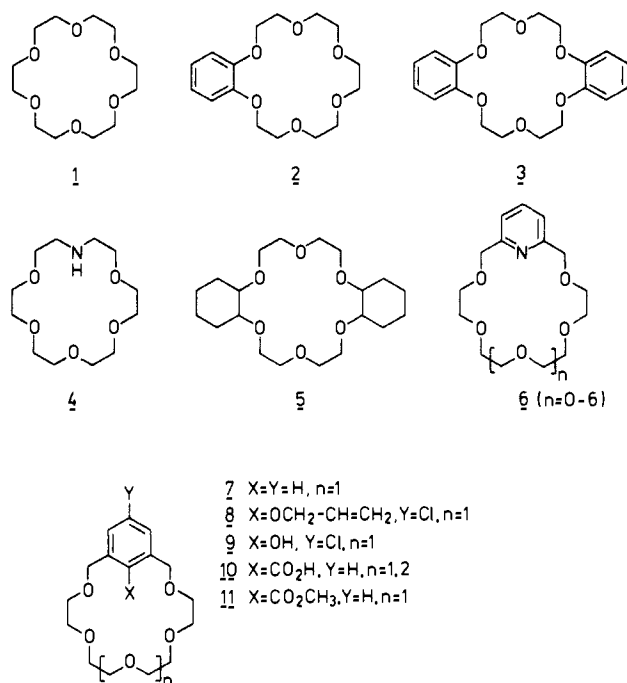
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Chart I



CH₃COCH₃,¹⁶ and CHCl₃¹⁶) and with a number of neutral molecules bearing NH or OH groups¹⁷ have been described. Recently complexes of a rigid host with CS₂^{18a} and of a cavitand with CH₂Cl₂, CH₂Br₂, and CH₂ClBr^{18b} were reported.

Stoddart et al.^{19a,b} have studied the effect of fixed conformations of substituted 18-crown-6 derivatives on the thermodynamic stabilities of complexes with *tert*-butylammonium salts. They concluded that constitution, configuration, and conformation must define the structures of noncovalently bonded species. Nevertheless our understanding of conformational behavior of macrocyclic polyethers in solution is very limited. Buchanan et al.^{19c} have studied conformations of free dicyclohexano-18-crown-6 isomers in solution.

Although much more work has been done on the complexation of cationic species, only a limited quantitative knowledge of the structure of macrocycles and their complexes in solution is available from the literature. Most studies in solution are based on ¹³C NMR T₁ relaxation techniques, which provide only qualitative information about mobility within the molecule.^{20a,b} Comparison of effects is limited to structurally closely related compounds.^{20c}

Therefore, a method that would allow us to determine conformational parameters in the uncomplexed ligands would be of great value for the design of host molecules. The complexation process will benefit from the relief of unfavorable interactions (e.g., oxygen-oxygen repulsion) and suffer from the rupture of favorable interactions in the uncomplexed state (e.g., intraannular H bonding).

In this paper we report the results of a quantitative systematic study of the thermodynamic stabilities of complexes of crown ethers with one neutral guest, viz., CH₂(CN)₂. Crown ethers with various functionalities and ring sizes (1-11) were studied in both C₆D₆ and CDCl₃ as solvents, using variable-temperature ¹H NMR spectroscopy. The objective of this work is to gain a better understanding of host-guest interactions in solution. Since we have used exclusively one guest species (malononitrile) and a variety of crown ethers, it turned out that such a study provides useful information about the conformations of the free crown ethers in solution.

Results and Discussion

Although CH₃NO₂ is more acidic than CH₂(CN)₂ (pK_a's 10.22 and 11.4, respectively²¹) and would be considered to exhibit stronger H bonding, our former studies⁷ show that complexation of CH₂(CN)₂ with 18-crown-6 is much stronger. We therefore decided to use CH₂(CN)₂ as a probe in our thermodynamic studies. When a crown ether is added to a solution of malononitrile in CDCl₃ or C₆D₆, a downfield chemical shift of the malononitrile protons is observed. This observation was used to determine association constants of malononitrile with a number of crown ethers at four temperatures in both solvents. In a typical experiment, 10 samples were prepared in which the crown ether concentration was kept constant (0.03 M) and the malononitrile concentration was varied from 0.01 to 0.1 M. The chemical shift of CH₂(CN)₂ in the samples was measured at four different temperatures. The chemical shift of the protons of CH₂(CN)₂ (taking into account only 1:1 complexation) is calculated to be

$$\delta_{\text{calcd}} = X_S \delta_S + X_{\text{CES}} \delta_{\text{CES}} \quad (1)$$

in which δ_S is the chemical shift of free CH₂(CN)₂ and δ_{CES} is the chemical shift of this molecule in the complex. X_S and X_{CES} are the mole fractions of free and complexed CH₂(CN)₂, respectively. For a series of samples in an iterative procedure a minimum is found for the function F given in eq 2, and X_S and X_{CES} can be calculated.⁷

$$F = \sum_i (\delta_{\text{obsd},i} - X_{S,i} \delta_S - X_{\text{CES},i} \delta_{\text{CES}})^2 \quad (2)$$

When both 1:1 and 1:2 complexes can be formed, eq 2 can easily be modified, assuming that the chemical shift of CH₂(CN)₂ in the 1:1 and in the 1:2 complexes is the same.⁷ Taking into account both 1:1 and 1:2 complexation we obtained K₁₁ values at four temperatures. From a plot of ln(K₁₁) vs. T⁻¹ the thermodynamic constants ΔH° and ΔS° for 1:1 complexation were calculated (Table I). In general 1:2 complexation was negligible, except in the case of 2,6-pyrido-18-crown-6, benzo-18-crown-6, and 18-crown-6 with K₁₂ = 21, 6, and 11 L/mol, respectively.

The results summarized in Table I show that the thermodynamic constants depend on several factors, viz., solvent, ring size, the nature of the donor atoms, and the presence of intraannular substituents.

Solvent. The influence of the solvent on the complexation of CH₂(CN)₂ was studied by comparing the complexation in CDCl₃ and in C₆D₆. The smaller enthalpy and entropy changes upon complexation in CDCl₃ reflect the greater polarity of CDCl₃, which means a stronger solvation of both CH₂(CN)₂ and the crown ether. These solvent interactions must be broken before complexation can occur, resulting in a less favorable enthalpy change. Desolvation of both the crown ether and CH₂(CN)₂ prior to com-

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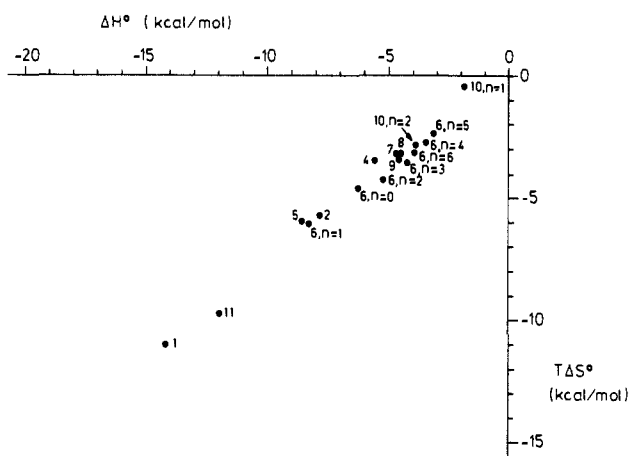
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Table I. Thermodynamic Constants for 1:1 Complexation of Crown Ethers with Malononitrile

crown ether	298 K, C ₆ D ₆				298 K, CDCl ₃			
	K ₁₁ , ^a L/mol	ΔH°, kcal/mol	TΔS°, kcal/mol	ΔG°, kcal/mol	K ₁₁ , ^a L/mol	ΔH°, kcal/mol	TΔS°, kcal/mol	ΔG°, kcal/mol
18-crown-6	159	-14.2	-11.0	-3.2	31	-5.3	-3.3	-2.0
benzo-18-crown-6	30	-8.0	-5.9	-2.0	50	-5.4	-3.1	-2.3
dibenzo-18-crown-6				<i>b</i>	113	-4.7	-1.9	-2.8
mono-aza-18-crown-6	34	-5.7	-3.6	-2.1				<i>c</i>
dicyclohexyl-18-crown-6	63	-8.6	-6.1	-2.5	43	-5.6	-3.3	-2.2
2,6-pyrido-15-crown-5	16	-6.3	-4.7	-1.6	11	-1.6	-0.2	-1.5
2,6-pyrido-18-crown-6	43	-8.3	-6.1	-2.2	31	-2.4	-0.3	-2.1
2,6-pyrido-21-crown-7	5	-5.2	-4.2	-1.0	7	-3.4	-2.2	-1.1
2,6-pyrido-24-crown-8	3	-4.3	-3.6	-0.7	2	-1.9	-1.4	-0.5
2,6-pyrido-27-crown-9	3	-3.5	-2.8	-0.7				<i>c</i>
2,6-pyrido-30-crown-10	3	-3.2	-2.5	-0.7				<i>c</i>
2,6-pyrido-33-crown-11	4	-4.0	-3.2	-0.8				<i>c</i>
1,3-xylyl-18-crown-5	10	-4.7	-3.3	-1.4	11	-5.2	-3.8	-1.4
2-allyloxy-5-chloro-1,3-xylyl-18-crown-5	11	-4.6	-3.2	-1.4				<i>c</i>
2-hydroxy-5-chloro-1,3-xylyl-18-crown-5	5	-4.4	-3.4	-1.0	5	-4.5	-3.6	-1.0
2-carboxyl-1,3-xylyl-18-crown-5	11	-1.9	-0.5	-1.4				<i>d</i>
2-carboxyl-1,3-xylyl-21-crown-6	5	-3.9	-2.9	-1.0				<i>d</i>
2-carbomethoxy-1,3-xylyl-18-crown-5	39	-12.0	-9.9	-2.2				<i>d</i>

^aAccuracy 10%. ^bInsoluble in C₆D₆. ^cChemical shift difference too small to obtain reliable results. ^dNot measured.

**Figure 1.** ΔH° vs. TΔS° for 1:1 complexation of crown ethers with malononitrile in C₆D₆.

plexation will result in a positive entropy change. Solvent interactions with CDCl₃ are especially pronounced in the case of the 2,6-pyrido crown ethers, where a D bond between CDCl₃ and the pyrido unit can be formed,^{22a,b} thus increasing the crown ether-solvent interactions. On the other hand, it is possible that because of this crown ether-solvent interaction the macrocycle adopts a suitable conformation for complexation of CH₂(CN)₂, which will correspond to a smaller negative value of ΔS°.

Compared with the complexation in C₆D₆, benzo-18-crown-6 and dibenzo-18-crown-6 are relatively efficient complexing agents for CH₂(CN)₂ in CDCl₃. It might be possible that interaction of the Cl atoms of CDCl₃ with the π-electrons of the benzo units^{23a,b} provides a preorganization of the macrocycle, and upon complexation, desolvation provides a favorable entropy change.

Entropy vs. Enthalpy. When all crown ethers are compared, both in CDCl₃ and C₆D₆ as a solvent, the large individual differences in ΔH° and TΔS° along the series are apparent. From a plot of ΔH° vs. TΔS° (Figure 1) it is obvious that there is an overall linear relationship between enthalpy and entropy of complexation. Such a compensating effect of TΔS° on ΔH° has recently also been observed for the complexation of cations by a large number of different macrocyclic polyethers.²⁴ It can, at

Table II. Fractional Atomic Coordinates for 2,6-Pyrido-18-crown-6-CH₂(CN)₂ (1:2) (NO = 0.5 N + 0.5 O; see Experimental Section)

atom	x	y	z
NO1	0.2795 (2)	0.3813 (2)	0.4642 (1)
C2	0.3839 (3)	0.3256 (4)	0.5332 (2)
C3	0.4047 (3)	0.4326 (4)	0.6070 (2)
O4	0.2645 (2)	0.4382 (2)	0.6349 (1)
C5	0.2719 (4)	0.5449 (4)	0.7033 (2)
C6	0.1191 (4)	0.5517 (4)	0.7262 (2)
O7	0.0058 (2)	0.6129 (3)	0.6572 (1)
C8	-0.1376 (4)	0.6459 (4)	0.6787 (2)
C9	-0.2479 (3)	0.7148 (4)	0.6054 (2)
C10	-0.3252 (7)	0.8307 (7)	0.6120 (4)
C11	-0.4358 (8)	0.8819 (8)	0.5431 (6)
C12	-0.4611 (7)	0.7913 (8)	0.4708 (5)
C13	-0.4248 (3)	0.7838 (3)	0.9707 (2)
C14	-0.3727 (4)	0.6595 (4)	1.0323 (2)
N15	-0.3292 (4)	0.5602 (4)	1.0785 (2)
C16	-0.3870 (3)	0.7405 (4)	0.8915 (2)
N17	-0.3554 (4)	0.7062 (4)	0.8307 (2)
H13A	-0.524 (3)	0.795 (3)	0.964 (2)
H13B	-0.374 (3)	0.883 (3)	0.993 (2)

least in part, be attributed to the rigidity of a complex. If the host-guest binding is strong, the flexibility of the macrocyclic ring in the complex will be limited, and consequently the loss of entropy upon complexation will be large. For complexation of cations the parameters *A* and *B* of the linear relation $T\Delta S^\circ = A(\Delta H^\circ) + B$ have been determined, $A = 0.76$ and $B = 2.4$ kcal/mol.²⁴ For complexation of CH₂(CN)₂ by the macrocycles 1-11 in C₆D₆ and CDCl₃ we find $A = 0.84$ and $B = 0.7$ kcal/mol ($n = 27$, $r = 0.95$). The parameter *B* represents the intrinsic entropy gain upon complexation and reflects mainly desolvation. Because neutral molecules are less strongly solvated than cations, *B* will be smaller for the complexation of CH₂(CN)₂. The difference in the values of *A* for the complexation of neutral molecules ($A = 0.84$) and cations ($A = 0.76$) may be due to the contribution of hydrogen bonds in the complexation of neutral molecules. This type of interaction requires a more defined relative orientation of the binding sites compared with the ion-dipole interactions in cation complexes.

Ring Size. The effect of the ring size on the complexation of CH₂(CN)₂ is obvious from the thermodynamic parameters for the series of 2,6-pyrido crown ethers with ring sizes of 15 to 33 ring atoms. The most stable complex is formed with 2,6-pyrido-18-crown-6, and in this case the 1:2 (host-guest) complex

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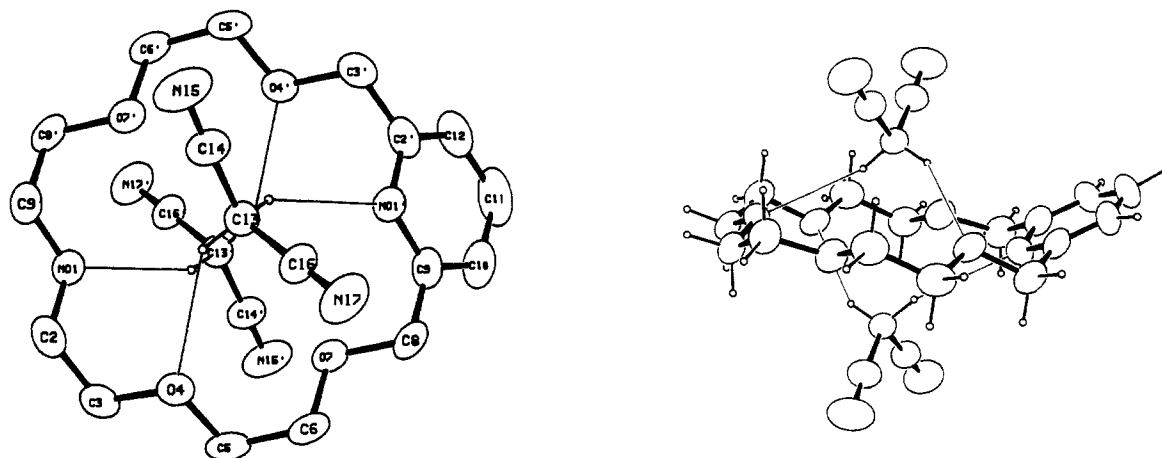


Figure 2. ORTEP³⁸ views of the crystal structure of 2,6-pyrido-18-crown-6-malononitrile (1:2). In the left view, the atom numbering is shown. The crown hydrogens are omitted for clarity. Hydrogen bonds are indicated by thin lines.

Table III. Selected Bond Distances (Å) and Angles (deg)

NO1	C2	1.367 (3)	C9	C10	1.203 (7)		
NO1	C9'	1.370 (4)	C10	C11	1.381 (10)		
C2	C3	1.481 (4)	C11	C12	1.380 (11)		
C2	C12'	1.200 (7)	C13	C14	1.449 (4)		
C3	O4	1.408 (4)	C13	C16	1.453 (4)		
O4	C5	1.421 (4)	C13	H13A	0.86 (2)		
C5	C6	1.475 (5)	C13	H13B	0.97 (3)		
C6	O7	1.422 (3)	C14	N15	1.130 (4)		
O7	C8	1.411 (4)	C16	N17	1.127 (5)		
C8	C9	1.479 (4)					
C9'	NO1	C2	117.3 (2)	C8	C9	NO1'	114.8 (3)
NO1	C2	C3	113.8 (3)	C10	C9	NO1'	122.2 (4)
NO1	C2	C12'	121.1 (4)	C8	C9	C10	121.6 (4)
C3	C2	C12'	124.7 (4)	C9	C10	C11	119.1 (6)
C2	C3	O4	109.0 (3)	C10	C11	C12	118.5 (6)
C3	O4	C5	112.7 (3)	C11	C12	C2'	120.6 (6)
O4	C5	C6	109.9 (2)	C14	C13	C16	109.9 (3)
C5	C6	O7	109.3 (2)	C13	C14	N15	177.5 (4)
C6	O7	C8	112.4 (2)	C13	C16	N17	178.9 (3)
O7	C8	C9	109.6 (3)				

could be isolated as a crystalline compound (*vide infra*). For either smaller or larger ring sizes, the enthalpy change upon complexation becomes less favorable, because the orientation of binding sites will be less favorable, giving a less ordered complex.²⁵

In this series, entropy changes also exhibit a predictable tendency with a most negative $T\Delta S^\circ$ for the 18-membered ligand. As the ring becomes larger or smaller the organization within the complex will become less rigid resulting in a $T\Delta S^\circ$ value which is less negative.

The crystal structure of 2,6-pyrido-18-crown-6- $\text{CH}_2(\text{CN})_2$ (1:2) was determined by X-ray diffraction. The atomic positional parameters are given in Table II. The corresponding atom numbering is shown in Figure 2 (primed atoms are related to unprimed atoms by a center of symmetry). Bond distances and angles, given in Table III, show some unusual values (see Experimental Section for details). The torsion angles given in Table IV indicate that the macrocycle has approximate D_{3d} symmetry. The structure of 2,6-pyrido-18-crown-6- $\text{CH}_2(\text{CN})_2$ (1:2) compares well with the 18-crown-6- $\text{CH}_2(\text{CN})_2$ (1:2) complex determined by Knöchel et al.⁵ The pyrido moiety does not seem to influence the mode of complexation much (this is also reflected by the positional disorder of the pyrido ring). The difference between the two structures is the H bonding between host and guest. The 2,6-pyrido-18-crown-6- $\text{CH}_2(\text{CN})_2$ (1:2) complex has a 1,3-H-bonding scheme (counting heteroatoms only): C13...NO1 3.342 (3) Å, 146 (3)° and C13...O4' 3.357 (3) Å, 141 (2)°, with the former of the two H bonds being somewhat stronger (H13B...NO1

Table IV. Torsion Angles (deg) in the Macrocycle

C9'	NO1	C2	C3	-176.8
NO1	C2	C3	O4	66.0
C2	C3	O4	C5	-177.1
C3	O4	C5	C6	176.8
O4	C5	C6	O7	-62.5
C5	C6	O7	C8	-170.9
C6	O7	C8	C9	177.9
O7	C8	C9	NO1'	59.4
C8	C9	NO1'	C2'	178.3

2.50 (3) Å vs. H13A...O4' 2.65 (2) Å). The 18-crown-6- $\text{CH}_2(\text{CN})_2$ (1:2) complex exhibits 1,4-hydrogen bonding with one strong and one weak H bond (distance between acceptor and H atom 2.24 (3) and 2.69 (4) Å, respectively).

Donor Atoms. The influence of donor atoms other than the ether oxygens can be studied in the series 2,6-pyrido-18-crown-6, monoaza-18-crown-6, 1,3-xylyl-18-crown-5, benzo- and dibenzo-18-crown-6, and 18-crown-6 in C_6D_6 .

The less negative enthalpy of complexation of $\text{CH}_2(\text{CN})_2$ with 1,3-xylyl-18-crown-5 compared with 18-crown-6 is due to the reduction of the number of oxygen atoms in the macrocyclic ligand. A similar difference in the free energy of complexation has been reported for the corresponding *tert*-butylammonium hexafluorophosphate complexes of these crown ethers.^{1a}

The presence of a nitrogen atom in the macrocyclic ligand reduces the enthalpy of complexation from $-14.2 \text{ kcal mol}^{-1}$ (18-crown-6) to -8.3 and $-5.7 \text{ kcal mol}^{-1}$ for the complexation by 2,6-pyrido-18-crown-6 and monoaza-18-crown-6, respectively. This seems surprising since in the solid state the pyridyl nitrogen is preferentially used as a binding site (Figure 2). However, the observed lower negative enthalpy data may be attributed to stronger intraannular interactions in the uncomplexed 2,6-pyrido-18-crown-6²⁶ ($\text{CH}\cdots\text{N}$) and monoaza-18-crown-6²⁷ ($\text{N}\cdots\text{H}\cdots\text{O}$).

Complexation of benzo-18-crown-6 with $\text{CH}_2(\text{CN})_2$ is weaker owing to electron-withdrawing properties of the benzo unit, which render the oxygen atoms next to the benzene ring weaker hydrogen bond acceptors.

Both diaza-18-crown-6 and dibenzo-18-crown-6 are nearly insoluble in C_6D_6 . Thermodynamic parameters could not be obtained.

Reorganization. Intraannular substituents can have a strong influence on complexation. Weak binding results from the introduction of a carboxylic group as in 2-carboxyl-1,3-xylyl-18-crown-5. From X-ray crystal structures²⁸ and pK_a measurements²⁹

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of this 18-membered macrocycle, we know that a strong intramolecular hydrogen bond is formed between the carboxylic group and an oxygen atom in the crown ether ring. Before complexation can take place this hydrogen bond must be broken.

In 2-carboxyl-1,3-xylyl-21-crown-6, the intraannular hydrogen bond is much weaker,²⁹ and consequently a more negative ΔH° of complexation is observed even though the ring lacks the optimum size of 18 atoms.

When compared with the acid, the methyl ester of 2-carboxyl-1,3-xylyl-18-crown-5 clearly shows the effect of an intramolecular H bond. The binding enthalpy of $\text{CH}_2(\text{CN})_2$ with the ester is much stronger than with the acid because no H bonds to the crown ether have to be broken. The additional binding site of the ester group can be used to form a H bond with the guest.

In the 2-hydroxy-5-chloro-1,3-xylyl-18-crown-5 there is also a hydrogen bond between the hydroxyl group and one of the benzylic oxygen atoms of the crown ether ring.³⁰ This interaction is probably not very strong as can be seen from the small influence of ring size on the acidity of 2-hydroxy-1,3-xylyl crown ethers.³⁰ Moreover, a phenolic hydroxyl group is not a very good H bond acceptor. Therefore, binding of $\text{CH}_2(\text{CN})_2$ to 2-hydroxy-5-chloro-1,3-xylyl-18-crown-5 resembles the complexation to 1,3-xylyl-18-crown-5. In 2-allyloxy-5-chloro-1,3-xylyl-18-crown-5, the situation is not much different. Although this macrocycle has one additional oxygen atom which might serve as an additional binding site,³¹ the allyl group uses much space and causes steric interaction with the guest molecule. Therefore $\text{CH}_2(\text{CN})_2$ is believed to bind to the crown ether only from the least hindered side, possibly using the allyl oxygen.

Conclusions

Complexation of neutral guest molecules such as malononitrile with macrocyclic polyethers provides the first method to predict intramolecular interactions within free macrocycles in solution and gives qualitative information about solvation of the free macrocycle. Both intramolecular hydrogen bonding and specific interactions of the crown ether with the solvent will be reflected in the thermodynamic parameters of the complex formed.

In general complexation is enthalpy stabilized and entropy destabilized. Therefore only part of the enthalpy gain will be reflected in the association constant. From the entropy loss the extent of reorganization of the host upon complexation can be inferred.

Crown ethers which form strong intramolecular hydrogen bonds are more stable than those which do not have these interactions. Therefore the complexation with malononitrile is less favorable for the former compounds.

When additional binding sites (e.g., C=O) for complexation without increase in steric interaction are available within the crown ether, hydrogen bonds will be formed to these functionalities to stabilize the complex.

18-Membered rings form the most stable complexes with malononitrile. Complexes of larger or smaller macrocycles are less stable.

In most cases complexation in C_6D_6 is favored over CDCl_3 , owing to specific interactions of crown ethers with CDCl_3 , which stabilize the free crown ether more than its complex.

Experimental Section

Materials. 18-Crown-6 was purified by complexation/decomplexation with nitromethane.⁷ Dibenzo-18-crown-6 and dicyclohexyl-18-crown-6 were purchased (Aldrich, Merck) and were used as received.

Benzo-18-crown-6,³² monoaza-18-crown-6,³³ 2,6-pyridocrown ethers,³⁴ 2-hydroxy-5-chloro-1,3-xylyl crown ethers,³⁵ 2-allyloxy-5-chloro-1,3-xylyl crown ethers,³⁵ and 2-carboxyl-1,3-xylyl crown ethers²⁸ were prepared by known methods.

$\text{CH}_2(\text{CN})_2$ was recrystallized from CHCl_3 before use. CDCl_3 was Merck 99 atom % and C_6D_6 was Janssen Chimica 99 atom %.

Preparation of Samples. Separate solutions of crown ether (0.1 M) and of $\text{CH}_2(\text{CN})_2$ (0.1 M) in CDCl_3 or C_6D_6 , containing 1% Me_4Si as an internal standard, were prepared in 5-mL volumetric flasks. Samples, containing 0.25 mL of crown ether solution and 0.05–0.50 mL of $\text{CH}_2(\text{CN})_2$ solution were prepared in 5-mm NMR tubes. By addition of CDCl_3 or C_6D_6 the total volume of all samples was adjusted to 0.75 mL. The tubes were closed, and NMR spectra were taken within 24 h of sample preparation.

Determination of Association Constants. All ^1H NMR spectra were recorded on a Bruker WM80 (80 MHz) apparatus equipped with a B-VT-1000 temperature accessor. Temperature was checked 3 times during a series of 8–10 samples and was constant within 0.3 K for a series. Temperature measurements were performed by inserting a copper-constantan thermocouple in an NMR tube with the appropriate solvent. ^1H NMR spectra were recorded at 285–315 K for samples in C_6D_6 and at 230–280 K for samples in CDCl_3 .

Calculations were carried out as reported earlier,⁷ taking into account both 1:1 and 1:2 complexation.

X-ray Diffraction. The crystal structure of 2,6-pyrido-18-crown-6- $\text{CH}_2(\text{CN})_2$ (1:2) was determined. Intensities were measured at room temperature on a CAD4 diffractometer (Mo $\text{K}\alpha$ radiation, graphite monochromator). Cell dimensions were obtained by least squares from 25 centered reflections ($3^\circ < \theta < 9^\circ$). Crystal data: monoclinic, $P2_1/n$, $a = 8.798$ (5) Å, $b = 8.363$ (3) Å, $c = 16.346$ (8) Å, $\beta = 102.94$ (5)°, $V = 1172$ (2) Å³, $Z = 2$, $f_w = 429.48$, $D_c = 1.22$ g cm⁻³, $F(000) = 456$, $\mu = 0.08$ mm⁻¹.

A total of 2051 reflections were measured in the $\omega/2\theta$ scan mode (scan width (1.0 + 0.35 tg θ)°; variable scan speed, 2–7 deg min⁻¹). The intensities were corrected for the decay of the 3 standard reflections (1.1% h⁻¹ during 30 h of data collection) and for Lorentz polarization.

The structure was solved by direct methods³⁶ and refined by full-matrix least squares. All calculations were done using SDP.³⁷ Reflections having $F_o^2 > 3\sigma(F_o^2)$ were included in the refinement (total number 1164). The weight for each reflection was calculated as $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma(F_o^2) = (\sigma(I)^2 + (0.06F_o^2)^2)^{1/2}$; $\sigma(I)$ based on counting statistics. All hydrogens were located on difference Fourier maps in the course of refinement. The $\text{CH}_2(\text{CN})_2$ hydrogens were included in the refinement, and the crown ether hydrogens were put in calculated positions (C–H distance 0.96 Å) and treated as riding on their parent C atoms, with fixed thermal parameters ($B_{\text{iso}}(\text{H}) = 1.1B_{\text{eq}}(\text{C})$). The number of parameters refined was 163: scale factor, isotropic extinction parameter, positional and anisotropic thermal parameters for the non-H atoms, positional and isotropic thermal parameters for the $\text{CH}_2(\text{CN})_2$ H atoms. Refinement converged at $R = 4.6\%$, $R_w = 7.0\%$. The largest shift/error ratio in the last cycle was 0.03. The highest peaks on the final Fourier difference map were 0.2 eÅ⁻³, near the $\text{CH}_2(\text{CN})_2$ nitrogen atoms.

The structure exhibits disorder: the asymmetric unit contains one $\text{CH}_2(\text{CN})_2$ and half a crown ether, the other half being generated by a center of symmetry. Consequently overlap of a C–O–C unit and the pyrido moiety, both having occupancy 0.5, is found. Separate refinement of this crown C–O–C unit and the pyrido C–N–C unit was not successful because of large correlations between parameters. Therefore they were merged into one C–NO–C unit (NO = 0.5N + 0.5O). Refinement of the structure with inclusion of this unit was successful, but it resulted in some unusual bond lengths and angles in the disordered part of the macrocycle.

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Registry No. 1, 17455-13-9; 2, 14098-24-9; 3, 14187-32-7; 4, 33941-15-0; 5, 16069-36-6; 6 ($n = 0$), 77877-86-2; 6 ($n = 1$), 53914-89-9; 6 ($n = 2$), 86309-73-1; 6 ($n = 3$), 86309-74-2; 6 ($n = 4$), 95216-11-8; 6 ($n = 5$), 95216-12-9; 6 ($n = 6$), 95216-13-0; 7, 53914-83-3; 8, 81336-37-0; 9, 81336-42-7; 10 ($n = 1$), 55440-83-0; 10 ($n = 2$), 55440-84-1; 11, 55440-80-7; 2,6-pyrido-18-crown-6(CN)₂CH₂, 103201-04-3.

Supplementary Material Available: Tables of atomic positional and thermal parameters and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

Excited-State Rearrangements of 1,3- and 1,5-Dienes in a Radio Frequency Plasma

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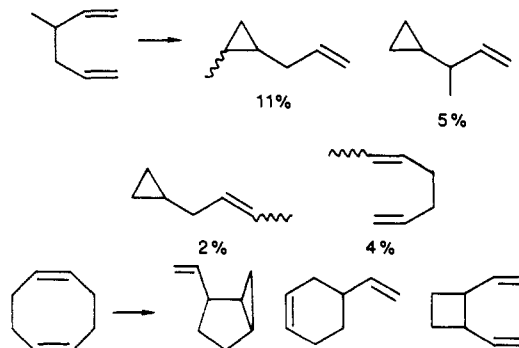
Abstract: 1,3- and 1,5-dienes were reacted by distilling them through an inductively coupled radio frequency plasma. The major liquid products from 1,5-dienes were allylcyclopropanes, and it is proposed that they were formed by a sigmatropic [1,4] vinyl shift. This mechanism accounts for the specific isomers formed from various methylated 1,5-hexadienes. Other isomerizations were observed. The *cis* and *trans* isomers of 1,3-hexadiene and 2,4-hexadiene are interconverted under these conditions, and 1,3-cyclooctadiene produced bicyclo[4.2.0]oct-2-ene. Kinetic data are reported.

The gaseous plasma generated by a radio frequency (13.56 MHz) discharge provides an unusual reaction medium and some unusual reactions.¹⁻³ These reactions are initiated by electron impact events. In the plasma, free electrons are accelerated by the electrical field and collide with neutral molecules. These collisions excite or ionize the molecules, and this naturally leads to chemical reactions. The initial reactions after excitation are often rearrangements or fragmentation and some analogies with photochemistry have been drawn.^{1,4-6} In the present study we set out to study rearrangements of hydrocarbon dienes and to compare the reaction products with those from UV photolysis. Previous studies have shown that the plasma products, formed from *cis*-2-butene (*trans*-2-butene and 1-butene), are also obtained by photolysis of *cis*-2-butene at 180 nm in the gas phase.⁵ Recently, we have reported the di- π -methane rearrangements of 1,4-pentadiene to vinylcyclopropane and allylbenzene to cyclopropylbenzene.⁶

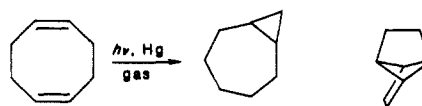


The present investigation focused on 1,3- and 1,5-dienes. Photochemical isomerizations of 1,3-butadienes to cyclobutenes are well-known for both acyclic⁷ and cyclic reactants like 1,3-cyclooctadiene.⁸ The rearrangement of 1,5-dienes has received a lot of attention.^{9,10} Of particular interest is conversion of

1,5-dienes to allylcyclopropanes in solution, which has been reported by Kropp and Manning.¹⁰ For example, 3-methyl-1,5-hexadiene and 1,5-cyclooctadiene gave the following results.



It was proposed¹⁰ that the higher yield allylcyclopropane products from acyclic 1,5-dienes came from a [1,2] sigmatropic shift mechanism. In the case of 1,5-cyclooctadiene, a [2,3] sigmatropic shift was proposed to explain the allylcyclopropane product.¹⁰ Interestingly, in the gas phase a mercury-sensitized photolysis gave different products from 1,5-cyclooctadiene.^{9f,s}



Experimental Section

Analysis. Quantitative analysis was carried out with use of a temperature programmed gas chromatograph (GC) equipped with a flame ionization detector. Isomer yields were computed relative to the peak area for reactant, which was calibrated. A 3 m length, 1/8 in o.d., 20% silicone OV-17 on acid washed and silylated Chromosorb W (80/100 mesh) was used. Gas chromatography-mass spectrometry (a Finnigan 4000 GC-MS interfaced to a VG M82L Multispace Data System) was performed for identification of the molecular weight of the major plasma products.

For the structural analysis of major plasma products, a GC equipped with thermal conductivity detector and preparative columns (3 and 6 m

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