obtained for proton tunneling in theoretical calculations,[50] we cannot know, at the present stage of the work, if $H_5O_2^+$ is or is not more favorable than H_3O^+. However, we can assume that some general conclusions would not be changed. For instance, if we replace, in Figure 3, H_3O^+ and molecule number 2 by $H_5O_2^+$, we may expect similar deformation of the position of molecules 1, 3, and 4 since H^+ should be shifted toward molecule 2. As mentioned in section II, further calculations will be performed to check this assumption but will not be available for some time.

The second peak around $d_{OI-OW} = 4.7$ Å is on the contrary very broad (Figure 1). This effect is illustrated in Figure 2 by the slope of the curve between $d_{OI-OW} = 4.0$ and 5.0 Å, compared to the nearly vertical wall at $d_{OI-OW} = 2.5$ Å. The peak is more pronounced for large values of n (Figure 1) and we can see, already for $n = 6$ or 7 but more clearly for $n = 8$ or 9, the formation of a third peak around $d_{OI-OW} = 6.8$ Å (the size of the box in Monte Carlo calculations has been chosen large enough to allow the study of this effect). It then exists some tendency to fill a third shell before the second one is complete. If we consider the limit of the three peaks are around 3.0, 5.9, and 10 Å, we find about 3.6, 4.2, and 1.2 molecules in each peak for $n = 9$. Figure 2 shows that the filling of the third shell is already noticeable for $n = 5$, with a very small number of molecules (0.1), this number increasing with n.

IV. Conclusions

As stated above, though the values of the cluster formation energies are not very good for small clusters, we expect that the description of the phenomena from the analysis of MC calculations is not strongly affected by this inaccuracy. A theoretical study of such clusters would be impossible without the use of approximate formulas, and the present treatment seems able to give interesting information about the structure and the filling of the solvation shells. Work is now in progress to extend this study to larger systems and to take into account three-body effects. Also, some studies considering $H_5O_2^+$ as the central ion, with the possibility of relaxing the geometry, will be undertaken.

Many questions are not yet answered about these systems. In this first step of our study, we have frozen the geometry of H_3O^+. We think that this treatment brings information which is essential for the understanding of these systems. The effect of the mobility of the proton in the clusters is of particular importance[11,14,15] and must be checked to get definitive answers.

Monte Carlo Study of the Conformation-Dependent Hydration of the 18-Crown-6 Macrocycle

G. Ranghino,[†] **S. Romano,**[‡] **J. M. Lehn,**[§] **and G. Wipff***[§]

Contribution from Montedison, G. Donegani, S.P.A., 28100 Novara, Italy, the Physics Department, The University, I-27100 Pavia, Italy, and the Laboratoire de Chimie Organique Physique, U.A. 422 au CNRS, Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pacal, 67000 Strasbourg, France. Received July 23, 1984

Abstract: The conformation-dependent hydration of the [18]-O_6 macrocycle has been studied by Monte Carlo calculations on a cluster made up of 100 water molecules surrounding the solute in the C_i, D_{3d}, and C_1 conformations. The intrinsically most stable C_i form, unefficient for ion binding, is the least well hydrated and should be the least stable form in water. The D_{3d} conformer, with a preformed cavity suitable for cation binding and transport, is solvated to the same extent as the C_1 conformer and should be the most stable in the aqueous environment. A computer graphics analysis of the supramolecular clusters shows conformation-dependent patterns of hydrogen bonds in the first solvation shell, corresponding to different hydration energies in that shell. In the D_{3d} form, a cooperativity between solvent molecules H bonded one to another is observed, analogous to what is found in the X-ray structure of a [18]-O_6/water/*p*-nitrophenol complex. For C_1 three independent water molecules in a bridging position maintain firmly the distorted solute. The weak solvation of C_i results from linear H bonds to the solute and unfavorable water–water interactions. These results have an important bearing on conformational analysis in solution and on solvent-dependent cation complexation by ionophores, since conformations found in the solid state may not be those favored in water.

The [18]-O_6 crown ether, a simple model foor macrocyclic ion receptors and carriers, is flexible and displays several conformations in crystals, depending on the nature of its environment and on the presence and nature of the complexed cation:[1-4] e.g., the uncomplexed crown has C_i symmetry, the Na^+ and K^+ complexes are C_1 and D_{3d}, respectively. Flexibility is important not

only to ensure the formation of the most favorable "cavity" for a given ion but also to facilitate the capture and release of the

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[†] Montedison, G. Donegani.
[‡] The University.
[§] Université Louis Pasteur.

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Table I. Parameters of the [18]-O_6 Water Interaction Potential[a,b]

	A	B	C	charge
C-O_w	10.20731	102467.8	0.993571	−0.155
C-H_w	3.560004	121598.2	0.992950	
O-O_w	11.29167	305269.3	0.999646	−0.410
O-H_w	84.53119	870.6007	1.0	
H-O_w	3.448793	3320.713	0.999967	+0.180
H-H_w	8.242525	1452.690	1.0	

[a] $E_T = \sum_{\text{atoms } i,j} - (A_{i,j}/r^6) + (B_{i,j}/r^{12}) + (Cq_iq_j/r)$. [b] The C, O, H atoms of the crown ether correspond to the classes O3, C15, and HB of ref 7.

ion in the process of transport at membrane interfaces.[5] Small energy gaps with low-energy barriers between different conformers are required. These quantities are not experimentally available; therefore theoretical evaluations provide a valuable insight into the conformational analysis of such ionophores. Indeed, the molecular mechanics technique indicates that C_i and D_{3d} forms of [18]-O_6 have comparable stabilities and that C_1 is about 6–9 kcal/mol higher in energy;[3,4] unfortunately, the solvent or molecular environment, which can modify the preferred conformation and the selectivity for complexation, has not been explicitly considered so far. It is thus important to assess the solvent effect on conformation: Does the solvent stabilize the different conformers to a similar extent? If not, can it stabilize structures relevant to ion transport (e.g., C_1 and D_{3d}) more than others with no cavity suitable for complexation (e.g., C_i)? Does it stabilize the high energy structures with a non-zero dipole moment (e.g., C_1) more than the centrosymmetric structures (e.g., C_i, D_{3d})?

As a first approach to the complex problem of specific carriers and of conformational analysis in solution, we present the results of a Monte Carlo study on the hydration of [18]-O_6 itself (without complexed cation) in the D_{3d}, C_i, and C_1 conformations.

Computational Technique

Three clusters made of 100 water molecules surrounding the [18]-O_6 "solute" have been considered. Each of them has been put in a cubic box of 32 Å, keeping the solute rigid and moving randomly the 100 water molecules. After an equilibration step of 300 000 moves at 500 K and 300 000 moves at 300 K, the production step has been performed with about 600 000 moves at 300 K. For each move, the "solute"–water and water–water interaction energies have been calculated, using a 6-12-1 interaction potential fitted from ab initio calculations. The water–water potential used is given in ref 6. The solute–water potential is derived from ref 7 and given in Table I.

In order to check the transferability of that potential to [18]-O_6, we compared the empirical with the ab initio interaction energy of one single water molecule in the field of the CH_3-O-CH_2-CH_2-O-CH_3 molecule. Two conformations, taken from fragments of C_i and D_{3d}, with trans and gauche OC-CO dihedral angle, respectively, have been considered. The position of water corresponding to the deepest potential has been determined first using the Monte Carlo force field (at −4.9 and −9.0 kcal/mol, respectively). The "ab initio" values calculated on the same geometries are in reasonable agreement with these values (−6.5 and −9.8 kcal/mol).

An examination of the three clusters on a computer graphics system revealed that C_i and D_{3d} are hydrated to a similar extent, forming a compact cluster (Figure 1), but C_1 presents a much
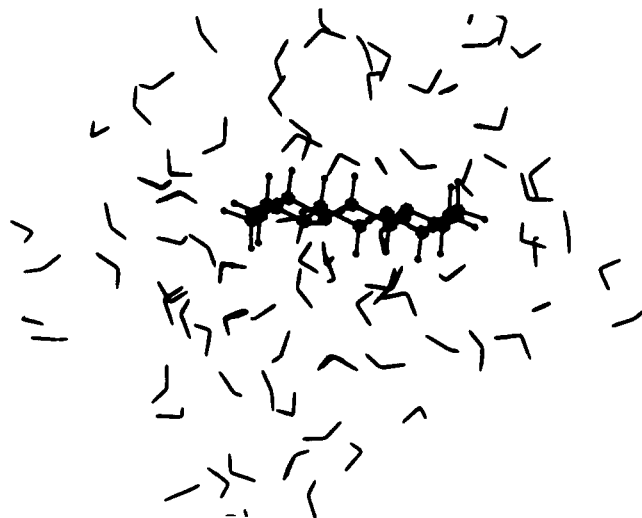
Figure 1. The [18]-O_6, 100 H_2O cluster with the D_{3d} conformer.

Table II. Monte Carlo Results: Average Water–Water (E_{WW}) and Solute–Water (E_{SW}) Interaction Energies[a]

	conformation		
	C_i	D_{3d}	C_1
E_{WW}[b]	−5.9	−6.0	−5.4
E_{SW}	−29.4	−52.4	−54.3

[a] Energies in kcal/mol. [b] E_{WW} for bulk water, calculated with the same potentials is 8.5 kcal/mol (Lye, G. C.; Clementi, E.; Yoshimine, M. *J. Chem. Phys.* **1976**, *64*, 2314).

more elongated shape. This may suggest that the number of water molecules, limited to 100 in order to avoid prohibitive computational times, is too small for C_1. This is, however, in itself an interesting feature of the solvatation in C_1, since we find that some water moves away from a hydrophobic region to arrange itself on the dipole axes of the solute. Because of the limited number of water molecules used in the simulation, the water–water interaction energy (Table II) cannot be compared directly with the values obtained in previous simulations of biological molecules in water.[8,9] This is why we cannot pretend to be quantitative and will focus mainly on the most significant results which are the conformation dependent solute–solvent interaction energy E_{SW} and the different pattern of water coordination in the first hydration shell of the oxygen atoms of [18]-O_6, for which more than enough water is included.

Energetic and Structural Results

We find that the solute–water interaction energy E_{SW} is strongly conformation dependent, and is much larger for C_1 and D_{3d} than for C_i (see Table II): it is thus clear that the intrinsically most stable form C_i is least well hydrated. The D_{3d} form, which is centrosymmetric like C_i, is stabilized by the solvent to about the same amount as C_1. Since C_i and D_{3d} have comparable intrinsic stabilities, C_i should become significantly less stable than D_{3d} in a water environment.

A second interesting result at this level of calculation is that there appears to be no relation between E_{SW} and the presence of a dipole moment: C_1 is not more solvated than D_{3d}, despite the difference in dipole moments. Since both conformers have comparable hydration energies, with D_{3d} intrinsically more stable than C_1, we predict D_{3d} to be still more stable than C_1 in an aqueous environment. It is thus likely that the observed dipole moment in solution comes from other conformers than C_1 (e.g., C_2, C_1'),

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Table III.[a] Contribution of Hydration Shells to Total Hydration Energy

	conformation					
	C_i		D_{3d}		C_1	
	N	E_{SW}	N	E_{SW}	N	E_{SW}
SH_{10X}	6.1	−18.5	5.5	−39.1	3.0	−33.5
SH_{1S}	16.6	−23.8	20.0	−45.0	12.8	−40.3
SH_{2S}	42.0	−25.7	46.4	−53.0	28.9	−44.6

[a] N is the average number of water molecules in the shell; E_{SW} is the average solute–water interaction energy for the N molecules.

as previously suggested.[3] This result should still hold with a larger cluster, since the first solvation shell of the oxygens is completed in C_1, in D_{3d}, and in C_i. Additional water in C_1 will go into the second shell, where it is not expected to compensate for the D_{3d}–C_1 difference in internal energies.

An analysis of the three clusters has been performed on the last 5000 supermolecules, considering three shells of water molecules: SH_{10X} is the first hydration shell of the oxygens, and SH_{1S} and SH_{2S} are the first and first + second solvation shells of the solute, respectively. The average number of molecules N and the corresponding solute–water interaction energies E_{SW} recalculated in each shell (Table III) are conformation dependent, with C_i displaying the weakest E_{SW} in each shell. Furthermore, there is no proportionality between N and E_{SW}.

Particularly in the first hydration shell SH_{10X} of the oxygens C_i is less well hydrated than D_{3d} or C_1 ($\Delta E \sim 15$ kcal/mol) despite the larger number of surrounding water molecules!

We sought to understand this paradoxical result and analyzed the probability density maps for water in selected planes. Peaks for oxygen and hydrogen atoms were indeed observed but difficult to interpret. A much clearer picture emerged from a dynamical representation of the clusters and shells on a color interactive graphics system, which revealed very different patterns of water coordination and of hydrogen bonding in SH_{10X} (Figure 2). In C_i, each oxygen is H bonded to about one H_2O in a linear arrangement. In C_1, each of the three H_2O molecules bridges two oxygen atoms (e.g., $O_1\cdots HOH\cdots O_{10}$, $O_4\cdots HOH\cdots O_{16}$, $O_7\cdots HOH\cdots O_{13}$). In D_{3d}, the situation is still different: among the three oxygens of each face of the ring, two are bridged by one H–O–H (e.g., $O_1\cdots HOH\cdots O_7$); another H_2O molecule is bound to the third oxygen (O_{13}) and to O of the H–O–H bridge. Without imposing any symmetry constraint to the simulation, we found the water molecules of SH_{10X} in D_{3d} to display a quasi-centrosymmetrical arrangement.

One also observes clearly conformation-dependent water–water interactions in SH_{10X}. For D_{3d}, there is a typical *cooperativity* between two water molecules on each face. We found it most encouraging, after this calculation was completed, that a crystal structure of $[18]\text{-}O_6/H_2O/\text{dinitrophenol}$ revealed a similar pattern of H bonding, with the H_2O molecule bridging $O_1\cdots O_7$ and the OH of phenol coordinated to H_2O.[11] This pattern contrasts markedly with that found around C_i where on each face of the molecule the approximately parallel arrangement of three H–OH dipoles is, at least, not favorable. In C_1 two of the three water molecules also have parallel H–O–H dipoles. The average solute/solvent interaction energy per water molecule in SH_{10X} changes from 3.1 to 11.2 kcal/mol, from C_i to C_1, which reflects these differences in structures. When compared to the average water–water interaction energy in the bulk solvent, these numbers indicate that, depending on the conformation of the solute, the water may have from a weak to a strong tendency to interact with the $[18]\text{-}O_6$ macrocycle and that its mobility around the hydrophilic groups is much larger for C_i than for D_{3d} and C_1. For D_{3d} and C_1, the firmly bound H_2O molecules may be considered as part of the structure itself.

Discussion

The cluster approximation cannot give a full account of the hydration process: in particular, the number of water molecules considered is small and the solute is kept rigid during the Monte
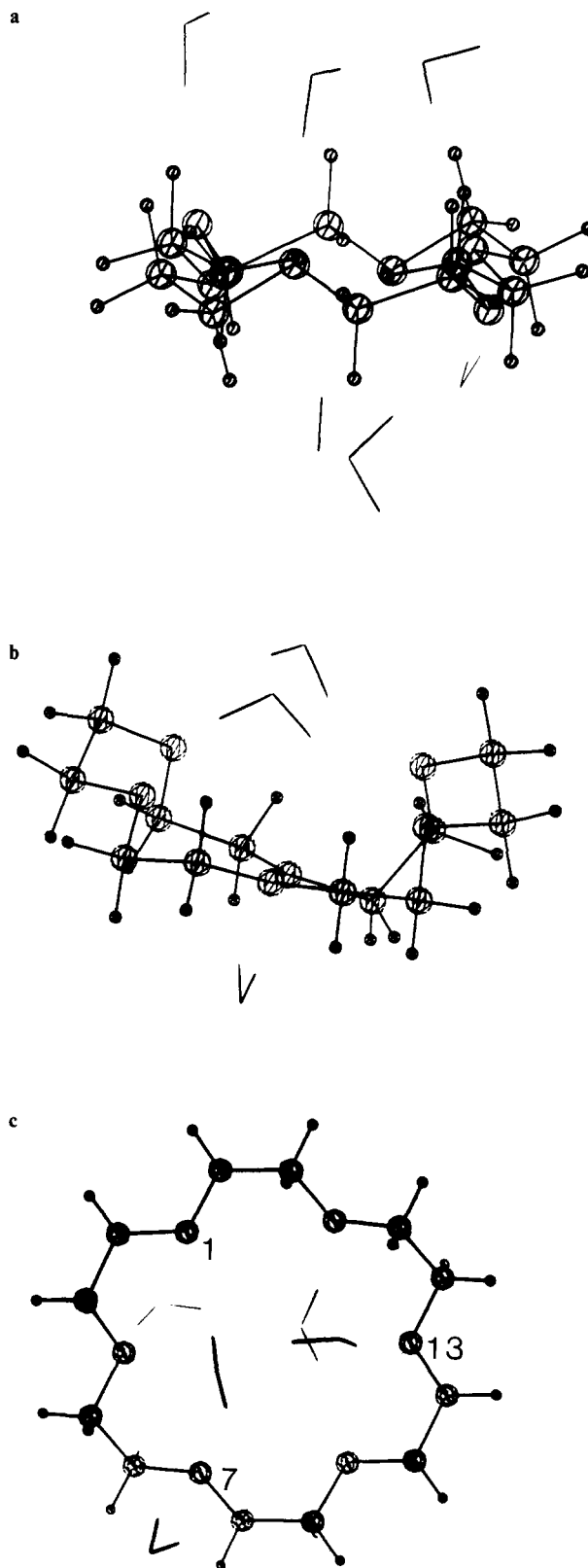
Figure 2. The first solvation shell of the oxygen atoms of $[18]\text{-}O_6$, in the C_i (a), C_1 (b), and D_{3d} conformations.

Carlo sampling; ideally, a great number of conformers, including those of low energy which can have a dipole moment, should be sampled. Our calculations, however, clearly reveal the environmental effect on relative stabilities of the macrocyclic receptor; it is particularly significant to find that *the intrinsically preferred C_i form, unefficient for ion binding, becomes less stable than D_{3d} and C_1 in water*; thus the $[18]\text{-}O_6$ macrocycle takes up in solution a conformation which contains a *preformed cavity* suitable for
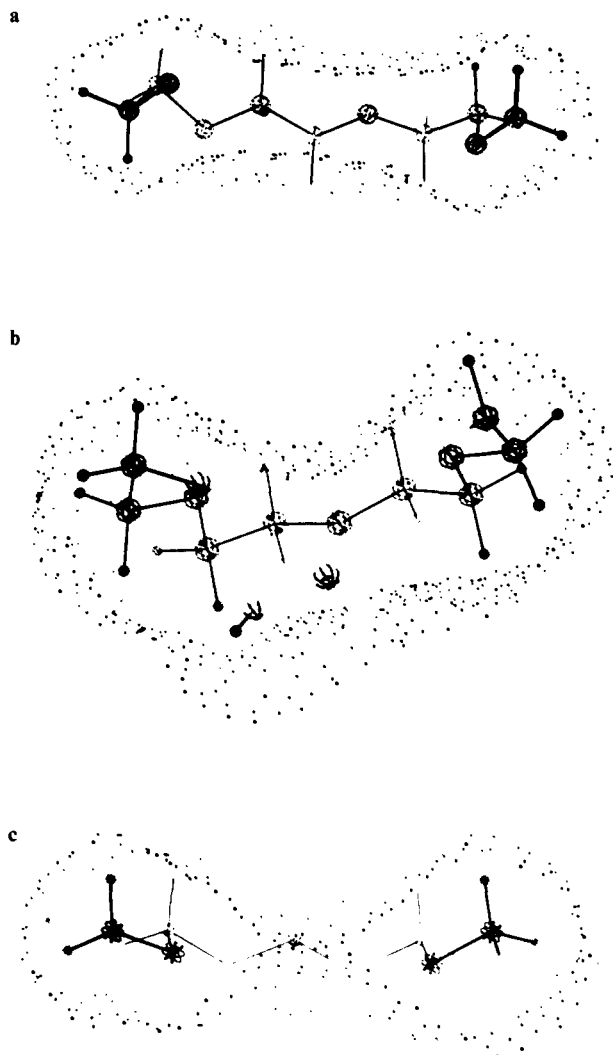
Figure 3. Clipping of the solvent accessible surface for C_i, C_1, and D_{3d}. The following radii have been used to calculate the surface: 1.8 Å for C (united atom representation of CH_2), 1.5 Å for O, 1.4 Å for H_2O (taken as a spherical probe; see ref 13).

cation binding. It is not clear to which extent this statement can be extended to other receptors. For instance, we predicted for the macrobicyclic [222]cryptand the intrinsically most stable conformation of the uncomplexed "in–in" form, unsuitable for cation complexation, to have about the same energy as the conformer found crystallographically in the K^+ complex, when the dielectric constant of the medium increases.[12] In fact these two "in–in" structures should be less well hydrated because of the bicyclic nature of [222] and of the orientation of the oxygens into the cavity. The effect of hydration on the relative stabilities of these forms will depend on accessibility of the heteroatoms to water molecules. For [18]-O_6 the solvation pattern is so intimately related to the arrangement of the ether binding sites that the generalization of this result would be hazardous.

Comparing now C_1 and D_{3d} in water, our calculations suggest that the difference in intrinsic stabilities is unlikely to be compensated by solvation effects, and thus D_{3d} should be more stable than C_1 in water. This result is nicely consistent with the observation of a D_{3d} structure in crystals where [18]-O_6 is surrounded by molecules with N–H^+, O–H^+, or even very weakly polar C–H bonds and with the structure of the water–dinitrophenol–[18]-O_6 crystal.[2,10,11]

Would it be possible to understand (or predict) at least trends in hydration processes from simple considerations? We have seen that the presence of a dipole moment for the solute cannot account
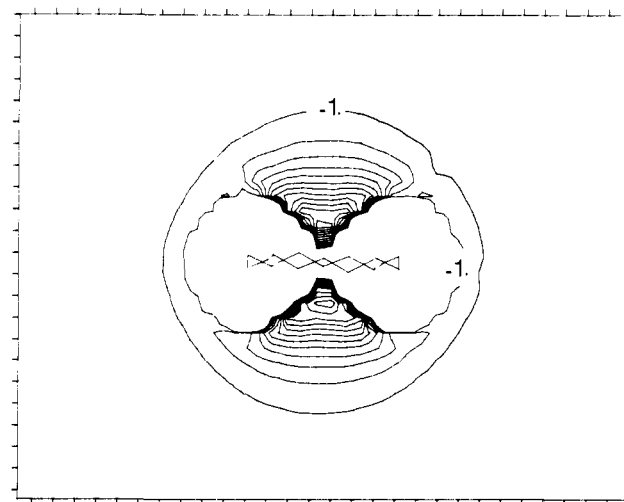
Figure 4. The calculated [18]-O_6/H_2O interaction energy for the D_{3d} conformer, perpendicular to the ring plane. The spacing between the contours is 1 kcal/mol.

for the order of E_{SW}. Other simple indices also have been tested.

The Molecular Surface. The van der Waals surface of the three conformers is calculated not to be very different for C_i, D_{3d}, C_1 (266 to 269 Å^2 for the molecule, 50–51 Å^2 for the oxygens only). However, the molecular surface defined as "accessible to the solvent"[13] is more conformation dependent, larger for C_i than for D_{3d} and C_1 (204, 199, 196 Å^2). If only the hydrophilic oxygen atoms are considered, D_{3d} is now clearly favored (49 Å^2) over C_i and C_1 (36 Å^2). A clipping of these surfaces shows (Figure 3) that for D_{3d} only there is a cavity in the center of the ring, accessible to the solvent.

The Deepest Energy Potential Around [18]-O_6. We calculated the interaction energy between [18]-O_6 and a single water molecule, placing the oxygen atom of H_2O at each point of a grid and optimizing the orientation of H_2O. A typical plot is shown in Figure 4 for D_{3d}. The very weak attraction found around the hydrophobic region (ca. -1 kcal/mol) contrasts markedly with the -12.7 kcal/mol energy minimum found inside the ring, corresponding to a bridging position of water. This value is close to the minimum found for C_1 (-12.8 kcal/mol) and about twice the value found for C_i (-5.5 kcal/mol), where an approximate linear hydrogen bond O···HOH is formed.

The analysis of the solvent-accessible surface and of the potential energy surface makes clear that the C_i conformation is less well hydrated than C_1 or D_{3d} because its conformation is such that the hydrophilic binding sites are less exposed to the solvent, making weaker hydrogen bonds. This is likely not caused only by the ring structure, since the CH_3–O–CH_2CH_2–O–CH_3 "fragment" of D_{3d} shows a deeper potential (-9.8 kcal/mol) than the fragment of C_i, with a trans OC–CO angle (-6.5 kcal/mol). Other important features of the conformation-dependent pattern of hydration, like cooperativity/noncooperativity between solvent molecules, cannot be accounted for by simple indices. On the basis of electrostatic potentials,[15] the solvation pattern would not have been predicted either.

The results of the Monte Carlo simulation are thus understable on a qualitative basis but were hardly predictable and cannot be simply extrapolated to other systems. More generally, this study points out the need to incorporate explicitly solvent effects to

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predict the preferred structures of ionophores, artificial molecular receptors, proteins, ..., in solution, even when relative conformations of species with identical binding sites are compared. It also makes it clear that the solvation pattern depends on the very nature of the solvent.[16] Particularly, the bridging position found for some water molecules is likely to be a specificity of that solvent. In mixed solvents containing water, or even when traces of water are present, such bridging water molecules are expected to become part of some of the structures. It is also clear that H_3O^+, which makes stronger H bonds to ethers than does H_2O, should also influence the conformation of crown ethers[10,17] and of other flexible

molecules, even in very weakly acid conditions.

Note Added in Proof. For the C_1 conformer, we have rerun a Monte Carlo simulation on a cluster of 250, instead of 100, water molecules. The energy results, after 10^6 moves, are as follows: $E_{ww} = -6.7$ kcal/mol per water molecule, $E_{sw} = -53.3$ kcal/mol. They show, as expected, an appreciable improvement of the water–water energy, while the solute–water interaction energy is very close to the previous one, indicating that 100 H_2O already account for the major part of the "solvation" of the 18-crown-6.

Registry No. 18-Crown-6, 17455-13-9.

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The Infrared Spectrum and Force Field of C₃O

Ronald D. Brown,* David E. Pullin, Edward H. N. Rice, and Martin Rodler

Contribution from the Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168. Received June 4, 1985

Abstract: The infrared spectra of matrix-isolated tricarbon monoxide and six isotopically substituted species have been recorded. C_3O was formed by pyrolyzing fumaroyl dichloride seeded in excess argon. The ν_1, ν_2, and ν_4 bands have been observed. A normal coordinate analysis has yielded a general harmonic force field. This has been compared with the force field from ab initio calculations.

We recently reported the pyrolytic generation of tricarbon monoxide and its characterization by its microwave spectrum,[1] followed by further microwave studies of various isotopic variations of the molecule leading to a substitution geometry.[2] The study was substantially assisted by a preceding theoretical investigation by ab initio molecular orbital methods.[3] This provides predictions of force constants and vibrational frequencies, the lowest of which, ν_5, could be estimated approximately from the *l*-doubling transitions observed in the microwave spectrum.[2] It seemed worthwhile to attempt to observe vibrational transitions in the infrared for C_3O by preparing low-temperature argon matrices, particularly since DeKock and Weltner[4] had tentatively proposed the presence of C_3O among the products obtained by deposition of CO and carbon vapor, mainly C or C_2, in cold argon matrices. Their evidence was an infrared band at 2244 cm⁻¹, which they assigned as the ν_1 of C_3O.

We now report the successful observation of the IR spectrum of matrix-isolated C_3O, including a number of different isotopic versions yielding a general harmonic force field, and more elaborate ab initio molecular orbital calculations of both vibrational frequencies and intensities that helped in the assignment of the bands.

Experimental Section

Apparatus. A closed cycle cryostat (model 21C cryodyne from CTI cryogenics) was used for all experiments. The cold stage of the cryostat, with which the copper block containing the CsI window was in direct contact, was at 9–10 K. Both deposition of the matrices and measurements of the infrared spectra were carried out at the lowest available temperature. The spectra were recorded in the region 4000–300 cm⁻¹

with a Perkin Elmer 180 spectrophotometer. The instrument was calibrated by measuring reference gases. The absolute frequencies of the absorption maxima are believed to be accurate to within 0.3 cm⁻¹.

Generation of C₃O. Gas mixtures of fumaroyl dichloride and argon (ratio 1:500) were prepared in advance and stored in a 1.6-L bulb at 0.5 atm. The argon used had a stated purity of 99.995%. The matrices were deposited at a rate of 40 mmol of argon per h. The mixtures were pyrolyzed in a silica tube of 16 mm inner diameter. A 30 cm long electric oven was used and the temperature measured with a thermocouple. Under these conditions the optimum temperature for the generation of C_3O was 1100–1200 °C. In some experiments a straight quartz tube was used, the oven ending about 25 cm in front of the cryostat. In order to reduce the influx of radiation from the oven to the CsI window, a 90° bend was later introduced between oven and cryostat. This had no noticeable influence on the yield of C_3O.

Chemicals. The preparation of isotopically enriched fumaroyl dichloride (fumaryl chloride, (*E*)-2-butenedioyl dichloride) has been described earlier.[2] The three enriched samples yielded mixtures of C_3O with the following isotopic ratios: 90% $CC^{13}CO$ + 10% CCCO, 45% $C^{13}CCO$ + 45% $^{13}CCCO$ + 10% CCCO, and 16% $CCC^{18}O$ + 84% CCCO.

Molecular Orbital Calculations. To obtain an improved prediction of the infrared spectrum we extended the previously reported ab initio calculations.[3] The 6-31G* basis set was used throughout this work. This basis set includes d-polarization functions on all atoms. The off-diagonal force constants were calculated at the Hartree–Fock level (HF) with the MP3/6-31G* geometry reported, while all diagonal force constants were computed at the MP3 level, which includes electron correlation. Due to the regular overshoot of the calculated frequencies a scaling factor of 0.958 was introduced which was obtained from similar calculations on known molecules.[5] The derivatives of the dipole moment with respect to the geometrical parameters were calculated numerically at the Har-

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