the ^{3}A and ^{1}A states of CPTMM have potential energy minima of C_2 symmetry. In any case, it is clear that twisting potentials of the ^{3}A and ^{1}A states of CPTMM are quite shallow.

F. Vertical Excitation Energies. The vertical excitation energies for CPTMM have been calculated at the MCSCF(8,8)/3-21G level of theory. For the $^3B_2$ species the predicted vertical excitation energies are 16.7, 27.9, and 32.2 kcal/mol for the transitions into $^1B_2$, $^1A_1$, and $^3A_1$ states, respectively. For the $^1A_1$ species vertical excitation energies of 3.2, 17.4, and 29.5 kcal/mol are predicted for the transitions into $^3A_1$, $^3B_2$, and $^1B_2$ states, respectively. Because of the large geometry differences between the A and B states, the state orderings as deduced from the vertical excitation spectra differ from those given in Figure 6, in which the energy of each state is reported at the optimized structure for that state.

Conclusions

The geometries of the lowest singlet and triplet states of CPTMM have been optimized by means of the UHF, MCSCF(2,2), and MSCSF(8,8)SD methods. The ground state of CPTMM is predicted to be $^3B_2$ and the first excited state to be $^1A_1$, with the $^3B_2$ state lying 4.9 kcal/mol below the $^1A_1$ state at the MCSCF(8,8)/6-31G* level of theory. Both of these states are found to be planar (at the MCSCF(8,8) level of theory). For the $^3B_2$ state there is a large (6.8 kcal/mol at the MCSCF(8,8)/3-21G level of theory) rotational barrier. On the other hand, the barrier for rotation in the $^1A_1$ state is predicted to be appreciably smaller (1.8 and 2.6 kcal/mol at the MCSCF(8,8)/3-21G and MCSCF(8,8)/6-31G* levels of theory, respectively).

The $^1A_1$ and $^3A_1$ states of CPTMM are closely analogous to the lowest energy singlet and triplet states of TME. In both cases the lower energy state is predicted to be a singlet. For CPTMM the $^1A_1$ state is predicted to be 2.8 kcal/mol below the $^3A_1$ (MCSCF(8,8)/3-21G results), whereas for TME the singlet is predicted to lie 1.3 kcal/mol below the triplet state (MCSCF(6,6)/3-21G results). For both TME and CPTMM the twisting potentials are quite shallow.

Electron correlation effects are found to be very important for predicting the spacing between the $^3B_2$ and $^1A_1$ states of CPTMM. However, the differences in the geometries as predicted in the MCSCF(2,2) and MCSCF(8,8)SD approximations are relatively unimportant for the state separation: in fact, MCSCF(8,8) calculations give nearly the same energy separation between the $^3B_2$ and $^1A_1$ states regardless of whether the MCSCF(2,2) or MCSCF(8,8)SD optimized geometries are employed.

All four states ($^1A_1$, $^3A_1$, $^3B_2$, and $^1B_2$) of CPTMM considered here are relatively nonpolar (with a dipole moments less than 0.4 D). Although an ionic allyl(+)–cyclopentadienyl(−) $^1A_1$ species is found in the HF approximation, the lowest $^1A_1$ state optimized by means of the MCSCF procedure is relatively nonpolar.

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Theoretical Calculations on 1,2-Ethanediol. 2. Equilibrium of the Gauche Conformers with and without an Intramolecular Hydrogen Bond in Aqueous Solution

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Abstract: Ab initio calculations were carried out on the tGg, tGt, and gGg conformers of 1,2-ethanediol in the gas phase and then Monte Carlo simulations were carried out in aqueous solution. MP2/6-31G*//6-31G* results with zero-point and thermal corrections (T = 298 K) show that these conformers without intramolecular hydrogen bonding are higher in free energy by 3–4 kcal/mol than the most stable tGg′ conformer. Hydration of the tGg conformer leads to stabilization by 5.2 kcal and is the most likely conformer in aqueous solution. It represents 64% of the conformer population considering tGg, gGg′, tGg′, tGt, tTt, and gGg conformers. This finding of the tGg-dominant conformer with a gauche O–C–C–O linkage and without intramolecular hydrogen bonding fits well with NMR and Raman experiments for the solution. The polar groups of the solute are hydrated by five to seven water molecules and form about four hydrogen bonds with them. The most stable bonds are nearly linear O–H(alc)···O(water) arrangments. Hydrogen bonds to O(alc) with donor water molecules exhibit less defined geometry. Water molecules hydrating the gauche hydroxyl group are more strictly localized than those for a trans one. The number of water molecules in the nonpolar region is not effected by conformational changes of the solute considering rotation either about the C–C axes or about the C–O bonds.

Introduction

1,2-Ethanediol is a very simple example of a system with possible intramolecular hydrogen bonds due to vicinal polar groups. Formation of an internal hydrogen bond in a gauche O–C–C–O conformation may be favorable, while the trans arrangement prohibits that formation. In our previous report[1] (part 1), we focused on studying the gauche–trans equilibrium of 1,2-ethanediol as the major conformational change of the molecule. To this end the most stable gauche and trans conformations, determined by

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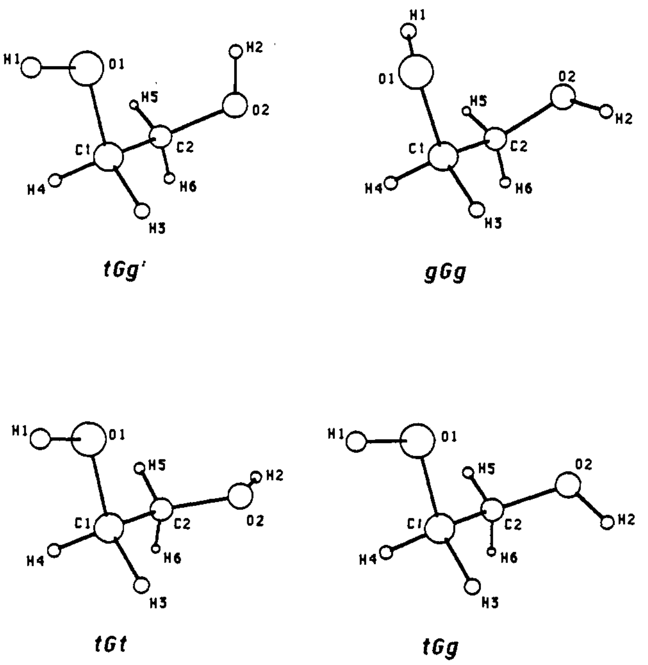

Figure 1. tGg′, gGg, tGt, and tGg conformations of 1,2-ethanediol.

ab initio calculations in the gas phase, were chosen for investigation. Using Monte Carlo simulations the relative hydration free energies were calculated in the solution phase. As a result the gauche conformers with an intramolecular hydrogen bond are considerably more stable than the trans form in both phases. The calculated ratios for the gas-phase conformers are consistent with electron diffraction, microwave and IR spectroscopic experiments.[2]

Experimental studies of the solution structure have been published.[3,4] Chidichimo et al.,[3] using NMR spectroscopy, found a gauche O–C–C–O linkage for the solute, studying the lyotropic liquid crystalline solution. Maleknia et al.[4] interpreted the Raman spectrum of an aqueous solution of 1,2-ethanediol as revealing the "virtually complete absence of any intramolecular hydrogen bonds" due to the apparent absence of a high-frequency shoulder around 3550–3660 cm^{-1} and the very broad, intense band around 3370 cm^{-1} due to intermolecularly hydrogen bonded hydroxyls. These experimental results are consistent with a gauche O–C–C–O structure having no intramolecular hydrogen bond. Our theoretical results in part 1 reflect correctly the domination of the gauche conformers over the trans one in aqueous solution, in accord with the NMR result.

The gauche conformers tGg, tGt, and gGg in Figure 1, without an intramolecular hydrogen bond, are the highest energy conformers in gas phase, as was found in ab initio calculations by Van Alsenoy et al.[5] Thus these conformations were considered as making small contributions to the equilibrium mixture. In fact, the small fraction of the trans conformer computed in the equilibrium solution, in accordance with the experiment, was successful without considering the tGg, tGt, and gGg conformations. Due to the Raman experimental result we have investigated the importance of conformers without intramolecular hydrogen bonds in the equilibrium solution. Despite their high conformational energy in the gas phase, hydration may stabilize them and their contribution to the equilibrium mixture in solution may be significant. Here we report our study of the relative stabilities of the tGg, tGt, and gGg structures in gas phase and aqueous solution.

Table I. Molecular Parameters for the 6-31G* Optimized Structures[a]

	tGg	tGt	gGg	tGg′[b]
		Bond Lengths		
C1–C2	1.516	1.510	1.521	1.514
C1–O1	1.398	1.401		1.408
C2–O2	1.398		1.398	1.397
H1–O1	0.947	0.946		0.946
H2–O2	0.947		0.947	0.949
C1–H3	1.091	1.087		1.087
C1–H4	1.090	1.087		1.088
C2–H5	1.081		1.085	1.088
C2–H6	1.090		1.089	1.083
		Bond Angles		
H1O1C1	109.77	109.75		110.24
H2O2C2	109.80		109.93	107.76
O1C1C2	109.12	108.86		106.72
O2C2C1	113.66		113.18	111.34
H3C1C2	109.57	108.71		109.54
H4C1C2	108.59	108.92		110.24
H5C2C1	109.10		110.07	109.13
H6C2C1	108.60		108.91	109.96
H3C1O1	110.97	111.38		110.73
H4C1O1	111.20	110.73		111.02
H5C2O2	106.24		105.87	111.06
H6C2O2	111.06		111.47	107.18
		Torsion Angles		
H1O1C1C2	−178.26	−166.22		−170.90
O1C1C2O2	63.99	72.63	49.01	60.56
H2O2C2C1	59.09		43.99	−53.92

[a] Distances in angstroms, angles in degrees. The structural parameters for tGg are give in a sequence of t, g. Conformers tGt and gGg are of C_2 symmetry. [b] Reference 1.

Table II. Vibrational Frequencies in cm^{-1} (6-31G* Basis Set)[a]

	tGg	tGt		gGg		tGg′[b]
1	142.5	176.6	a	120.2	a	189.0
2	267.3	204.9	a	121.9	b	290.6
3	293.3	211.7	a	305.9	a	350.9
4	361.7	363.4	a	338.4	a	457.5
5	556.1	540.4	b	582.9	b	569.6
6	945.4	958.4	a	948.6	a	954.9
7	987.6	1007.2	b	971.5	b	975.8
8	1146.0	1154.6	a	1149.4	a	1170.5
9	1208.3	1204.8	b	1211.7	b	1209.5
10	1244.3	1234.6	a	1254.7	a	1241.5
11	1300.7	1329.5	b	1267.1	b	1273.7
12	1375.9	1377.4	a	1410.1	a	1384.2
13	1437.2	1425.7	b	1456.4	a	1416.9
14	1511.9	1448.0	a	1507.9	b	1516.2
15	1567.1	1580.5	b	1568.3	b	1565.7
16	1622.5	1642.2	a	1594.9	a	1613.3
17	1652.4	1664.1	b	1666.5	b	1658.1
18	1670.9	1666.7	a	1671.7	a	1669.5
19	3150.7	3169.3	b	3176.9	b	3189.3
20	3177.2	3190.9	a	3195.6	a	3198.7
21	3193.3	3219.7	a	3233.8	a	3234.0
22	3296.5	3236.6	b	3256.7	b	3278.3
23	4103.8	4123.0	b	4102.9	b	4094.5
24	4116.3	4123.5	a	4103.7	a	4122.8

[a] Normal modes of the vibrations are indicated for tGt and gGg with C_2 symmetry. [b] Reference 1.

The method used follows that in part 1.[1] The gas-phase conformational free energy was calculated by using results from the MP2/6-31G*//6-31G* calculations. The relative solvation free energy was computed with Monte Carlo simulations and statistical perturbation theory.[6] Analysis of the solution structures around the solute in the tGg, tGt, and gGg conformations was carried

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Table III. Energy Contributions Relative to the tGg′ Conformer (in kcal/mol)[a]

	tGg	tGt	gGg
HF	4.20	3.76	3.42
MP2	4.65	4.45	3.55
ZPE	−0.38 (−0.42)	−0.48 (−0.53)	−0.52 (−0.58)
MP2 + ZPE	4.27	3.97	3.03
thermal corrections (T = 298 K)			
H	0.17 (0.17)	0.26 (0.27)	0.32 (0.34)
$-TS$	−0.43 (−0.42)	−0.21 (−0.19)	−0.55 (−0.53)
G	−0.26	0.05	−0.23
MP2 + ZPE + G	4.01	4.02	2.80
ΔG_{solv}	−5.23 ± 0.27 (−5.12 f, 5.34 b)	−3.40 ± 0.31 (−3.61 f, 3.19 b)	−0.24 ± 0.41
ΔG_{tot}	−1.22 ± 0.27	0.62 ± 0.31	2.56 ± 0.41

[a] Energies for tGg′ in the gas phase: HF = −228.925 725 au, ZPE = 0.092 551 au, MP2 = −229.540 613 au. Values in parentheses are calculated by using unscaled frequencies. Letters f and b stand for the forward and backward simulations for the relative solvation free energy.

Table IV. Coordination Numbers, Number of Hydrogen Bonds, and Hydration Sphere Data

	Ot/Ow	Og/Ow	Ot/Hw	Og/Hw	Ht/Ow	Hg/Ow
tGg	3.8	2.9	1.4	1.5	0.9	1.0
tGt[a]	3.5–3.7		1.8–1.9		0.9–1.0	
gGg[b]	2.6–2.9		1.3–1.6		0.9–1.0	

	$E \leq E_{\text{min}}$	$E \leq -0.25$	$E \geq 1.00$	$\sum$O/Ow
tGg	4.4	58.4	1.3	6.6
tGt	4.2	53.5	1.3	7.1
gGg	4.0	46.6	1.2	5.6
tGg′[c]	3.5	49.7	0.8	6.4

[a] For the tGt conformer Hg and Og correspond to Ht and Ot, respectively. [b] For the gGg conformer Ht and Ot correspond to Hg and Og, respectively. [c] Reference 1.

Table V. Average Bond Lengths, Bond Angles, and Torsion Angles for the Intermolecular Hydrogen Bonds in the Hydrated 1,2-Ethanediol[a]

	tGg	tGt[b]	gGg[c]
O(w)···Ht	1.84 (58%)	1.82 (72%)	1.84 (83%)
O(w)···Hg	1.84 (89%)	1.86 (71%)	1.87 (70%)
H(w)···Ot	1.86 (35%)	1.80 (40%), 1.90 (36%)	1.81 (46%)
H(w)···Og	1.80 (49%)	1.92 (48%), 1.84 (37%)	1.82 (33%)
O(w)···Ht–O	173°	175°	171°
O(w)···Hg–O	175°	176°	175°
O–H(w)···Ot	172°	168°, 165°	171°
O–H(w)···Og	165°	162°, 168°	167°
O(w)··(H)Ot–C–C	−174°	−169°	49°
O(w)··(H)Og–C–C	57°	−169°	48°
O(w)(H)··Ht–Ot–C	160°	−142°, 141°	−156°
O(w)(H)··Hg–Og–C	148°	−118°, 173°	−145°

[a] The percent in parentheses is the fraction of snapshots with water in this position. [b] g corresponds to t in tGt. [c] t corresponds to g in gGg. Bond distances in angstroms. For designating the solute atoms see Figures 6–8.

out by interpretation of radial distribution functions, energy pair distributions, and statistical averaging of water positions in the first hydration shell.

Methods and Calculations

Both the ab initio and Monte Carlo calculations used have been described.[1] Here only the main points and departures from the previous study are mentioned.

The geometries of the tGg, tGt, and gGg conformers (Figure 1) were optimized by using the 6-31G* basis set and the UNIX version of the Gaussian '86 program package[7] running on a Gould NP1 computer. Normal frequencies and MP2 energies were determined by using these optimized geometries. Zero-point energies and H, S, and G at T = 298 K were calculated by using scaled frequencies with a scaling factor of 0.9. The results are summarized in Tables I–III.

Monte Carlo simulations were carried out for N,P,T ensembles with one solute and 262 water molecules at 298 K and 1 atm. The 12-6-1 OPLS potential function was applied with the parameterization of Jorgensen for alcohols.[8] The free energy perturbation calculations transformed tGg′ to tGg and tGt in eight steps each, by rotating the C–O bond and transforming the ab initio geometry parameters. Both forward and backward calculations were carried out by using double-wide sampling. tGt was the starting conformation and was transformed into gGg in six steps in a forward simulation. Intermediate points were obtained considering 2000K configurations in the equilibrium phase and 3000K configurations in the averaging phase. Radial and energy pair distribution functions for the tGg, tGt, and gGg conformers were obtained after considering 4500K configurations in the equilibration and averaging phases each (Figures 2–5 and 9). Calculated average values of coordination numbers, number of hydrogen bonds, and geometric data of the first hydration spheres are given in Tables IV and V. Thermodynamic data of solvation, in relation to the solution structure, are summarized in Table VI.

Results and Discussion

Molecular Structure and Equilibrium. Geometric data for the optimized structures (Table I) indicate that by breaking the intramolecular hydrogen bond, the two H–O–C segments become nearly equivalent. This is trivial for the tGt and gGg conformers with C_2 symmetry. Most of the pairs of bond lengths and angles are nearly equal also in the tGg form. The C–O bond lengths found earlier[1] are 1.408 and 1.409 Å in tGg′ and gGg′, respectively, for the acceptor oxygens. This bond is considerably shorter, 1.398 Å, in tGg without an internal hydrogen bond. The same value was found for the C–O bond length bearing the gauche hydrogen atom. The C–O bonds are 1.401 Å in tGt and 1.398 Å in gGg. In the rest of this paper the Og and Hg symbols will be used for

Table VI. Computed Thermodynamic Data of Solvation[a]

	tGg′	tGg	tGt	gGg
H	−2661.2 ± 1.9	−2665.5 ± 2.5	−2662.8 ± 2.7	−2667.6 ± 2.3
ΔH		−4.3 ± 3.1	−1.6 ± 3.3	−6.4 ± 3.0
ΔG		−5.2 ± 0.3	−3.4 ± 0.3	−0.2 ± 0.4
$T\Delta S$		0.9 ± 3.1	1.8 ± 3.3	−6.2 ± 3.0
E_{SX}	−31.4 ± 0.4	−43.4 ± 0.5	−39.8 ± 0.4	−34.3 ± 0.4
ΔE_{SX}		−12.0 ± 0.6	−8.4 ± 0.6	−2.9 ± 0.6
ΔE_{SS}		7.7 ± 3.2	6.8 ± 3.4	−3.5 ± 3.1
DM (gas)	2.70	3.51	1.69	1.68
DM (sol)[b]	3.14	4.33	2.12	1.96

[a] Relative values refer to the tGg′ conformer. Energy in kilocalories per mole, dipole moments in debye. [b] Atomic charge parameters for the 1,2-ethanediol solute result in dipole moments for the conformers consistently larger by about 20% than the values obtained from the ab initio wave function for the isolated molecule in the gas phase.

the OH group with gauche hydrogen and Ot and Ht with the trans hydrogen. The small difference found for the O–H bonds in tGg′ (0.946 and 0.949 Å) disappear in the conformers studied here, where the O–H bond lengths are 0.946–0.947 Å. There is, however, a remarkable C–C bond shortening in tGt, 1.510 Å, in comparison with 1.521 Å in gGg.

All H–O–C angles are 109.8–109.9° for the three conformers. The O–C–C angles differ by 4.5° in tGg but the Ot–C–C angles are close in tGg and tGt and the Og–C–C angles in tGg and gGg. Corresponding torsion angles differ moderately in all three conformers. While Ht has an almost perfectly trans position in tGg, it is rotated by about 14° in tGt. Hg is in a nearly ideal gauche position in tGg, but it is rotated by 15° toward an eclipsed position in gGg. Also there are gradual changes in the O–C–C–O torsion angle values when going from gGg (49°) to tGt (73°). To avoid the repulsion of the oxygen lone pairs, the tGt structure is most torsioned about the C–C bond, as might be expected. The relatively short C–C bond is, therefore, surprising. In gGg the O–C–C–O torsion angle is the smallest within the series (Table I). This way the hydrogen atoms can approach the lone pair regions of the other oxygen that may stabilize the conformation.

Our rigid model in the Monte Carlo simulations prohibits evaluating the change in the solute geometry upon hydration. Palinkas et al.[9] considered methanol–water mixtures using flexible molecular models in molecular dynamics calculations. The change in the methanol geometry due to hydrogen bond formation was considered in liquid methanol as compared to the gas-phase structure.[9a] The O–H bond length increases by about 0.02 Å, while increases of the other bonds are of 0.001 Å. The decrease in the HOC bond angle is about 1°. These values are larger than the changes in the bond lengths and bond angles for the 1,2-ethanediol conformers in Table I (see t and g hydrogens), indicating that the solute geometry is more effected by the solvent environment than by conformational changes in the hydrogen bond region. These geometry changes are negligible in considering the solution structure in the nearest environment of the solutes but may slightly influence the relative solute internal energies.

The normal frequencies (Table II) are similar to those of the previous conformers and, after scaling, are generally within the range found experimentally (Table II in part 1). The lowest frequencies show, however, a definite decrease when compared to those in tGg′ (see below).

Hartree–Fock energies (Table III) are high in comparison with the tGg′ energy. The relative energies are 4.20, 3.76, and 3.42 kcal/mol for tGg, tGt, and gGg, respectively. Considering electron correlation, the MP2 values are even higher: 4.65 kcal/mol for tGg, 4.45 kcal/mol for tGt, and 3.55 kcal/mol for gGg. Thus the same tendency was found here as in the case of tTt[1]: consideration of electron correlation stabilizes the internally hydrogen bonded system with respect to conformers without it. Zero-point corrections are −0.4 to −0.5 kcal/mol. The negative sign is mainly due to the considerably decreased lowest normal frequencies. They contain those of the H–O–C–C and O–C–C–O torsions that are released by removing the hydrogen bond. At the same time there are only small or moderate changes in the O–H stretching frequencies (highest two values in Table II).

As a result, the relative MP2 + ZPE(scaled) values are 4.27, 3.97, and 3.03 kcal/mol for tGg, tGt, and gGg, respectively, not very different from the corresponding Hartree–Fock values. These relative values are lowered by 1.3–2.2 kcal/mol when compared to those of Van Alsenoy et al.[3]

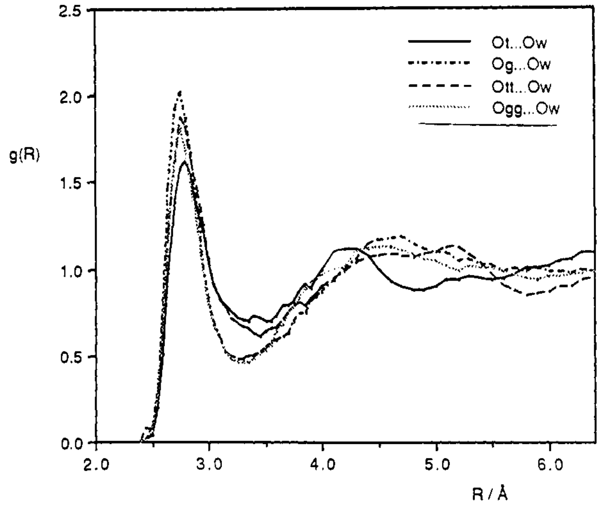

Figure 2. O···O(w) radial distribution functions. Solid line tGg, *t*-OH; dash–dot line tGg, *g*-OH; dashed line tGt (average); dotted line gGg (average).

Thermal corrections, affecting rather the energy of conformers with a gauche hydrogen, are of some tenth of a kilocalorie per mole with a compensating effect from the enthalpy and entropy. As a result, the relative free energies of both the tGg and tGt conformers are 4.0 kcal in the gas phase, while that of gGg decreases to 2.8 kcal/mol.

Relative solvation free energies are −5.2 kcal for tGg and −3.4 kcal/mol for tGt. These are the means of the forward and backward simulations that differed by less than 0.4 kcal in any case. The accuracy of the relative free energy calculated along a single path is 0.3 kcal, in good accord with the value of ±0.2 kcal/mol obtained from the forward and backward calculations.

Thus, in solution, the tGg′ is intermediate in free energy to tGt and tGg, with tGt being 0.62 kcal/mol higher in free energy and tGg being 1.22 kcal/mol lower. The relative free energy for the gGg conformer is 2.56 kcal/mol. Considering that the gGg′ conformer has a free energy of −0.66 kcal/mol relative to tGg′,[1] in solution tGg is preferred by 0.56 kcal/mol with respect to gGg′.

These results are consistent with an equilibrium mixture with the following fractional concentration of conformers at 298 K: tGg 63.7%, gGg′ 24.7%, tGg′ 8.1%, tGt 2.9%, tTt 0.5%, gGg 0.1%. Thus 99.5% of the conformers existing in the aqueous solution are in a gauche conformation and 66.7% of the equilibrium mixture is without an intramolecular hydrogen bond. This conclusion is consistent with the experimental results for the 1,2-ethanediol conformation in solution. Chidichimo et al.[7] in their NMR investigations concluded a O–C–C–O gauche conformer is dominant in the lyotropic liquid crystalline solution, and Maleknia et al.[4] proposed that this gauche conformer probably does not have intramolecular hydrogen bonds in aqueous solution. Our calculations support the results. Thus, of the conformers investigated, the tGg is the dominant conformer in aqueous solution.

In a study taking into account the solvation of the 1,2-ethanediol conformers,[10] performed with the solvent described as a continuous dielectric medium,[11] the ordering of the solvent effect on the various rotamers (tGg > tGt > gGg > gGg′ > tTt > tGg′) turned out to be analogous to that obtained by using the free energy perturbation method for all the conformers considered here and in part 1, with an inversion of gGg and tTt. The rationale of this result is related to the shape of the solvent reaction field acting on the solute. In the case of the tTt rotamer the oxygen atoms point toward different and opposite regions of the cavity surface, giving rise to a quadrupolar-like reaction field, which thus produces a weak effect on the solute. On the contrary, when the lone pairs of both oxygens are directed toward close regions of the cavity surface, the solvent electrostatic effect is reinforced and the reaction field shows a decidely strong dipolar trend[12] that produces

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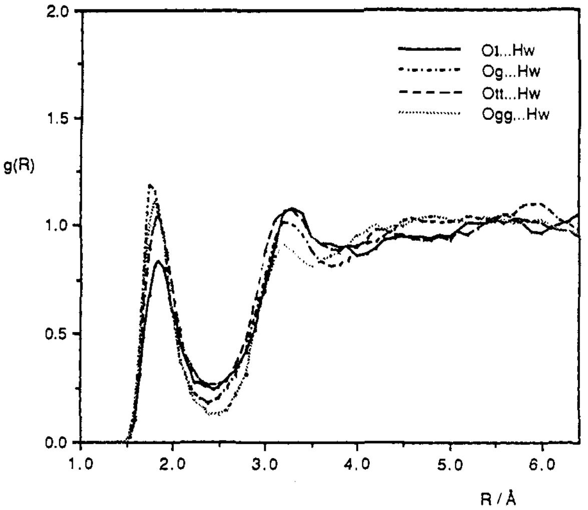

Figure 3. O···H(w) radial distribution functions. For the meanings of the lines see Figure 2.

a noticable solvent stabilizing effect, as in the tGg and tGt cases.

The magnitude of the solvent stabilizing effect on the tGg rotamer obtained by employing the continuum, however, is not sufficient to make the tGg solvated species more stable than the tGg′ one, because of the large vacuo energy group.

Interestingly, the tGg′, gGg′, and tGg conformers turn out to be the most stable conformers with either method: the free energy perturbation method predicts the tGg conformer to be the most stable, whereas the continuum model favors the gGg′ conformer.

Solution Structure and Solvation Thermodynamics. The general shapes of the radial distribution functions for tGg, tGt, and gGg are rather similar to those for tTt, tGg′, and gGg′ in part 1. There are small differences in the locations of extrema and in the $g(R)$ values at these points.

The O···O(w) radial distribution functions (Figure 2) show that the water oxygens are more ordered around Og than Ot in tGg. Both peaks are at 2.75–2.80 Å, but the heights are different: 2.0 for Og and 1.6 for Ot. The minimum for Og is deeper and is at a shorter distance, $R = 3.3$ Å, than the poorly defined one for Ot in the R range of 3.4–3.6 Å. As a result there are 2.9 more strongly localized water molecules in the first hydration shell of Og and 3.8 water molecules around Ot (Table IV). Peak values of the radial distribution functions at 2.75 Å are similar for tGt and gGg, with a $g(R)$ of about 1.8. The minima are at 3.6 Å for tGt and 3.3 Å for gGg. As a result the first hydration shells for tGt have 3.5–3.7 water molecules around each oxygen and there are 2.6–2.9 water molecules around the oxygens of the gGg conformer. Broad second bands are there in the 4-5-Å range, having contributions from the second hydration shell of the O atoms and the first shells of the CH_2 groups (Figure 9). The more definite second peak for Ot in tGg is considered a contribution from water molecules in Og–Hg···Ow hydrogen bonds. The absence of the corresponding peak for Og may be explained by the less stable hydrogen bond formation around the trans hydroxyl group in tGg. (See Table V and discussion later.)

O···H(w) (Figure 3) and H···O(w) (Figure 4) radial distribution functions have first peaks at 1.8–1.9 Å with, however, considerably different peak values. Highest peaks are for Og and Hg and the lowest ones for Ot and Ht in tGg. The Hg··O(w) peak for tGg is 1.7; the peak value for Og···H(w) is 1.2. This indicates a ~50% greater probability of finding a water molecule in the Og–Hg···Ow position than in the Og···H–O(w) form. This difference is less pronounced for the Ot and Ht atoms. The characteristic second peaks were discussed earlier.[1] These peaks have contributions from the second hydrogen atom of the connecting water molecule (Figure 3) or from the neighboring O···H–O(w) hydrogen bond (Figure 4). The coordination numbers were obtained by integrating the curves up to the first minima

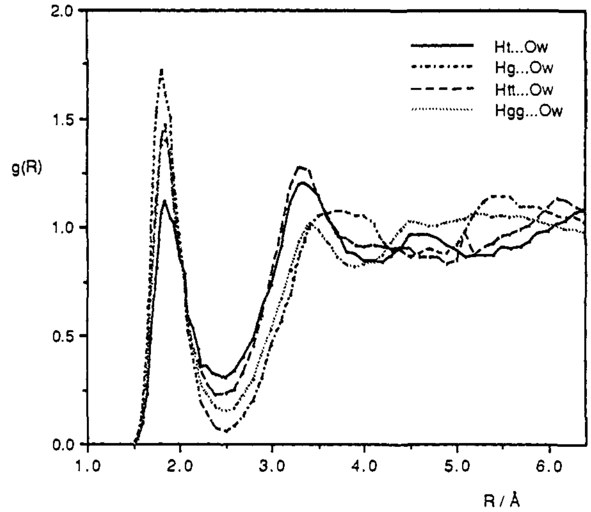

Figure 4. H···O(w) radial distribution functions. For the meanings of the lines see Figure 2.

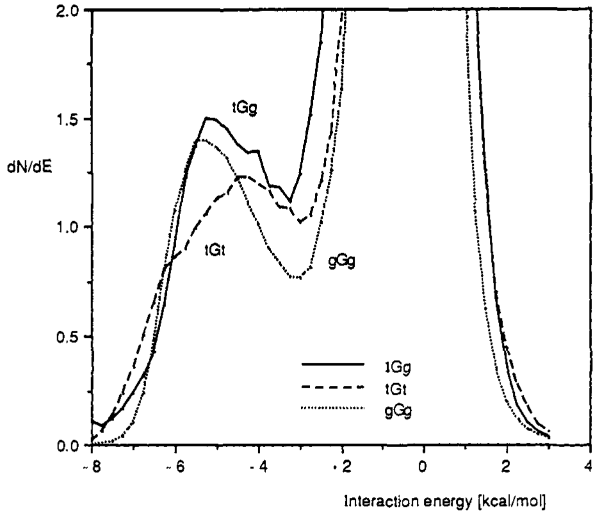

Figure 5. Solute–solvent pair interaction energy distribution for the tGg, tGt, and gGg conformers of 1,2-ethanediol.

at 2.4–2.5 Å. Hydration of the hydrogen atoms by water oxygens gives coordination number of uniformly 0.9–1.0 (Table IV). This suggests one O–H···O(w) hydrogen bond at each site. Each solute oxygen is hydrated by 1.4–1.5 water hydrogens in tGg. This value is 1.8–1.9 for tGt and 1.3–1.6 for gGg. Since their location sites are less definite than those for the acceptor water oxygens (Table V), one may not expect hydrogen bonding by all of them. This is the reason the number of the hydrogen bonds is lower than the number of the water oxygens in the first hydration shells.

The numbers of the hydrogen bonds were determined by integrating the pair energy distribution functions (Figure 5) up to their minima at −3.25 kcal/mol for tGg and at −3.00 kcal/mol for tGt and gGg. The calculated values are 4.4, 4.2, and 4.0, respectively (Table IV). The pair interaction energy is more confined into a range for tGg and gGg with gauche hydrogens. The distribution function for tGt is flatter with a smaller peak value, allowing a more diverse energy distribution. Also the site of the peak for tGt is shifted to the less negative values. This means that the water–solute interaction is more restricted to an energy interval and probably to a spatial domain with gauche than with the trans hydroxyl group. It was reflected in the findings that all values of the radial distribution functions are higher for the gauche than for the trans OH group.

Snapshots support the above interpretation. Figure 6 shows the water molecules closest to the oxygens in the tGg conformation. There are two water molecules around Og and four connecting to Ot. There are seven hydrogen bonds shown with five of them

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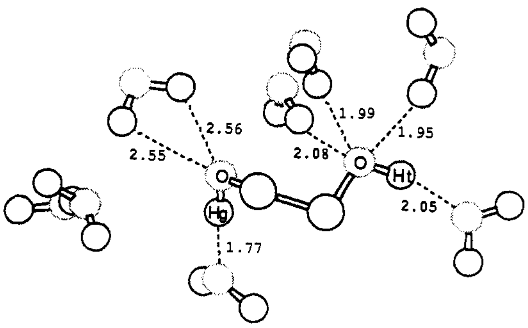
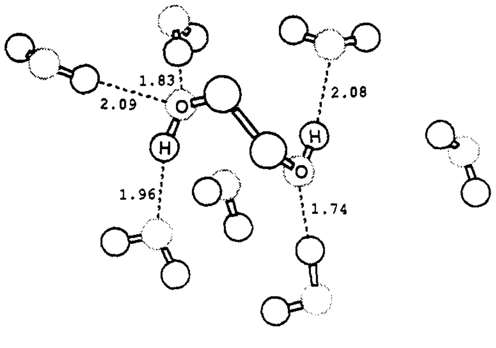


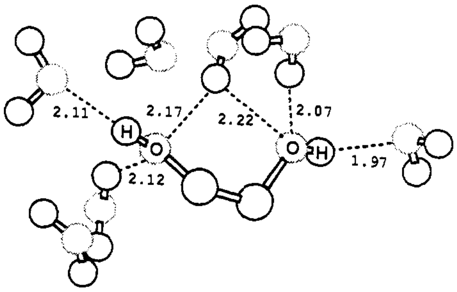
tGg

Figure 6. Snapshot for the tGg conformer with water molecules satisfying criterium O(alc)··O(water) ≤ 3.5 Å.



gGg

Figure 7. Same as Figure 6 for gGg.



tGt

Figure 8. Same as Figure 6 for tGt.

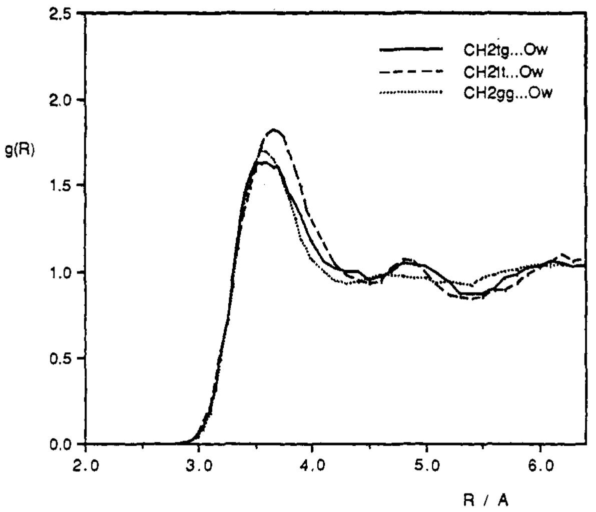


Figure 9. CH_2···O(w) radial distribution functions, averaged for the two CH_2 groups. Solid line, tGg; dashed line, tGt; dotted line, gGg.

close to 2 Å. Both solute hydrogens are bonded to a single water oxygen. The difference in the hydration numbers comes from the different numbers of the donor water molecules. The snapshot is in accord with 0.9 and 1 water molecules calculated for hydrating Ht and Hg, respectively, and the larger Ot/Ow than Og/Ow coordination number in Table IV. The snapshot for gGg (Figure 7) correctly reflects a water molecule in an O–H···Ow hydrogen bond for each hydroxyl. Three donor water molecules bonded to the two solute oxygen atoms are in good agreement with the calculated average value of 2.6–3.2 in Table IV. The total of five water molecules in the first hydration shells of the polar functions of the solute is also in agreement with the calculated average value of 5.6. The tGt snapshot (Figure 8) shows a hydration scheme of correct C_2 symmetry. There are five water molecules hydrogen bonded to the solute. One of them in a bridge position. Thus it belongs to both hydroxyl groups and might be counted twice in the sum O/Ow in Table IV. This means that the total number of water molecules in the first shells of the OH groups is probably less than 7 and may be closer to our previous value of 6 and to the value for tGg. The hydrogen bond distances are generally longer than most O···H distances in the tGg snapshot. It should mean weaker bonds for tGt explaining the shift of the peak of the energy pair distribution function toward a less negative value. At the same time the rather uniform hydrogen bond distances are contrary to a diverse energy pair distribution found for tGt. This points out the limited utility of a single snapshot in explaining average values or distributions.

To overcome the above 4500 snapshots were considered for determining average intermolecular bond lengths, bond angles, and torsion angles with the water molecules in the first hydration shells (Table V). The averaging procedures was the same described earlier.[1] It was found here, in accord with the previous results, that the O–H···O(w) bond is more stable than the O-(alc)····H–O(w) bond. The population for the former, 58–89%, was significantly higher for all three conformers than that of the O···H–O(w) type hydrogen bond, 33–49%. Also, hydration of the gauche OH by acceptor water is favored compared to that of a trans conformer.

O··H··O bond angles are nearly linear. There are a few departures of 5–15° from linearity. Torsion angles are least well defined. Values obtained for the acceptor waters confirm the near linearity for the O–H···O(w) bond. Oxygens of the donor water molecules are in the lone pair regions of the alcoholic oxygens (±120°) but considerable departures are easy. This is in line with the relatively low populations of their average positions.

The radial distribution functions characterizing the nonpolar regions of the three conformers (Figure 9) show only small differences when compared to the corresponding functions for tTt, tGg′, and gGg′. Sites of maxima and minima differ, if at all, by about 0.1 Å. The calculated number of the water molecules is between 10 and 11, considering 4.5 Å for the hydration shell radius around one CH_2 group. The first water shells of the nonpolar groups should contain fewer than 2 × 10.5 = 21 water molecules due to the strong overlap of the CH_2 hydration spheres. (The C–C separation is 1.5 Å as compared to 4.5 Å, the hydration shell radius.) Since similar values were obtained by using the radial distribution functions for tTt, tGg′, and gGg′, it may be concluded that the solvent structure is little effected in the nonpolar region either by the G to T rotation or by breaking or forming intramolecular hydrogen bonds.

Solvation thermodynamic data (Table VI) show that the free energies of the tGg, tGt, and gGg conformers relative to tGg′ are basically determined by their relative solute–solvent interaction energies, ΔE_{SX}. Contrary to our previous finding for tTt and gGg′, where ΔE_{SX} amounted to only about 1 kcal/mol, the E_{SX} differences for the present conformers are 3–12 kcal/mol. ΔE_{SX} is −12.0 kcal/mol for tGg, where the number of hydrogen bonds is larger by 0.9 units as compared to tGg′ (Table IV). The number of water molecules in attractive interactions ($E \leq -0.25$ kcal/mol) is 58, the largest value within the series, and is related to the largest dipole moment for tGg (Table VI). ΔE_{SX} for gGg is −2.9 kcal/mol. The number of hydrogen bonds is larger by 0.5, and the number of the water molecules in attractive interactions is lower by 3 than those for tGg′. Thus it is concluded for the conformers studied here that the number of the waters hydrogen bonding to the solute is a more important parameter in defining the sign of ΔE_{SX} and of ΔG than the number of the water molecules in attractive interactions. For the tGt conformer the two effects act in the same direction, resulting in considerable stabilization by 8.4 kcal/mol for ΔE_{SX} and by 3.4 kcal/mol for ΔG.

While trends in ΔE_{SX} and ΔG are in line with the solution structure parameters, no correlation to these parameters was found considering the ΔH, $T\Delta S$, and ΔE_{SS} (solvent reorganization) terms in Table VI. The values obtained by direct comparison of the H values for solutions after considering 4500K configurations show large relative errors for the ΔH, $T\Delta S = \Delta H - \Delta G$, and $\Delta E_{SS} = \Delta H - \Delta E_{SX}$ terms. These errors make uncertain even the sign of the above terms for the tGg and tGt conformers. Results obtained in the perturbation calculations showed poorly converged values after considering 3000K configurations in the subsequent steps. Despite the uncertainty in the $T\Delta S$ values for tGt and gGg, more positive entropy, thus a less ordered solution structure, is expected when the solute is in the tGt rather than in the gGg conformation. On the contrary, the radial distribution functions are similar around the first peaks for these conformers (Figures 2-4 and 9). The number of hydrogen bonds to the solute and the number of the water molecules in the first hydration shell, where the water molecules are expected to be strongly bound to the solute, are larger for tGt than gGg (Table V). This suggests a more ordered structure for tGt, contrary to the above interpretation of the entropy values. So we consider the calculated entropy difference as characterizing the differences in the bulk solution structure and not directly correlating with the first hydration shell structure parameters. The effect that dominates the relative entropies of the solutions with these two conformers may be determined by the solvent-solvent interactions rather than solute-solvent interactions.

Conclusions

In studying the tGg, tGt, and gGg conformers of 1,2-ethanediol in the gas phase, it was found that these structures without intramolecular hydrogen bonds are higher in free energy by 3-4 kcal/mol than the most stable tGg′ conformer. On hydration tGg is stabilized by 5.2 kcal and becomes the dominant conformer, thus the most likely conformer in aqueous solution is an O-C-C-O gauche form without intramolecular hydrogen bonding. This fits well the NMR and Raman spectroscopic experiments.

The polar groups of the solute are hydrated by five to seven water molecules and form about four hydrogen bonds with them. The most stable bonds are the nearly linear O-H(alc)···O(water) ones. Hydrogen bonds to O(alc) with donor water molecules are much more mobile. Water molecules hydrating a gauche hydroxyl group are more strongly localized than those for a trans one. The number of water molecules in the nonpolar region is insensitive to conformational changes of the solute considering rotation either about the C-C axes or about the C-O bonds.

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Registry No. 1,2-Ethanediol, 107-21-1.

Cyclopentadienylideneketene: Theoretical Consideration of an Infrared Spectrum Frequently Mistaken for That of Benzyne

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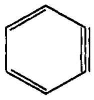
Abstract: Ab initio molecular quantum mechanics has been applied to the cyclopentadienylideneketene molecule, a C_7H_4O isomer. Until very recently, it was thought that this molecule had not been observed spectroscopically. However, recent experiments appear to show that an infrared feature near 2085 cm^{-1} (and often attributed to benzyne) is due to cyclopentadienylideneketene. Here the structure of the latter molecule has been optimized using three theoretical methods, including second-order perturbation theory with a triple-ζ plus double-polarization (TZ2P) basis set. Harmonic vibrational frequencies and infrared intensities have also been evaluated, and the ketene C=C plus C=O stretch is indeed consistent with the 2085-cm^{-1} assignment previously identified with benzyne.

Introduction

o-Benzyne has been an important molecule in the history of physical organic chemistry. Most respected contemporary organic chemistry texts[1-3] are in agreement, on the basis of the infrared spectrum, that the triple-bond valence structure



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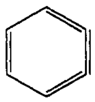
is more important than other possibilities, such as



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The section in Vollhardt's text[2] entitled "Benzyne is a Strained Cycloalkyne" summarizes the current understanding.

The basis for the identification of benzyne with the triple-bond structure **1** is a series of independent experiments[4-9] that yielded

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