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Bifurcated vs. Linear Hydrogen Bonds: Dimethyl Phosphate and Formate Anion Interactions with Water

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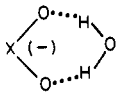
Abstract: We present molecular mechanical and quantum mechanical studies of the interactions of H_2O with dimethyl phosphate $(CH_3O)_2PO_2^-$ and formate $HCOO^-$ anions. In contrast to the results suggested earlier on the basis of STO-3G ab initio calculations on dimethyl phosphate$\cdots$water interactions, molecular mechanics and 4-31G ab initio calculations show that the bifurcated two hydrogen bonded geometry of H_2O is more stable than the optimal linear H-bonded structure for $(CH_3O)_2PO_2^-\cdots H_2O$. A parallel study on $HCOO^-\cdots N_2O$ shows that the preference for the bifurcated structure is found there as well. The reason for the failure of the STO-3G basis set to predict the correct geometry lies in its poor representation of charge transfer energies. For $HCOO^-\cdots H_2O$, we also carried out extended basis set 6-31G** correlation calculations (MP2) to confirm the greater stability of the bifurcated geometry as well as carrying out Morokuma component analyses to further elucidate its nature.

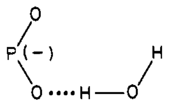
Introduction

The question of "bifurcated" vs. "linear" hydrogen bonds has been of interest to structural chemists and theoreticians for some time. The central question has been: under what circumstances (if any) will bifurcated hydrogen bonds be preferred over linear ones? In the case of the water dimer[1] all ab initio studies find the linear dimer more stable than the bifurcated. Umeyama and Morokuma[2] have carried out energy component analyses on bifurcated and linear $(H_2O)_2$ and find the linear dimer greater stability to lie in its more favorable electrostatic and charge transfer components, compensated by its less favorable exchange repulsion. Thus, in the water dimer, the bifurcated structure is less stable than the linear and we know why. However, the relative instability of the bifurcated water dimer is likely to be related to the large deviation of its O–H$\cdots$O angles from the ideal 180° value.

In the case of a water molecule interacting with the biologically very important phosphate and carboxylate anions, the situation is not so clear, since the two water hydrogens can interact with a different anionic oxygen and the geometry for this "bifurcated"



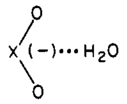
structure might be quite favorable. However, there is some evidence in the literature that, in the case of dimethylphosphate$\cdots H_2O$, such a bifurcated structure is (1–2 kcal/mol) less stable than a linear



structure. Pullman et al.[3,4] have carried out ab initio calculations on dimethylphosphate $(DMP^-)\cdots$water interactions using an STO-3G basis set, and have found a linear H-bonded structure to be more stable than a bifurcated one for $DMP^-\cdots H_2O$.

We had begun a study of the aqueous solvation of DMP^- by Monte Carlo techniques[5] and, in the course of testing our simple molecular mechanics potential for $DMP^-\cdots H_2O$ interactions,[5] we found that no matter what our choice of partial atomic charges (within reason), the bifurcated structure was more stable than the linear by 3–5 kcal/mol. We thus decided to reexamine the results of the study of Pullman et al.[4] using a more extended (4-31G basis set). As a preliminary test case we studied $H_2PO_4^-\cdots H_2O$ with both STO-3G and 4-31G basis sets. At STO-3G, the linear geometry was more stable, as has been found in ref 4; at 4-31G, the bifurcated geometry was more stable, as had been found on molecular mechanics studies of $DMP^-\cdots H_2O$. We then confirmed that the $DMP^-\cdots H_2O$ ab initio results are essentially analogous to those for $H_2PO_4^-\cdots H_2O$. To test the generality of our results, we also studied $HCOO^-\cdots H_2O$ using a more extended basis set as well as correlation energy calculations.

The results of these calculations on the interactions of $H_2PO_4^-$, DMP^-, and $HCOO^-$ with H_2O are presented below. The calculations seem to definitely establish the bifurcated structure as the energetically more stable for



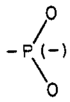
interactions.

Experimental Methods

We used the quantum chemistry program Gaussian 80 UCSF[6] in these studies. This is an extension of the Gaussian 80 designed to be version of operating system independent on a VAX 11/780 computer. It also has improvements on the original Gaussian 80 in its SCF convergence routines and also includes the facilities for Morokuma component analysis,[7] molecular properties, and electrostatic potential/point charge[8] fitting. These calculations were carried out on the Structural Biology VMS VAX 11/780 at UC, San Francisco.

Results

In Table I we present the optimum or nearly optimum (see Figure 1a and b) distance and energy found respectively in $H_2PO_4^-$ and $DMP^-\cdots H_2O$ interactions of both the bifurcated (B) and extended (E and E″) type initially considered by Pullman et al.[4] E and E″ correspond to water bound by one hydrogen bond to oxygen in the plane



E stands for water pointing roughly in the direction of the O lone-pair external to ∠OPO angle; E″ water points in the direction

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Table I. Monohydration of $H_2PO_4^-$ and $(CH_3O)_2PO_2^-$(DMP$^-$)

basis set	molecule	type[a]	$R_{O...H}$, Å	$-E^b$	$-\Delta E^c$
STO-3G	$H_2PO_4^-\cdots H_2O$	E	1.45	708.129106	26.96
		E″	1.45	708.127525	25.97
		B	1.75	708.125986	25.01
	DMP$^-\cdots H_2O$	E	1.47	785.296847	23.99
		E″	1.45	785.298233	24.86
		B	1.75	785.296848	23.99
4-31G	$H_2PO_4^-\cdots H_2O$	E	1.70	716.451208	19.10
		E″	1.75	716.452359	19.82
		B	2.05	716.456293	22.29
	DMP$^-\cdots H_2O$	E	1.75	794.376955	17.95
		E″	1.75	794.379717	19.68
		B	2.10	794.383702	22.19
molecular mechanics[d]	DMP$^-\cdots H_2O^e$	E	1.50		16.89
		B	1.74		23.06
	DMP$^-\cdots H_2O^f$	E	1.72		14.55
		B	1.87		19.40

[a] See text and ref 4. [b] Hartrees. [c] kcal/mol. [d] Used molecular mechanics software in ref 11. [e] For DMP$^-$ charges from STO-3G electrostatic potential best fitting (ref 6); for H_2O TIPS2 model (W. L. Jorgensen, *J. Chem Phys.*, 77, 4156 (1982)). [f] For DMP$^-$ charges from STO-3G* electrostatic potential best fitting (ref 6); for H_2O as in footnote *e*. $E^b_{\textbf{STO-3G}}$: $H_2PO_4^-$ = −633.123210; DMP$^-$ = −710.295684; H_2O = −74.962928; $E^b_{\textbf{4-31G}}$: $H_2PO_4^-$ = −640.513381; DMP$^-$ = −718.440957; H_2O = −75.907391.

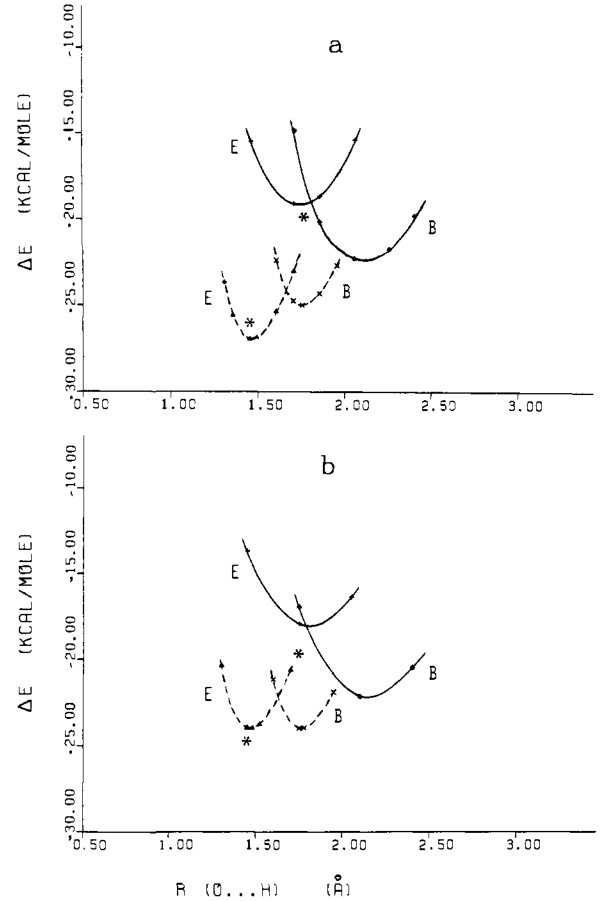
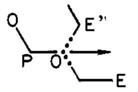


Figure 1. Interaction energy dependence on O···H separation at STO-3G (dashed lines) and 4-31G (full lines) levels for B and E type structures (see the text). The values contained in Table I for the E″ structure are displayed with a star. (a) $H_2PO_4^-\cdots H_2O$; (b) $(CH_3O)_2PO_2^-\cdots H_2O$.

of the other lone-pair. The second hydrogen in the E structure makes a dihedral angle of 0° with the P–O direction, while in the E structure the same dihedral is 180°, as depicted in the following scheme



For the phosphate anions we used the geometry computed by Newton[9] and for water we adopted 0.9572 Å and 104.52° for the bond length and angle, respectively.[10]

In contrast to ref 4 we found that the E type geometry is less stable than the E″ in DMP$^-\cdots H_2O$ interaction. This result seems reasonable, because of the greater repulsion between water H and $-CH_3$ group, in the E geometry. The results are also presented for molecular mechanics calculations[11] of the energies and structures of B and E complexes in Table I. In the case of these molecular mechanics studies, we carried out complete geometry optimization of all degrees of freedom and demonstrated that, at that level of calculation, the E structure is not a true local minimum.[12] For the ab initio calculations described in Table I, we have not determined whether the E″ structure is a true local minimum, but it is clearly more stable than the B at the STO-3G level and less stable than the B at 4-31G level.

The agreement between the results of the 4-31G calculations and the molecular mechanics is encouraging, particularly since the latter is such a simple model. Pullman et al.[4] STO-3G calculations found water interactions with the ester oxygens significantly less favorable than with the $-O^{\delta-}$ oxygens and our molecular mechanical model finds this as well.

Because we wished to further understand these results, we turned to another important ion···H_2O interaction, that of $HCOO^-\cdots H_2O$, to which one can apply a somewhat higher level of theory at a modest cost of computer time. We first studied the geometries B, E, and E″ at both the STO-3G (Figure 2a) and 4-31G (Figure 2b) level. As in the phosphate case, the internal molecular geometries have been kept constant throughout the calculations at the values previously determined by one of us.[13] The results are essentially analogous to those found for the in-

Table II. Monohydration of $HCOO^-$

basis set	type[a]	$R_{O\cdots H}$, Å	$-E^b$	$-\Delta E^c$
STO-3G	E	1.50	260.459113	25.04
	E″	1.50	260.460943	26.19
	B	1.773	260.458336	24.56
4-31G	E	1.75	263.838885	19.39
	E″	1.75	263.842843	21.87
	B	2.10	263.847634	24.88

[a] See text and ref 4. [b] Hartrees. [c] In kcal/mol. $E^b_{\textbf{STO-3G}}$: $HCOO^-$ = −185.456277; H_2O = −74.962928; $E^b_{\textbf{4-31G}}$: $HCOO^-$ = −187.900598; H_2O = −75.907391.

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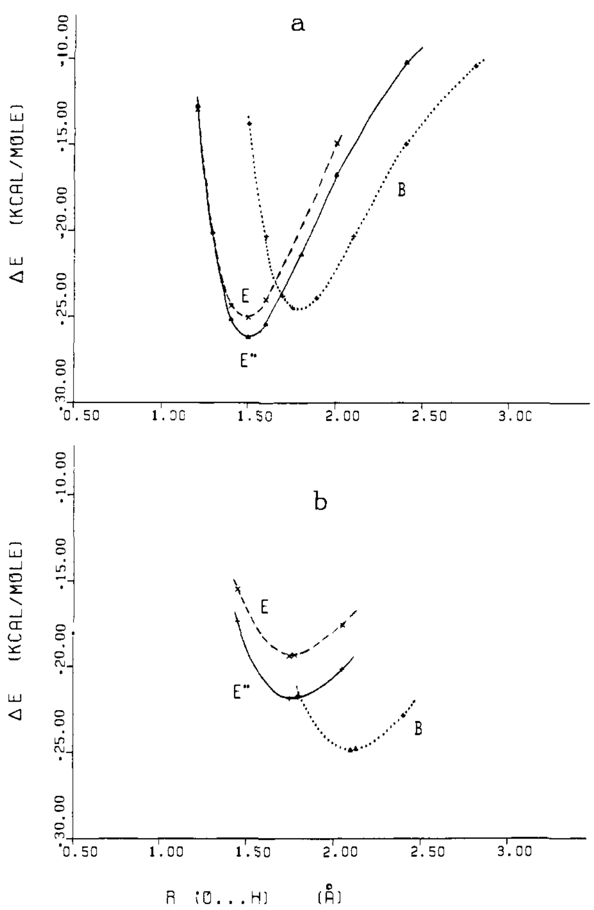

Figure 2. Interaction energy dependence on O···H separation of HCO-O^-···H_2O B (dotted line), E (dashed line), and E″ (full line) type structures. (a) STO-3G level; (b) 4-31G level.

teraction of DMP^-···H_2O, with the bifurcated structure more stable at 4-31G and the extended structure more stable at STO-3G. The results of Port and Pullman[14] with a (7s 3p/3s) basis set are consistent with our 4-31G calculations.

The next question we addressed is: why does the STO-3G basis set incorrectly exaggerate the stability of the extended compared to the bifurcated structure? The most obvious explanation is the counterpoise error,[15] since the minimum energy distances found with STO-3G are significantly (~0.3–0.4 Å) shorter than found with 4-31G and rather unrealistically small (1.45 Å for E, 1.75 Å for B; the pertinent data are shown in Table II). We thus carried out counterpoise calculations as a function of O···H separation on the E″ and B structures, and the results are presented in Table III and Figure 3. As one can see, the counterpoise correction does bring the minimum energy distances of both structures into much more reasonable agreement with the 4-31G values, but the energies still favor the extended structure by a small amount. Interestingly, the Moller Plesset (MP2) correlation[16] correction, also displayed in Table III and Figure 3, at the (most reasonable) distances of 2.1 Å for B and 1.8 Å for E″, slightly favors the B structure, even at the STO-3G level.

Table III. Energy (kcal/mol) as a Function of Distance and Basis Set for $HCOO^-$···H_2O

basis set	type[a]	$R_{O\cdots H}$, Å	$-\Delta E_{SCF}$[b]	$-\Delta E_{CP}$[c]	$-\Delta E_{MP_2}$[d]
STO-3G	E″	1.20	12.72	−10.82	13.02
		1.40	25.17	6.01	26.46
		1.50	26.19	9.53	27.57
		1.60	25.43	11.32	26.73
		1.80	21.39	12.03	22.28
		2.00	16.76	11.13	17.16
		2.40	10.21	8.61	10.02
	B	1.50	13.78	−20.31	17.77
		1.694	23.79	−0.23	26.92
		1.75	24.46	3.12	27.29
		1.89	23.90	8.49	25.95
		2.10	20.32	11.64	21.37
		2.13	19.74	11.80	20.67
		2.40	14.95	11.61	15.09
		2.80	10.38	9.61	10.04
4-31G	E″	1.45	17.37		17.73
		1.75	21.87		23.03
		1.80	21.81		23.04
		2.05	20.18		21.53
	B	1.80	21.69		23.35
		2.10	24.88		26.74
		2.13	24.81		26.67
		2.40	22.87		24.53
6 31G**	E″	1.80	18.67		20.89
	B	2.13	20.91		23.58

[a] See text and ref 4. [b] Interaction energy at the SCF level. [c] Interaction energy at the SCF level after counterpoise correction (ref 15). [d] Interaction energy at the MP2 level (ref 16). [e] Hartrees. $E^e{}_{\text{STO-3G}}$(MP2): $HCOO^-$ = −185.607928; H_2O = −74.998321; $E^e{}_{\text{4-31G}}$(MP2): $HCOO^-$ = −188.246938; H_2O = −76.035717; $E^e{}_{\text{6-31G**}}$(SCF): $HCOO^-$ = −188.180058; H_2O = −76.023163; $E^e{}_{\text{6-31G**}}$(MP2). $HCOO^-$ = −188.675955; H_2O = −76.219744.

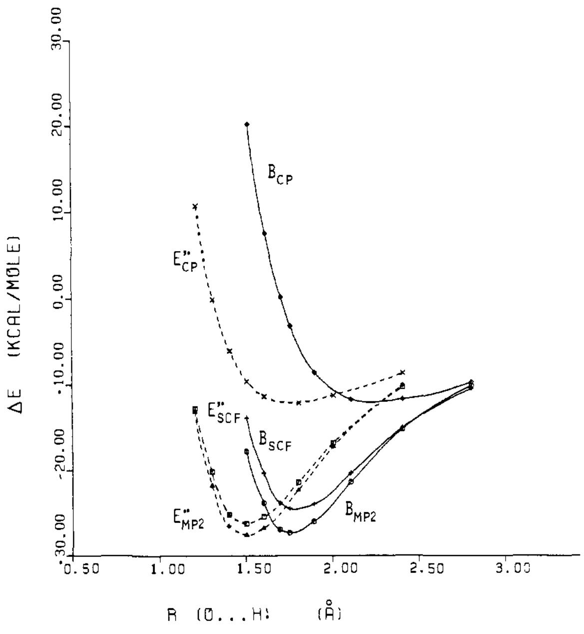

Figure 3. Interaction energy variation with O···H distance of $HCOO^-$ and H_2O at STO-3G level for B (full lines) and E″ (dashed lines) type structures. Middle curves refer to SCF results; bottom curves include MP2 correlation corrections, while top ones include counterpoise correction.

We carried out two further extensions of these results. First, at the 4-31G distances, we calculated the SCF and MP2 energies for the B and E″ geometries with a 6-31G** basis set. These results (bottom lines of Table III) corroborate those found at 4-31G; the B structure is 2.2 kcal/mol (SCF) and 2.7 kcal/mol (MP2) more stable at 6-31**, with corresponding relative energies 3.0 and 3.7 kcal/mol at 4-31G.

In an attempt to understand the nature of these interactions and to see if we could understand more clearly the failure of the STO-3G basis set to rationalize the relative energies of these structures, we carried out Morokuma component analysis calculations[7] on the $HCOO^-$···H_2O B and E″ structures at both the

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Table IV. Energy Decomposition[a] (kcal/mol for $HCOO^- \cdots H_2O$)

type[b]	E″			B		
basis set	STO-3G		6-31G**	STO-3G		6-31G**
$R_{O \cdots H}$, Å	1.50[c]	1.80[d]	1.80[d]	1.773[c]	2.13[d]	2.13[d]
E_{ES}	−25.28	−14.52	−20.93	−25.09	−15.38	−21.88
E_{POL}	−1.88	−1.52	−2.83	−0.99	−0.69	−2.02
$E_{CT(A\text{-}B)}$	−0.17	−0.05	−0.76	−0.05	−0.01	−0.26
$E_{CT(B\text{-}A)}$	−24.19	−13.79	−3.50	−24.94	−9.82	−4.03
E_{EX}	32.36	9.89	10.51	26.92	6.02	8.27
E_{MIX}	−7.03	−1.40	−1.16	−0.41	0.15	−0.99
ΔE_{tot}	−26.19	−21.39	−18.67	−24.56	−19.73	−20.91

[a] $\Delta E_{tot} = E_{ES} + E_{POL} + E_{CT} + E_{EX} + E_{MIX}$, where E_{ES} is the electrostatic interaction, E_{POL} is the polarization interaction, $E_{CT(A\text{-}B)}$ is the charge transfer from A to B and $E_{CT(B\text{-}A)}$ from B to A (A = $HCOO^-$ and B = H_2O), E_{EX} is the exchange repulsion, and E_{MIX} is the coupling term (see ref 2). [b] See text and ref 4. [c] Equilibrium distance at STO-3G level. [d] Estimated equilibrium distance at 6-31G** level. Note that these are ~0.05 Å longer than the 4-31G optimized distances listed in Table III.

STO-3G and 6-31G** level (Table IV). At the 6-31G** level, it is clear that the two major components which favor B over E″ are the electrostatic (by 0.95 kcal/mol) and exchange repulsion (2.24 kcal/mol), whereas polarization favors E″. Interestingly, the $HCOO^- \rightarrow H_2O$ charge transfer (see $E_{CT(B\text{-}A)}$) is more favorable for B, but this is almost exactly compensated by more favorable "back transfer" $HOH \rightarrow HCOO^-$ (see $E_{CT(A\text{-}B)}$) for the E″ structure.

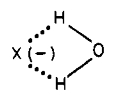
We focus on the STO-3G energy components at the 6-31G** geometries, since even there, the incorrect orderings of E″ and B are found by STO-3G. Here the electrostatic and polarization energies for E″ and B are too small in magnitude compared to the 6-31G** values, but the difference between the sum of electrostatic and polarization energies is ~0 for STO-3G and ~0.1 kcal/mol for 6-31G**. The main difference between the 6-31G** and STO-3G shows up in the charge-transfer term, which greatly favors E″ for STO-3G by ~4 kcal/mol. If one makes the (crude) assumption that the counterpoise correction just affects the charge-transfer term and we add this energy to the STO-3G charge transfer energy, we find a charge transfer energy for the E″ structure of −4.5 kcal/mol and for the B −1.9 kcal/mol. This E″ charge transfer energy is surprisingly close to the 6-31G** value, but the B value is grossly underestimated. This makes some sense physically, in that a minimal basis set would be less likely to have the flexibility to represent charge transfer in bent O–H⋯O bonds. Thus, it is both in the large counterpoise error and in the poor representation of true charge transfer that the STO-3G basis set is inadequate at differentiating the bifurcated and linear hydrogen bonded systems.

Discussion and Conclusions

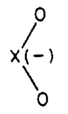
We have demonstrated, in calculations on DMP^-, $H_2PO_4^-$, and $HCOO^- \cdots H_2O$ interactions, that the minimum energy structure is bifurcated. This result was found in molecular mechanics calculations and in ab initio calculations employing 4-31G and 6-31G** basis sets; minimal STO-3G basis sets are not able to correctly reproduce this effect.

The basis for the preference of the bifurcated structure lies in its more favorable electrostatic and exchange repulsion energies (Table IV). Since its minimum energy H⋯O distances were ~0.3 Å longer than the linear H bonded E type structure, the more favorable exchange energy for the bifurcated structure is predominantly due simply to less penetration of the charge clouds at the longer distances. If one compares the bifurcated and linear structures at the longer O⋯H distance, even at the STO-3G level the electrostatic energy for the B structure is more favorable than for the E.

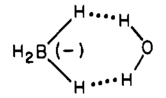
It is worth relating this result to the interaction of H_2O with F^- and Cl^-, which have been studied with extended basis sets by Kistenmacher et al.[17] and with a 4-31G basis set and simple charge models by us.[18] The minimum energy $F^- \cdots H\text{–}O$ angle is ~170°, whereas that of Cl^- is ~150°. The longer $X^- \cdots H$ distance in the $Cl^- \cdots HOH$ interaction (2.2 Å) compared to that of $F^- \cdots HOH$ (1.5 Å) obviously favors an interaction closer to the idealized ion–dipole geometry, which the bifurcated structure



is. With the two anionic oxygens in

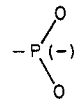


one can form such a bifurcated geometry with significantly more nearly linear and thus more favorable $O^{\delta-} \cdots H\text{–}O$ angles. We have earlier studied[18] $BH_4^- \cdots H_2O$ interactions at the double ζ level using a 4-31G basis set, and, as we would expect from the results presented here, the

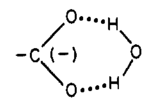


geometry is more stable than various other $BH_4^- \cdots HOH$ structures. This is further support for the generality of the greater stability of bifurcated (doubly) H-bonded structures over singly H-bonded structures when the $X^- \cdots H\text{–}O$ angles are not too far from linearity.

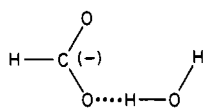
The overall significance of the bifurcated H bonds studied here is not clear. When one adds more waters to the anion, it is clear from both STO-3G ab initio calculations[4] and Monte Carlo simulations[5] that the coordination around



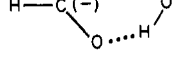
involves three water O–H hydrogen bonds to each anionic oxygen. Even for a



in a protein, one could imaging that the water could rotate and form a second hydrogen bond that would easily compensate for the fact that the



interaction is not as strong as



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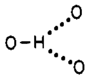
(17) H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, **58**, 5627 (1973).

(18) P. Kollman, *J. Am. Chem. Soc.*, **99**, 4875 (1977).

Entropy considerations also would be expected to favor E over B.[19] The freezing out of an internal rotational mode of HOH by forming a bifurcated structure rather than a linear one plus the double degeneracy of the linear H-bonded structure would be expected to stabilize the E structure by ~1 kcal/mol at 298 K, thus reducing the preference for the B relative to the E″ structure of $HCOO^-\cdots H_2O$ and $(CH_3O)_2PO_2^-\cdots H_2O$.

However, such a bifurcated structure may be kinetically important in general base catalysis by $HCOO^-$. For example, in the 6-31G** calculations, Mulliken populations suggest that the B structure H_2O has a slightly more negative charge (−0.071) than the E″ (−0.067) as well as a somewhat more negative oxygen (−0.783 (B) and −0.771 (E″)). Thus, the B H_2O may be slightly more effective than E in its nucleophilic attacks on electrophiles.

Finally, it is worth relating our calculations to the analysis of bifurcated carbohydrate H bonds by Jeffrey and Maluszynska.[20] These authors have found many examples of



bifurcated H bonds in these crystals, attributing this to the greater density of –O– acceptors than hydroxyl hydrogens. Ab initio calculations by Newton et al.[21] support the notion that such "nonoptimal" bifurcated hydrogen bonds can be more stable than a single linear H bond (see Table II in ref 21), analogously to what has been found in this study.

There are three important points to emerge from this study. First, it represents the most definitive demonstration of how the lowest energy structure determined from single solvation site calculations (B structure) is very little represented[4,5] when one considers multiple solvation. This underscores the danger of extrapolating single water hydration studies to infer properties of the aqueous solution structure and the importance of Monte Carlo or Molecular Dynamics simulations of each solutions. In such a Monte Carlo study[5] of the aqueous solvation of $(CH_3O)_2PO_2^-$, we have shown that the water interactions with the PO_2^- are predominantly of the E type.

Secondly, this study supports the preferential use of molecular mechanical (empirical potential) methods over minimal basis set ab initio (STO-3G) or, by inference, semiempirical MO methods that are based on reproducing minimal basis set ab initio studies, for studying molecular interactions. We should emphasize, however, that minimal basis sets derived by SCF atom calculations (e.g., those used in ref 14) do not suffer the same defect as STO-3G.

Finally, the calculations suggest that, for cases in which a single water molecule interactions with molecules where there is more than one center of partial negative charge, e.g., BH_4^-, $RCOO^-$, RPO_2^-, the bifurcated structure will be the one of minimum energy. In the case of the bifurcated $RPO_2^-\cdots H_2O$ structure, each $O^{\delta-}\cdots H{-}O$ hydrogen bond is significantly ($\angle OOH = 26.2°$ for $R_{O\text{-}H} = 2.10$ Å) bent, but two bent bonds appear to be more stabilizing that one ideal linear one. Thus, in systems such as $-XO_2^-$, one could imagine a dependence of the relative stabilities of B and E on OXO angle and XO bond length. Those geometrical changes which would allow more linear $O{-}H\cdots O^{\delta-}$ interactions in the B structure would tend to stabilize this structure; those that make these interactions less linear would stabilize the E structures.

Note Added in Proof. We have been made aware of ab initio calculations on nitrate and nitrite anion hydration using a 6-31G basis set (J. M. Howell, A. M. Sapse, E. Singman, and G. Snyder, *J. Chem. Phys.*, **86**, 2345–2349 (1982)), which found more stable bifurcated than linear structures for NO_2^- and NO_3^-.

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Registry No. $(CH_3O)_2PO_2^-$, 7351-83-9; $HCOO^-$, 71-47-6; H_2O, 7732-18-5.

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[19] Assuming the relative 4-31G energies of E and E″ in Table II, only the E″ would contribute to the thermodynamic properties and there would be one E″ structure for each oxygen. Thus, the degeneracy of 2 for E″. In addition, the internal rotation of the external water O–H in the E″ structure, but not the B, would lead to an additional contribution of 0.5 entropy unit (assuming a frequency of 300 cm^{-1}) for this structure. The sum of these two would be 2 e.u. or 0.6 kcal/mol at 300 K.

[20] G. Jeffrey and H. Maluszynska, *Int. J. Quant. Chem., Quant. Biol. Symp.*, **8**, 231 (1981).

[21] M. Newton, G. Jeffrey, and S. Takagi, *J. Am. Chem. Soc.*, **101**, 1997 (1979).

Luminescence Quenching Studies in NaLS Micellar Systems at 77 K

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Abstract: The formation of a micellar structure of sodium lauryl sulfate (NaLS) in an ethylene glycol–water mixture (EGW) both at room temperature and at 77 K was confirmed by using photochemical techniques. An aggregation number of 29 was determined in 0.050 M NaLS in 45% v/v ethylene glycol–water both at room temperature (20 °C) and at 77 K. Luminescence studies of the quenching reactions of the lowest excited state of tris(2,2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$) by Cu^{2+}, Cr^{3+}, and Fe(III) in NaLS–EGW micellar solutions at 77 K exhibited unusual kinetics, which are attributed to energy transfer or electron-transfer processes from the excited Ru(II) complex to metal ions, all of which are randomly distributed on the micellar surface. In contrast to behavior at 77 K, the quenching of $^*Ru(bpy)_3^{2+}$ by Cu^{2+} in a NaLS–EGW system at room temperature was explicable by simple Stern–Volmer kinetics, as observed in a NaLS micellar solution. On the other hand, the quenching behavior of the singlet excited pyrene by 1-ethyl-1′-hexadecyl-4,4′-bypyridinium ($C_{16}C_2V^{2+}$) ion appeared to be quite similar, both at room temperature and at 77 K. This latter effect was explained by an electron-tunneling mechanism where electron transfer takes place between species which are separated by distances that are larger than that of the closest contact of the quenchee–quencher pair at room temperature. Consequently, the micellar system at 77 K offers a reaction medium, being unique in its rigidity which fixes reactants in a known geometry in space, a situation which does not occur in homogeneous systems at this temperature. This effect can also be ascribed to a "catalytic" feature of micelles.

There have been numerous studies over the past several years of photochemical reactions in organized assemblies such as micelles, microemulsions, vesicles, etc.[1] Micelles have attracted much attention by two inherent and important properties, first, their

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