

Quantitative Structure-Stability Relationship for Potassium Ion Complexation by Crown Ethers. A Molecular Mechanics and *ab Initio* Study

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Abstract: Molecular mechanics calculations with the MM2 program were used to examine the structures and strain energies 11 hexadentate crown ether ligands and their potassium complexes. With the exception of K-O stretching parameters, all force field parameters for interactions involving the potassium ion were obtained by fitting to *ab initio* potential energy surfaces for selected distortions in K-O(Me)₂ and K-O(Me)(Et). The K-O stretching parameters were optimized relative to crystallographic data. Comparison of the molecular mechanics results to experimental log *K* values that were available for all 11 crown ethers revealed the complex stability to be strongly correlated with the difference in strain energy between the uncomplexed ligand and its potassium complex. The results establish that both the K-O length preference and bonding directionality at the ether oxygen donor atom are important factors in the determination of complex stability. It is concluded that the failure to consider the orientation of the ether C-O-C moiety, relative to the metal ion, is a serious flaw in the size-match selectivity theory.

I. Introduction

The quest for ligands that exhibit selectivity for specific metal ions has been an active and growing field of research.¹ Much effort has been focused on the development of macrocyclic ethers that are able to selectively complex the alkali and alkaline earth cations.²⁻⁵ Many factors, including cavity size, shape and topology, substituent effects, and conformational flexibility have been invoked to explain trends in complex stability.²⁻¹¹ In addition, molecular mechanics (MM) and molecular dynamics calculations have been used to compute interaction energies for series of metal ions with a single crown ether in an effort to rationalize observed selectivity patterns.¹²⁻¹⁷ Yet, despite these extensive investigations, quantitative relationships for predicting how the three-

dimensional structure of a crown ether will affect the stability of its complexes have not been reported.

Quantitative structure-stability relationships have, however, been developed successfully for other types of coordination compounds including nickel amine complexes,¹⁸ cobalt amine complexes,¹⁹ and copper thioether complexes.²⁰ These relationships are based on MM models that have been used both to predict the structures of ligands and their metal complexes and to evaluate the magnitude of the steric strain within them. For series of ligands that differ in molecular structure but have the same number and types of donor atoms, these studies have demonstrated that calculated strain energies provide a basis for understanding the effect of the spatial orientation of donor atoms on complex stability. It has been proposed that the increase in strain energy that is associated with metal ion complexation can be used to evaluate how well a ligand will coordinate to a metal ion and can therefore serve as a basis for the design of ligands with increased binding strength and increased metal ion selectivity.¹

In the present study, we have investigated the utility of the strain energy approach in rationalizing the effect of crown ether structure on complex stability. The 11 crown ethers shown in Chart I, and their potassium complexes were examined with use of MM calculations. These ligands were chosen for two reasons. First, each ligand possesses a set of six aliphatic ether donor atoms. Therefore, differences in complex stability would be expected to arise from differences in the spatial orientation of the donor atoms rather than from differences in donor atom basicity. Second, experimental stability constants for potassium complexes have been reported for each of the ligands in the same solvent and at the same temperature (methanol solvent, 25 °C), providing a consistent set of thermodynamic data for evaluation of the model. In what follows, we present the development and detailed

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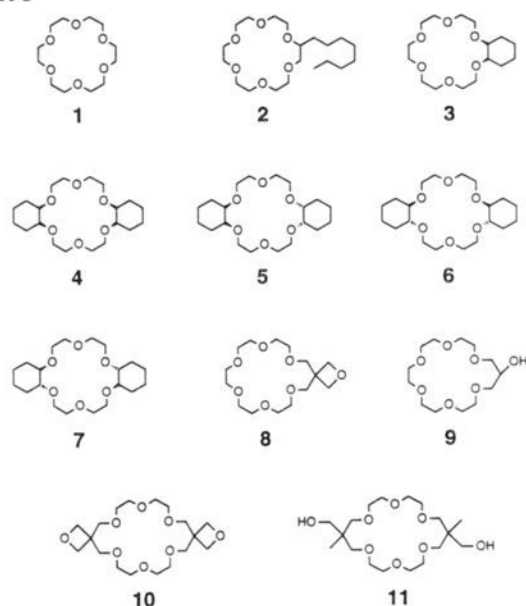
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Chart I



description of the MM model, the application of the model, and results that demonstrate that the stability of the potassium complexes is related to the increase in strain energy associated with the coordination of the metal ion.

II. Development of the Molecular Model

1. Hardware and Software. The MM calculations were carried out with use of the MM2 program,²¹ available through the Quantum Chemistry Program Exchange (QCPE) at Indiana University. After minor alteration of the TIME and DATE subroutines, the VAX version of the code received from QCPE was compiled and linked with use of MacFortran/020 Fortran 77 obtained from Absoft Corporation for a Macintosh IICI personal computer. *Ab initio* quantum calculations were performed with the Gaussian 90 program²² on a Sun SparcII workstation. The molecular graphics program Chem3D Plus²³ was used to build initial sets of molecular coordinates for Gaussian 90 and MM2 and to plot the energy-minimized molecular coordinates obtained from such calculations.

2. Potential Energy Functions. The MM2 program contains a default set of potential functions designed for use with organic molecules. The default set of potential functions was modified for this study. First, bond-stretching terms were switched to a harmonic rather than the default cubic equation because the default cubic equation goes to minus infinity when the atoms separate beyond a certain limit. This causes a problem with K-O bonds because they exhibit a much greater variability in bond length than in normally encountered in organic structures and frequently exceed the useful range of the cubic stretching equation. Second, stretch-bend terms were excluded from the calculations because when stretch-bend terms are present, unrealistically large stretch-bend energies develop due to the coupling of the K-O bond lengths and K-O-C bond angles, both of which vary over a wide range of values.

It was found that these two modifications to the default set of MM2 potential functions yielded a potential energy equation that was suitable for modeling the potassium complexes and, at the same time, did not greatly impact the performance of the force field on metal-free aliphatic ethers. These modifications are easily implemented within the MM2 program through a choice of options in the input files (supplementary material).

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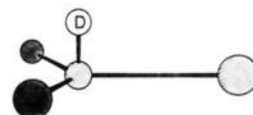


Figure 1. Attachment of a dummy atom (D) to oxygen. In practice, the dummy atom is always attached to oxygen such that the K-O-D and K-O-C angles are $\leq 90^\circ$.

With the two modifications indicated above, the potential energy equation used in this work was restricted to the sum of five terms as shown in eqs 1-9:

$$U = \sum U_r + \sum U_\theta + \sum U_\phi + \sum U_{vdw} + \sum U_{dipole} \quad (1)$$

$$U_r = 1/2 k_r (r - r_0)^2 \quad (2)$$

$$U_\theta = 1/2 k_\theta (\theta - \theta_0)^2 [1 + (7 \times 10^{-8}) (\theta - \theta_0)^4] \quad (3)$$

$$U_\phi = V_1/2(1 + \cos \phi) + V_2/2(1 - \cos 2\theta) + V_3/2(1 + \cos 3\phi) \quad (4)$$

$$U_{vdw} = A \exp(-Bd) - C/d^6 \quad (5)$$

$$A = 2.9 \times 10^5 \epsilon^* \quad (6)$$

$$B = 12.5/d^* \quad (7)$$

$$C = 2.25 \epsilon^* (d^*)^6 \quad (8)$$

$$U_{dipole} = [\mu_a \mu_b / (1.5r^3)] (\cos X - 3 \cos \alpha_a \cos \alpha_b) \quad (9)$$

U_r gives the stretching energy arising from bond length deformations. U_θ gives the bending energy arising from bond angle deformations. U_ϕ gives the torsional energy arising from rotation about bonds. U_{vdw} gives the nonbonded interaction energy arising from van der Waals interactions between all atom pairs that are neither attached to one another nor to a common atom. For a given atom pair, atom_i and atom_j, the nonbonded parameters A , B , and C are generated from values of ϵ^* and d^* , which in turn are obtained from the expressions $\epsilon^* = (\epsilon_i \epsilon_j)^{1/2}$ and $d^* = d_i + d_j$. U_{dipole} gives the energy arising from the interactions between all pairs of dipoles that do not share a common atom.

For the computations on the potassium complexes, interactions at the metal ion were handled with the approach deployed by Hambley et al. in their studies of cobalt hexamines.²⁴ This approach entails the replacement of all O-K-O bond angle terms with 1,3 van der Waals interactions between the ligated oxygens, the neglect of torsional interactions about K-O bonds, and the neglect of all nonbonded interactions (both van der Waals and electrostatic) that involve the potassium ion. With one exception, other interactions such as K-O stretches, K-O-C bends, K-O-C-H torsions, and K-O-C-C torsions are treated in the same way as the corresponding organic interactions.

The exception concerns the assignment of an out-of-plane bending interaction at oxygen. The standard MM2 out-of-plane bending function, intended for use with sp^2 carbon and nitrogen atoms, proved to be too stiff for this application. We therefore adopted the following alternative. A dummy atom (D) is attached to each coordinated oxygen atom such that the K-O-D and C-O-D angles are $\leq 90^\circ$ (see Figure 1). The dummy atom is defined such that the only contribution to the strain energy total comes from K-O-D and K-O-C bending interactions. An energetic preference for the potassium ion to lie in the plane defined by the C-O-C moiety is achieved by assigning a strain-free value of 90° to the K-O-D and C-O-D angles.

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As with the modifications to the default potential functions, all options described above for the assignment of potential functions for interactions that involve potassium were specified in a standard MM2 input file according to methods reported elsewhere.²⁵ An example MM2 input file is available as supplementary material.

3. Metal-Independent Parameters. We adopted the assumption that force field parameters used for modeling organic compounds are transferable to the organic portion of a metal complex. Thus, the parameters that are used for metal-free crown ethers are the same parameters used for the crown ether portion of their potassium complexes. These metal-independent parameters were derived by updating the standard MM2 parameter set to include several improvements reported for aliphatic ethers in the MM3 force field.²⁶ First, the ideal lengths of C–C bonds were adjusted to account for the shortening that occurs when an electronegative atom is attached to the bond. This was accomplished by redefining atom type 27 to be an “ether carbon” to distinguish it from an alkane sp³ carbon, atom type 1. Separate stretching parameters were assigned for bonds of the type 1–1, 1–27, and 27–27. Second, lone pairs were removed from ether oxygens, atom type 6. With the removal of lone pairs from the force field, it was necessary to alter the van der Waals parameters for oxygen, the dipole moment for bond type 6–27, and the torsional parameters for rotations involving atom type 6. The resulting parameter set is given in Table I.

The accuracy of this updated parameter set was confirmed by examining the structure and, where data were available, the conformational equilibria of simple ethers including dimethyl ether, ethyl methyl ether, diethyl ether, methyl isopropyl ether, and diisopropyl ether. Our modifications to the MM2 force field yielded results comparable to those reported for the MM3 force field.²⁶ The parameter set was further validated by examining metal-free crown ethers for which X-ray data are available, i.e., 12-crown-4,²⁷ 1,1'-bis(13-crown-4),²⁸ 3,3'-hexamethylenebis(13-crown-4),²⁹ *cis-syn-cis*-dicyclohexyl-14-crown-4,³⁰ *cis-anti-cis*-dicyclohexyl-14-crown-4,³⁰ and 18-crown-6.³¹ Structural features of these crown ethers were adequately reproduced (bond length rmsd = ±0.005 Å, bond angle rmsd = ±1.0°, and torsion angle rmsd = ±2.5°).

4. Metal-Dependent Parameters. Having established a working force field for aliphatic ethers, the next step in model construction was to develop the parameters for the interactions that involve potassium. These include the K–O stretch, the K–O–C bend, the oxygen out-of-plane interaction (K–O–D and C–O–D bends), the K–O–C–H torsion, and the K–O–C–C torsion. With the exception of the K–O stretch (*vide infra*), *ab initio* molecular orbital calculations were used to derive all of the parameters for the metal-dependent interactions. This task was accomplished in two phases.

In the first phase of the metal-dependent parameter development, Hartree–Fock calculations were performed to determine the optimized geometries and potential surfaces for selected distortions in the simple molecular fragments K–O(Me)₂ and K–O(Me)(Et). During the *ab initio* calculations, K–O bond lengths were constrained to a value of 2.80 Å, which is the average K–O distance in crown ether complexes.³² These calculations were performed with use of the STO-3G basis set. This basis set is known to yield C–H and C–O bond lengths that are slightly too long³³ and known to give a poor representation of highly polar molecules and bonds.³⁴ However, we felt this level of theory to be adequate for the current application since the goal was to reproduce relative potential energy surfaces rather than absolute energies.^{35,36} Because no electron

Table I. Metal-Independent Parameter Set for Aliphatic Crown Ethers^a

| | | van der Waals | | | |
|------------------------------|-----------|--|---------------------------|---------------------------|-------------------------|
| | | atom type | ε (kcal/mol) | d (Å) | |
| sp ³ carbon | 1 | | 0.044 | 1.900 | |
| hydrogen | 5 | | 0.047 | 1.500 | |
| oxygen | 6 | | 0.050 | 1.960 | |
| ether sp ³ carbon | 27 | | 0.044 | 1.900 | |
| Bond Stretching | | | | | |
| bond type | | k _r (mdyn/Å) | r ₀ (Å) | μ (D) | |
| 1 | 1 | 4.400 | 1.523 | | |
| 1 | 5 | 4.600 | 1.113 | | |
| 1 | 27 | 4.800 | 1.505 | | |
| 5 | 6 | 4.500 | 0.940 | -1.115 | |
| 5 | 27 | 4.600 | 1.113 | | |
| 6 | 27 | 5.360 | 1.407 | 1.168 | |
| 27 | 27 | 5.000 | 1.485 | | |
| Angle Bending | | | | | |
| bond type | | k _θ (mdynÅ/rad ²) | θ ₀ (type 1) | θ ₀ (type 2) | θ ₀ (type 3) |
| 1 | 1 1 | 0.670 | 109.5 | 110.2 | 111.0 |
| 1 | 1 5 | 0.590 | 109.8 | 109.3 | 110.7 |
| 1 | 1 27 | 0.670 | 109.5 | 110.2 | 111.0 |
| 5 | 1 5 | 0.550 | 107.6 | 107.8 | 109.5 |
| 5 | 1 27 | 0.590 | 109.8 | 109.3 | 110.7 |
| 27 | 1 27 | 0.670 | 109.5 | 110.2 | 111.0 |
| 5 | 6 27 | 0.350 | 106.9 | | |
| 27 | 6 27 | 0.820 | 106.4 | | |
| 1 | 27 1 | 0.670 | 109.5 | 110.2 | 111.0 |
| 1 | 27 5 | 0.590 | 109.8 | 109.3 | 110.7 |
| 1 | 27 6 | 0.830 | 107.5 | 107.0 | 107.9 |
| 5 | 27 5 | 0.550 | 107.6 | 107.8 | 109.5 |
| 5 | 27 6 | 0.820 | 110.0 | 108.9 | 108.7 |
| 1 | 27 27 | 0.670 | 109.5 | 110.2 | 111.0 |
| 5 | 27 27 | 0.590 | 109.8 | 109.3 | 110.7 |
| 6 | 27 27 | 0.830 | 107.5 | 107.0 | 107.9 |
| 4 | 27 1 27 | 0.192 | 109.5 | 110.3 | 110.6 |
| 4 | 27 6 27 | 0.424 | 107.0 | | |
| 4 | 1 27 6 | 0.340 | 109.3 | 109.2 | 108.4 |
| Torsional | | | | | |
| bond type | | V ₁ (kcal/mol) | V ₂ (kcal/mol) | V ₃ (kcal/mol) | |
| 1 | 1 1 1 1 | 0.185 | 0.170 | 0.520 | |
| 1 | 1 1 1 5 | 0.000 | 0.000 | 0.280 | |
| 1 | 1 1 1 27 | 0.185 | 0.170 | 0.520 | |
| 5 | 1 1 1 5 | 0.000 | 0.000 | 0.237 | |
| 5 | 1 1 1 27 | 0.000 | 0.000 | 0.280 | |
| 27 | 1 1 1 27 | 0.185 | 0.170 | 0.520 | |
| 1 | 1 1 27 1 | 0.185 | 0.170 | 0.520 | |
| 1 | 1 1 27 5 | 0.000 | 0.000 | 0.267 | |
| 1 | 1 1 27 6 | 0.200 | 0.000 | 0.300 | |
| 1 | 1 1 27 27 | 0.185 | 0.170 | 0.520 | |
| 5 | 1 1 27 1 | 0.000 | 0.000 | 0.280 | |
| 5 | 1 1 27 5 | 0.000 | 0.000 | 0.237 | |
| 5 | 1 1 27 6 | 0.000 | 0.000 | 0.300 | |
| 5 | 1 1 27 27 | 0.000 | 0.000 | 0.280 | |
| 27 | 1 1 27 5 | 0.000 | 0.000 | 0.280 | |
| 27 | 1 1 27 6 | 0.200 | 0.000 | 0.300 | |
| 5 | 6 27 1 | 0.400 | 0.000 | 0.100 | |
| 5 | 6 27 5 | 0.000 | 0.000 | 0.200 | |
| 5 | 6 27 27 | 0.400 | 0.000 | 0.100 | |
| 27 | 6 27 1 | 0.450 | 0.050 | 0.757 | |
| 27 | 6 27 5 | 0.000 | 0.000 | 0.680 | |
| 27 | 6 27 27 | 0.450 | 0.050 | 0.757 | |
| 1 | 27 27 1 | 0.185 | 0.170 | 0.520 | |
| 1 | 27 27 5 | 0.000 | 0.000 | 0.280 | |
| 1 | 27 27 6 | 0.200 | 0.000 | 0.300 | |
| 5 | 27 27 5 | 0.000 | 0.000 | 0.237 | |
| 5 | 27 27 6 | 0.000 | 0.000 | 0.300 | |
| 5 | 27 27 27 | 0.000 | 0.000 | 0.280 | |
| 6 | 27 27 6 | 3.360 | -4.820 | 3.840 | |
| 6 | 27 27 27 | 0.200 | 0.000 | 0.300 | |
| 4 | 27 1 27 6 | 0.000 | 0.000 | 1.830 | |
| 4 | 27 6 27 1 | 0.000 | 0.000 | 1.830 | |

^a Parameters are presented in standard MM2 format. For additional information, refer to the users' manual (ref 21).

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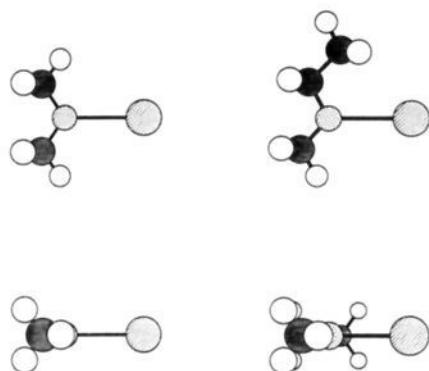


Figure 2. Geometry-optimized *ab initio* structures for $\text{K-O}(\text{Me})_2$ and $\text{K-O}(\text{Me})(\text{Et})$ with the K-O length constrained to 2.80 Å. Average structural features are as follows: C-O length, 1.438 Å; C-H length, 1.092 Å; H-C-H angle, 108.8°; K-O-C angle, 124.7°; C-O-C angle, 110.6°; O-C-C angle, 108.5°; and O-C-H angle, 110.0°.

pairs are disturbed during the distortions, the associated energy error is expected to be approximately constant over the range of the distortion.

Figure 2 illustrates the geometry-optimized *ab initio* structures for $\text{K-O}(\text{Me})_2$ and $\text{K-O}(\text{Me})(\text{Et})$. In both cases, the minimum energy structure is obtained when the potassium ion lies within the plane defined by the C-O-C moiety. This finding establishes that the metal ion prefers to lie between the two oxygen lone pairs to give a trigonal-planar geometry rather than to bind to one of the oxygen lone pairs to give a tetrahedral geometry, as has been suggested elsewhere.³⁷

Five potential energy surfaces were generated from selected distortions of $\text{K-O}(\text{Me})_2$ and $\text{K-O}(\text{Me})(\text{Et})$. These include movement of the potassium ion out of the C-O-C plane, movement of the potassium ion within the C-O-C plane, and rotations about the O-C bonds. At each point along the distortion, the geometry was optimized subject to the following constraints. For the out-of-plane distortion, the two K-O-C bond angles were constrained to have the same value such that a projection of the K-O bond vector upon the C-O-C plane bisected the C-O-C angle, and the distortion was driven by changing this K-O-C angle. For the in-plane distortion, the potassium ion and the C-O-C moiety were constrained to remain coplanar, and the distortion was driven by constraining one of the K-O-C angles to a specified value. For the rotations about the O-C bonds, the potassium ion and the C-O-C moiety were constrained to remain coplanar, and the rotation was driven by constraining the appropriate torsion angle to a specified value.

The *ab initio* calculations yielded potential energy surfaces that were used as a basis for fitting the metal-dependent parameters. In this second phase, a series of MM2 calculations was performed for the same structural distortions of $\text{K-O}(\text{Me})_2$ and $\text{K-O}(\text{Me})(\text{Et})$. As with the *ab initio* calculations, the K-O lengths were constrained to a value of 2.80 Å during the MM2 calculations. The metal-dependent parameters were adjusted to achieve the best fit to the potential energy surfaces. Parameters that were varied during the fitting process were θ_0 and K_θ for the K-O-C angle; K_θ for the K-O-D and C-O-D angles (θ_0 fixed at 90°); V_3 for the K-O-C-H torsion (V_1 and V_2 fixed at 0 kcal/mol); and V_1 , V_2 , and V_3 for the K-O-C-C torsion. The adjustments to these parameters were made according to the downhill Simplex method,³⁸ with all seven parameters free to vary and all five *ab initio* potential energy surfaces included. Figures 3–7 illustrate the *ab initio* potential energy surfaces for the five distortions of $\text{K-O}(\text{Me})_2$ and $\text{K-O}(\text{Me})(\text{Et})$ and the fit obtained after MM2 parameter optimization. The resulting metal-dependent parameters are presented in Table II.

The K-O stretching parameters were the last to be assigned. This assignment was accomplished through an iterative process in which the strain-free length and the stretching force constant were manually adjusted to give the best overall agreement with a series of known structures. Crystal structure data for potassium complexes of **1**,^{39–57} **4**,^{58,59} and **5**^{47,60} served as the basis for this process. Atomic positional coordinates for

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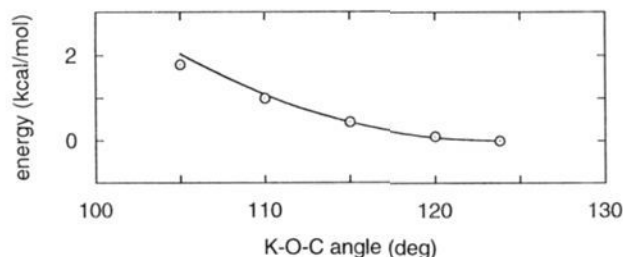


Figure 3. Comparison of the *ab initio* (○) and MM2 (—) potential energy surfaces for the movement of the potassium ion within the C-O-C plane in $\text{K-O}(\text{Me})_2$.

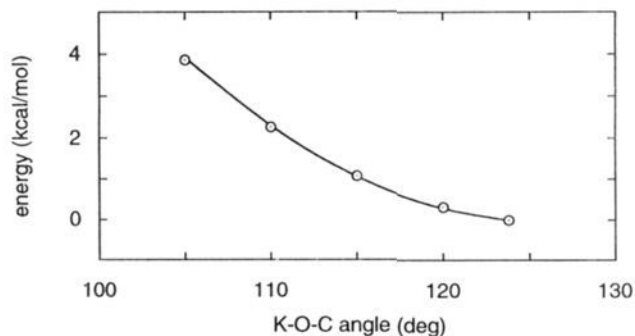


Figure 4. Comparison of the *ab initio* (○) and MM2 (—) potential energy surfaces for the movement of the potassium ion out of the C-O-C plane in $\text{K-O}(\text{Me})_2$.

each of the three complexes were taken from the crystal structures and used as a starting point for the calculations. Axial ligands were omitted. A series of MM2 calculations was performed on each of the three complexes with the strain-free length set from 2.6 to 2.9 Å at 0.1-Å intervals. For each strain-free length, the stretching force constant was varied, and the calculated structures were compared with the experimental data. A good agreement with the experimental K-O lengths was obtained with the ideal length set at 2.725 Å and the stretching force constant set at 0.170 mdyn/Å.

A comparison of experimental and calculated bond lengths, bond angles, and torsion angles for **1**, **4**, and **5** is presented in Table III. Examination

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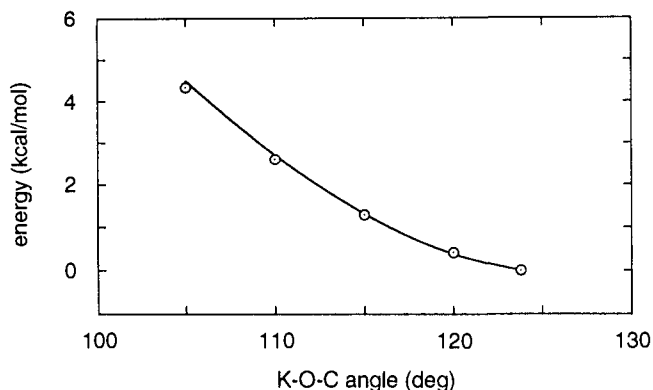


Figure 5. Comparison of the *ab initio* (○) and MM2 (—) potential energy surfaces for the movement of the potassium ion out of the C—O—C plane in K—O(Me)(Et).

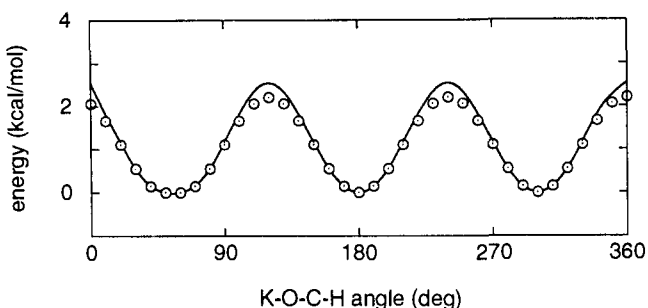


Figure 6. Comparison of the *ab initio* (○) and MM2 (—) potential energy surfaces for rotation about the C—O bond in K—O(Me)₂.

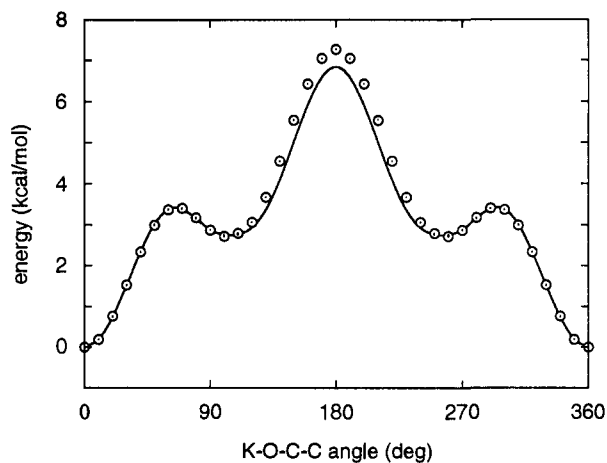


Figure 7. Comparison of the *ab initio* (○) and MM2 (—) potential energy surfaces for rotation about the C—O(Et) bond in K—O(Me)(Et).

of these data reveals that the model reproduces the structure of these potassium complexes to a level of accuracy that is comparable to that obtained with the metal-free crown ethers (*vide supra*).

III. Application of the Molecular Model

The MM model described above was used to calculate the structure and strain energies for compounds 1–11, both with and without a potassium ion in the cavity. Because of a lack of experimental data for the majority of these structures, it was necessary, in most cases, to assume a conformation for the macrocyclic ring. From the results of crystallographic studies,^{39–57,61} it is clear that the *D*_{3d} conformation is preferred for potassium complexes of 1. In this conformation, the O—C—C—O torsion angles alternate $\pm 60^\circ$ and the C—O—C—C torsion angles alternate $\pm 180^\circ$ such that the oxygen atoms are alternately positioned above and below the plane of the ring. Spectroscopic studies

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Table II. Metal-Dependent Parameters for Aliphatic Crown Ether/Potassium Complexes^a

| van der Waals | | | | | |
|-----------------|---------|--------------------------------------|---------------------|---------------------|---------------------|
| atom type | | ϵ (kcal/mol) | d (Å) | | |
| dummy atom | | 11 | 0.000 | | |
| potassium | | 19 | 0.000 | | |
| | | 3.800 | | | |
| Bond Stretching | | | | | |
| bond type | | k_r (mdyn/Å) | r_0 (Å) | μ (D) | |
| 6 | 11 | 99.999 | 1.000 | | |
| 6 | 19 | 0.170 | 2.725 | | |
| Angle Bending | | | | | |
| bond type | | k_θ (mdynÅ/rad ²) | θ_0 (type 1) | θ_0 (type 2) | θ_0 (type 3) |
| 11 | 6 19 | 0.079 | 90.0 | | |
| 11 | 6 27 | 0.079 | 90.0 | | |
| 19 | 6 27 | 0.120 | 123.5 | | |
| Torsional | | | | | |
| bond type | | V_1 (kcal/mol) | V_2 (kcal/mol) | V_3 (kcal/mol) | |
| 11 | 6 27 1 | 0.000 | 0.000 | 0.000 | |
| 11 | 6 27 5 | 0.000 | 0.000 | 0.000 | |
| 11 | 6 27 27 | 0.000 | 0.000 | 0.000 | |
| 19 | 6 27 1 | -1.100 | 0.880 | 0.200 | |
| 19 | 6 27 5 | 0.000 | 0.000 | 0.060 | |
| 19 | 6 27 27 | -1.100 | 0.880 | 0.200 | |

^a Parameters are presented in standard MM2 format. For additional information, refer to the users' manual (ref 21).

indicate that the *D*_{3d} conformation of 1, both for the potassium complex and for the free ligand, is also the predominant conformation in protic solvents.⁶² Therefore, we have chosen to use, where possible, the *D*_{3d} conformation for all calculations involving 18-membered rings. Analogous conformations were adopted for the larger 19- and 20-membered rings. These ring conformations are illustrated in Figure 8.

The input atomic coordinates used to achieve these conformations in the potassium complexes of 1–11 were derived by using the following procedure. Atomic positional coordinates from crystallographic data on the potassium complex of 1 were used as a foundation for the construction of the other molecules.^{39–57} With use of the Chem3D Plus program, additional atoms were added to this foundation to obtain the desired compound.⁶³ The resulting crude set of coordinates was then subjected to a two-step minimization procedure. In the first step, the motion of all the original ring carbons and oxygens was restricted, allowing the added atoms to adopt a structure that is compatible with that of the ring. In the second step, the structure of the entire complex was energy-minimized. By removing the metal ion and dummy atoms from these structures, the input atomic coordinates for the crown ethers in the absence of potassium were obtained. In every case, the metal-free crown ether minimized to the same ring conformation as that obtained for the corresponding potassium complex. Input coordinates for each crown ether are available as supplementary material.

With the exception of 7, this procedure was successful at generating the ring conformations for the potassium complexes shown in Figure 8. Due to the *trans-anti-trans* attachment of the cyclohexyl rings, it is not possible to locate the *D*_{3d} ring conformation for 7. The procedure outlined above gave a ring conformation of *ag*⁻*a ag*⁺*g*⁺*ag*⁺*a ag*⁺*a ag*⁻*a ag*⁺*a*.⁶⁴ Other likely

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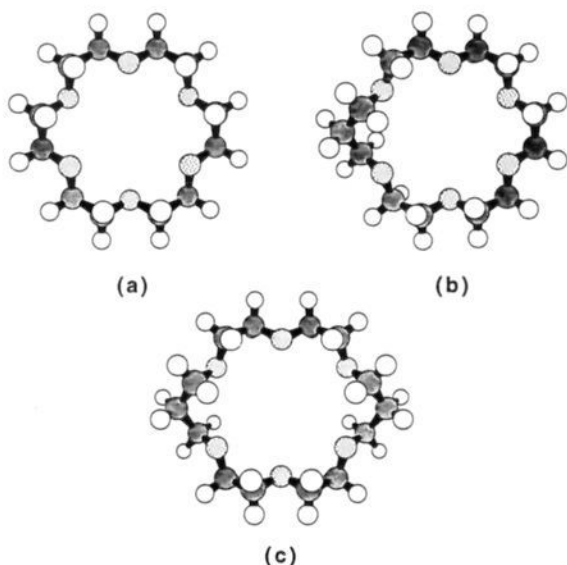
(63) Both the *cis* and *trans* isomers were examined for 11. The difference in ring conformation and strain energy proved to be insignificant for the two isomers.

(64) (a) We have adopted the notation of Dale.^{64b} Italics are used to indicate the location of the cyclohexyl rings. (b) Dale, J. *Isr. J. Chem.* 1980, 20, 3.

Table III. Comparison of Experimental vs Calculated Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for Crown Complexes of Potassium^a

| | 1 | | 4 | | 5 | |
|---------|----------------------|-------------------|----------------------|-------------------|----------------------|-------------------|
| | exp ³⁹⁻⁵⁷ | calc ^b | exp ^{58,59} | calc ^b | exp ^{47,60} | calc ^b |
| K-O | 2.80(0.06) | 2.80(0.01) | 2.82(0.05) | 2.80(0.06) | 2.81(0.10) | 2.81(0.06) |
| O-K-O | 60(1) | 60.3(0.2) | 59(2) | 60.0(0.3) | 60(2) | 60(1) |
| K-O-C | 114(4) | 115.2(0.3) | 115(5) | 115(2) | 114(6) | 115(2) |
| C-O-C | 113(2) | 113.4(0.1) | 115(5) | 115(1) | 113(1) | 114(1) |
| C-C-O | 109(2) | 109.0(0.1) | 111(5) | 109(1) | 109(2) | 109(1) |
| C-O-C-C | 176(2) | 176(1) | 173(6) | 171(5) | 172(7) | 174(4) |
| O-C-C-O | 65(3) | 63.7(0.1) | 62(9) | 62(3) | 66(6) | 64(2) |

^a Experimental data were obtained by averaging data for 19 structures of 1, two structures of 4, and two structures of 5. Distance and angle information was calculated from atomic positional coordinates taken from the Cambridge Structural Database. Root mean square deviations are given in parentheses. ^b This work.

**Figure 8.** D_{3d} symmetry conformation of the 18-membered rings (a) and analogous conformations of the 19-membered rings (b) and 20-membered rings (c).

conformations,^{65,66} including $ag^+g^+ag^+aag^-ag^+g^+ag^+aag^-$, $ag^+aag^-ag^+g^+ag^+aag^-ag^+g^+$, $ag^-ag^-ag^-ag^+g^+ag^+aag^-ag^+g^+$, and $ag^-ag^+ag^+g^+aag^-ag^-ag^+a$, were examined. The $ag^-ag^+ag^+g^+aag^-ag^-ag^+a$ conformation was the most stable (≤ 2 kcal/mol lower in energy than the other four conformations) and was used for comparison with the other crown ethers.

Strain energies for 1-11 and their potassium complexes are presented in Table IV. In addition, Table IV contains experimental $\log K$ values for complexation of potassium in CH₃OH at 25 °C.^{2,4,67-72} In cases where more than one value has been reported, the values have been averaged. The large amount of data for 1, in which 23 determinations yield an average value of 6.1 ± 0.1 (1σ), provides a measure of the uncertainty associated with these $\log K$ values. We have assumed that a comparable uncertainty of ± 0.1 (1σ) applies to all $\log K$ values listed in Table IV, and the values have thus been presented with two significant figures.

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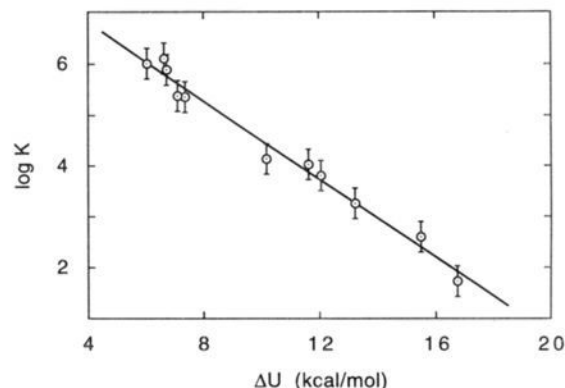
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Table IV. Calculated Strain Energies and Experimental Potassium Stability Constants

| ligand | strain in metal-free ligand (kcal/mol) | strain in potassium complex (kcal/mol) | ΔU^a (kcal/mol) | $\log K$ (exp) | $\log K^b$ (calc) |
|--------|--|--|-------------------------|----------------------|-------------------|
| 1 | 28.06 | 34.70 | 6.64 | 6.1 ^{2,4} | 5.8 |
| 4 | 51.31 | 57.36 | 6.05 | 6.0 ⁶⁷ | 6.0 |
| 3 | 39.80 | 46.53 | 6.73 | 5.9 ⁶⁷ | 5.8 |
| 5 | 51.42 | 58.53 | 7.11 | 5.4 ⁶⁷ | 5.6 |
| 2 | 37.55 | 44.92 | 7.37 | 5.4 ⁶⁸ | 5.5 |
| 6 | 50.26 | 60.46 | 10.20 | 4.1 ⁶⁹ | 4.4 |
| 9 | 35.74 | 47.39 | 11.65 | 4.0 ⁷⁰ | 3.8 |
| 8 | 70.52 | 82.60 | 12.08 | 3.8 ⁷¹ | 3.7 |
| 7 | 51.22 | 64.46 | 13.24 | 3.3 ⁶⁹ | 3.3 |
| 11 | 52.34 | 67.84 | 15.50 | 2.6 ⁷² | 2.4 |
| 10 | 114.89 | 131.64 | 16.75 | 1.7 ^{71,72} | 1.9 |

^a ΔU = strain in potassium complex - strain in metal-free ligand.

^b Calculated from the regression line shown in Figure 9.

**Figure 9.** Experimentally determined potassium stability constants, $\log K$, as a function of the increase in strain energy associated with potassium ion complexation, ΔU . Error bars reflect a confidence level of $\pm 3\sigma$. Regression line: $\log K = 8.35 - 0.384\Delta U$ ($r = 0.991$).

Given the strain energies in Table IV, it is possible to define the increase in strain energy that accompanies potassium complexation, ΔU , as the difference between the strain energy of the potassium complex and the strain energy of the metal-free ligand. Figure 9 shows the experimentally determined potassium stability constants, $\log K$, as a function of ΔU for the 11 crown ethers. A definite linear relationship is revealed ($r = 0.991$), with the regression line passing through all 11 points within experimental error.

IV. Discussion

We have presented the development of a MM model for aliphatic crown ethers and their potassium complexes. Our model differs from the MM models that have been previously applied to crown ether metal complexes^{12-17,37} in two respects. First, we have used a force field that explicitly includes terms for K-O

stretches, K–O–C bends, K–O–C–H and K–O–C–C torsions, and out-of-plane bending at oxygen. With one exception,³⁷ previous modeling studies have relied upon a pair potential treatment where metal-dependent terms are limited to van der Waals and electrostatic interactions. Second, we have employed *ab initio* calculations to identify the preferred geometry for an ether ligand coordinated to potassium and to generate potential surfaces for structural distortions in simple models. Metal-dependent parameters were optimized relative to the *ab initio* results. This represents a unique approach for the parameterization of MM force fields for coordination compounds.

The MM model developed in this study was applied to compute the structure and associated strain energies in 11 crown ethers and their potassium complexes. By assuming that the macrocyclic ring would adopt, where possible, a conformation with *gauche* O–C–C–O torsion angles and *anti* C–O–C–C torsion angles,^{64b} we have shown that a MM model can be successfully applied to explain the observed trend in complex stability. The correlation between the experimental stability constant, $\log K$, and the increase in strain that accompanies the coordination of potassium, ΔU , represents the first quantitative structure–stability relationship that has been reported for crown ethers. By combining computed values of ΔU with the linear correlation from Figure 9, we believe it is now possible to predict the stability constant, $\log K$ (CH₃OH, 25 °C), for potassium complexation with other aliphatic hexadentate crown ethers to within ± 0.3 log units.

It is important to note that the quantity ΔU was determined for isolated molecules. Neither inner- nor outer-sphere solvent effects were included. Given the correlation that was obtained, we conclude that the major factor in controlling the differences in reactivity for this series of ligands is the relative orientation of the oxygen donor atoms within the ligand cavity, i.e., the structure of the crown ether, and that the solvent effects may be ignored in this type of comparison.

The calculations presented in this study did not include entropic effects. Yet we find that the quantity ΔU , which is related to the change in enthalpy,¹⁸ is linearly related to the $\log K$ values or the change in free energy. We conclude either that the entropy change for all 11 complexation reactions is relatively constant or that for this series of similar reactions, the entropy change is linearly related to the enthalpy change. Numerous examples of such entropy and enthalpy relationships have been reported.⁷³

A significant finding of this study is the importance of the bonding directionality at the ether oxygen. The *ab initio* calculations on K–O(Me)₂ and K–O(Me)(Et) reveal a preference for the potassium ion to lie within the plane defined by the C–O–C moiety. In addition, the calculations show that significant strain develops on distortion from this preferred orientation. This hitherto unrecognized orientational preference must modify the

way in which we have traditionally thought about the influence of crown ether structure on complex stability.

Soon after the discovery of crown ethers, it was noticed that picrate extraction constants showed a correlation between the size of the cation and the size of the crown ether cavity.⁷⁴ This observation gave rise to the size-match selectivity theory. This theory states that a metal ion will form the most stable complex with the member of a series of macrocycles that has the cavity size that most closely matches the metal size. Despite studies that have demonstrated that size-match selectivity fails to correctly predict the reactivity of crown ethers^{75–77} and other macrocycles,⁷⁸ the size-match concept remains widely accepted and is frequently the only criterion cited in the attempted design of metal ion-selective crown ethers.

While it is clear that a match between the preferred M–O bond length and cavity size is an important requirement for energy efficient complexation, the results of the present study reveal that the consideration of M–O bond length preferences alone is a poor basis for crown ether design. We conclude that it is also necessary to consider the orientation of the C–O–C groups, relative to the metal ion, to understand the relationship between structure and reactivity.

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Supplementary Material Available: Example MM2 input file for the potassium complex of **1** and the connectivity and input coordinates for the potassium complexes of **2–11** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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