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QUANTUM CHEMICAL INVESTIGATION OF HYDROGEN-BONDED SPECIES OF ACETIC ACID

VITHAYA W. RUANGPORNVISUTI

Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10500, Thailand.

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ABSTRACT

The hydration and internal rotation energies of monomeric acetic acid were computed to obtain an understanding of the other co-existing species of acetic acid in water. Stabilization energies of hydrogen-bonded species of acetic acid were determined by means of ab initio calculations. In dilute aqueous acetic acid, a linear dimer is the most stable species but, at higher concentrations, a cyclic dimer is the dominant species. The first hydration energies of monomeric and linear dimeric acids are -82.0 to -136.8 and -223.0 kJ/mol, respectively.

INTRODUCTION

Several years ago, Karle and Brockway found a cyclic dimer of acetic acid in the gas phase by means of electron diffraction.[1] A simple equilibrium model of monomer and dimer of acetic acid, in solution, has been proposed and quantitatively studied in terms of the equilibrium constant.[2-7]

The presence of long chain linear polymer in crystalline acetic acid,[8] as indicated by infrared and Raman spectroscopy,[9-11] led to the postulation that acetic acid in the liquid state was composed of a mixture of monomers, linear dimers, cyclic dimers and linear polymers. Due to the H-nmr chemical shift dependence on the concentration of the hydrogen bonding System[12] and the postulation of the co-existence of hydrogen-bonded species of acetic acid, Goldman and Emerson[13] proposed a quantitative model for acetic acid in inert solvents; more recently, a similar quantitative model has been applied to aqueous solutions of acetic acid.[14]

In this work, stabilization energies of the hydrogen-bonded species of acetic acid have been computed by means of quantum chemical calculations, in order to support the results obtained from previous work[14] and develop an understanding of such a system via the results of the calculations, e.g. dipole moments.

METHOD

Ab initio MO-SCF calculation with minimal basis set[15] via the HONDO programme,[16] which has been widely used in quantum chemical work (e.g. ref. 17), was performed to obtain the stabilization nergies of hydrogen-bonded species of acetic acid.

The geometrical parameters of acetic acid taken from ref. 18 (listed in Table 1) were kept constant throughout the calculations but some rotation angles of the methyl group about its C-C bond were varied in order that calculations of the internal rotation energies can be carried out. The hydrated structure of acetic acid and its hydrogen-bonded species were optimized only in the distances and angles of the hydrogen bonds.

The computations were performed using the IBM 3031/08 computer of Chulalongkorn University and CDC and Cyber 835 computer of the University of Innsbruck.

RESULTS AND DISCUSSION

The total energies of different conformations of acetic acid shown in Table 2 indicate that the staggered conformation (S) is the most stable one (in the gas phase) while the energies of internal rotation for the perpendicular (P) and eclipsed (E) conformations, relative to the staggered form, are 3.3 and 5.9 kJ/mol, respectively.

However, both the staggered and eclipsed conformations can be considered as existing in the acetic acid aqueous solution because of the small energy barrier, especially when compared to the available thermal energy (2.5 kJ/mol at room temperature), the calculations of such rotational barriers compared to the thermal energy having been commonly done.[19] The optimized positions of the six water molecules (symbolized in Table 1 as W1, W2,...W6) interacting with the staggered and eclipsed conformations of acetic acid, together with their total energies, were obtained as shown in Table 3. The various binding energies ($\triangle E_n$) between Wn-water (n = 1, 2,...6) and acetic acid (S and E conformations), determined from the total energies in Table 3 via eqs. 1, 2 and 3, are shown in Table 4.

$$HOAc^E + Wn \xrightarrow{\triangle E_n^{EE}} (Wn) \cdot HOAc^E \quad (1)$$

$$HOAc^E + Wn \xrightarrow{\triangle E_n^{ES}} (Wn) \cdot HOAc^S \quad (2)$$

$$HOAc^S + Wn \xrightarrow{\triangle E_n^{SS}} (Wn) \cdot HOAc^S \quad (3)$$

As the water/water interaction potential (-44.2 kJ /mole with the same basis set)[20] was used for comparison with the interaction between monomeric acid and water molecule, only the interaction between W1-water and monomeric acetic acid will be taken as first hydration energy, although, sometimes, W2-water can also be included into the first hydration sphere.

The interaction between a water molecule and a methyl group of acetic acid, compared to the water/water interaction, is very weak and hardly affects the main interaction between W1-water and monomeric acid. This corresponds with nmr measurements at any concentration of acetic acid in water,[14] as reflected by the small change in the nmr chemical shift of the methyl protons (δ = 1.59-2.06 ppm, DSS as external reference) compared to the shifts of the acid proton (δ = 4.70-11.06 ppm).

The simple first-hydration model of (W1)· HOAc for the monomer, (W2). $(HOAc)_2$ (Fig. 2) for the linear dimer, (W1)· $(HOAc)_3$ for the trimer (Fig. 3) and the optimized structure of cyclic dimer (Fig. 4) are therefore proposed. Because of the symmetry, no water prefers solvating to the cyclic dimer. Also, due to the lack of the polarity of the cyclic dimer (dipole moment = 0 D, see Table 5), it can hardly dissolve in water, as indicated by the stabilization energy of the hydrated linear dimer relative to the cyclic dimer, $\triangle E_1$ (see Table 6 and eq. 4).

$$HOAc\frown HOAc + H_2O \xrightarrow{\triangle E_1} (H_2O)\cdot HOAc\text{-}HOAc \quad (4)$$

This means that the cyclic dimer prefers not to be located near water molecules; instead, ti prefers to be among other molecules of cyclic dimer. In the case of the cyclic dimer, comparison of its stability with that of the linear dimer can only be made for the non-hydrated form. According to eqs. 5 and 6, the cyclic dimer is, therefore, more stable than the hydrated linear dimer.

$$HOAc + HOAc \xrightarrow{\triangle E_2} HOAc\frown HOAc \quad (5)$$

$$HOAc + HOAc \xrightarrow{\triangle E_3} HOAc\text{-}HOAc \quad (6)$$

The stabilization energies, $\triangle E_3$, $\triangle E_4$ and $\triangle E_5$ corresponding to eqs. 6, 7 and 8 respectively (tabulated in Table 6), show that the hydrated linear dimer is more stable than its non-hydrated species and both the hydrated and non-hydrated monomer.

$$(H_2O)\cdot HOAc + HOAc \xrightarrow{\triangle E_4} (H_2O)\cdot HOAc\text{-}HOAc \quad (7)$$

$$HOAc\text{-}HOAc + H_2O \xrightarrow{\triangle E_5} (H_2O)\cdot HOAc\text{-}HOAc \quad (8)$$

The lower stability of the hydrated trimeric acid relative to the hydrated linear dimer (according to eq. 9) also argues for the lower stability of long chain polymers, when compared with the shorter chain polymers, due to weakness of their hydrogen bonds.

$$(H_2O)\cdot HOAc\text{-}HOAc + HOAc \xrightarrow{\triangle E_6} (H_2O)\cdot HOAc\text{-}HOAc\text{-}HOAc \quad (9)$$

It can therefore be concluded that in dilute solutions of aqueous acetic acid, the linear dimer is the most stable species but, at high concentrations, the cyclic dimer becomes the dominant species. That the linear dimer has the highest stability is clearly demonstrated by its dipole moment (μ = 1.04 D, Table 5), whose order of magnitude is close to that of water (μ = 1.61 D) and monomeric acetic acid (μ = 1.26 D), while the dipole moments of other species are quite different. In summary, it can be said that the species distribution of hydrogen-bonded species of acetic acid depends strongly on the polarity of the solution. The first hydration energies of the monomeric and linear dimeric acetic acids are approximately -82.0 to -136.8 and -223.0 kJ/mol (Table 4) respectively.

ACKNOWLEDGEMENT

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บทคัดย่อ

การศึกษาพลังงาน hydration และ internal rotation ของ monomeric acetic acid รวมทั้งพลังงานเสถียรภาพของ hydrogen-bonded species ของกรดน้ำส้ม โดยวิธี ab initio LCAO-MO-SCF calculation พบว่า linear dimer มีเสถียรภาพมากที่สุดในสารละลายเจือจางของกรดน้ำส้ม แต่ในสารละลายเข้มข้นของกรดน้ำส้ม cyclic dimer จะมีเสถียรภาพมากที่สุด พลังงาน first hydration ของ monomer และ linear dimer มีค่าเท่ากับ -82.0 ถึง -136.8 และ -223.0 kJ/mol ตามลำดับ

TABLE 1 Geometrical parameters used in the calculations.

Bond lengths (Å)		Bond angles (degrees)	
C1-O1	1.321	OĈO	121.9
C1-O2	1.206	CĈO1	113.2
C1-C2	1.501	CĈO2	124.9
C2-H2	1.050	CÔH	110.5
C2-H3	1.050	CĈH	109.47
C2-H4	1.050		
O1-H1	1.011		

TABLE 2 Total energies and rotational barriers of monomeric acid.

Rotation angles (ϕ)[a] (degrees)	Total energy (kJ/mol)	Barrier (kJ/mol)
0 (S)[b]	-507754.6	0.0
10	-507753.3	1.3
20	-507752.9	1.7
30 (P)[b]	-507751.3	3.3
40	-507750.0	4.6
50	-507749.2	5.4
60 (E)[b]	-507748.7	5.9

[a] defined in Figure 1

[b] S, P and E indicate that they belong to the staggered perpendicular and eclipsed conformations respectively.

TABLE 3 Optimization of hydrogen-bond distance of six water molecules around various conformations of acetic acid and their total energies.

Hydrogen bond	Optimized distance (Å)	Total energy (kJ/mol)	
		Eclipsed	Staggered
O1...O(W 1)	2.60	-677240.5	-677294.2
O2 ..O(W 2)	2.70	-677248.7	-677254.7
O1...O(W 3)	2.91	-677240.5	-677246.4
C2...O(W 4)	2.90	-677223.7	-677232.2
C2...O(W 5)	2.90	-677225.0	-677232.2
C2 ...O(W 6)	2.90	-677224.4	-677226.2

TABLE 4 Binding energies between water and acetic acid of two different conformations.

Type of interaction	Binding energy (kJ/mol)		
	$\triangle E_n^{EE}$	$\triangle E_n^{ES}$	$\triangle E_n^{SS}$
HOAc (W 1)	-84.1	-88.3	-82.0
HOAc (W 2)	-80.3	-48.5	-42.7
HOAc (W 3)	-34.7	-40.6	-34.3
HOAc (W 4)	-18.0	-26.8	-20.1
HOAc (W 5)	-18.8	-26.8	-20.1
HOAc (W 6)	-18.0	-20.5	-14.2
(W1)HOAc(W2)	-126.8	-136.8	-124.7

TABLE 5 Total energies of hydrated and non-hydrated hydrogen-bonded species of acetic acid.

Species	Total energy (kJ/mol)	Dipole moment (Debye)
H_2O	-169457.2	1.61
HOAc	-507754.8	1.26
(H_2O) HOAc	-677294.2	3.88
HOAc⁀HOAc	-1015670.0	0.00
HOAc-HOAc	-1015578.3	3.24
(H_2O) - HOAc-HOAc	-1185190.2	1.04
HOAc-HOAc-HOAc	-1520673.7	7.35
(H_2O) - HOAc-HOAc-HOAc	-1690242.0	8.71

TABLE 6 Stabilisation energy of interesting species, according to eqs. 4 to 9.

Stabilisation energy $\triangle E$	kJ/mol
$\triangle E_1$	-62.8
$\triangle E_2$	-151.9
$\triangle E_3$	-72.4
$\triangle E_4$	-141.0
$\triangle E_5$	-223.0
$\triangle E_6$	destabilized (+2702.0)

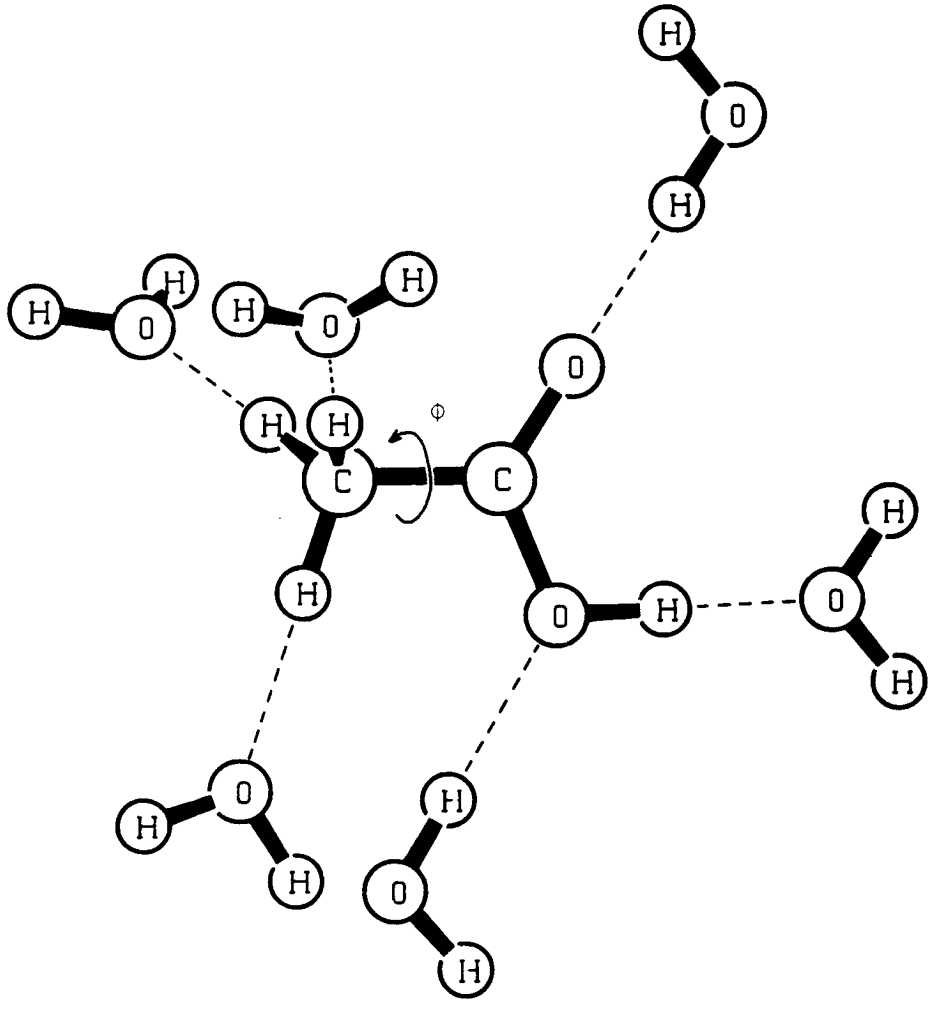
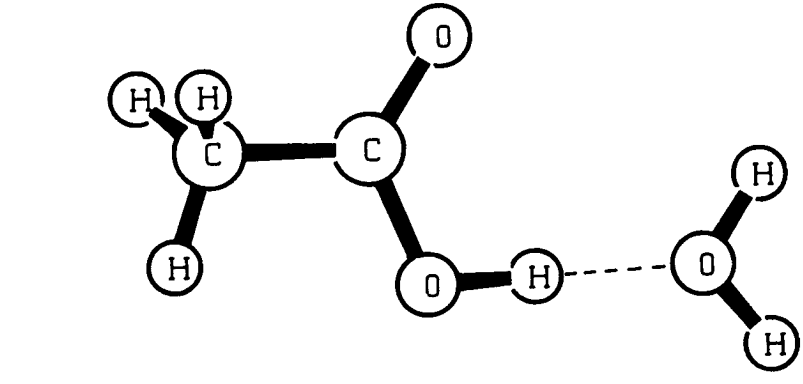
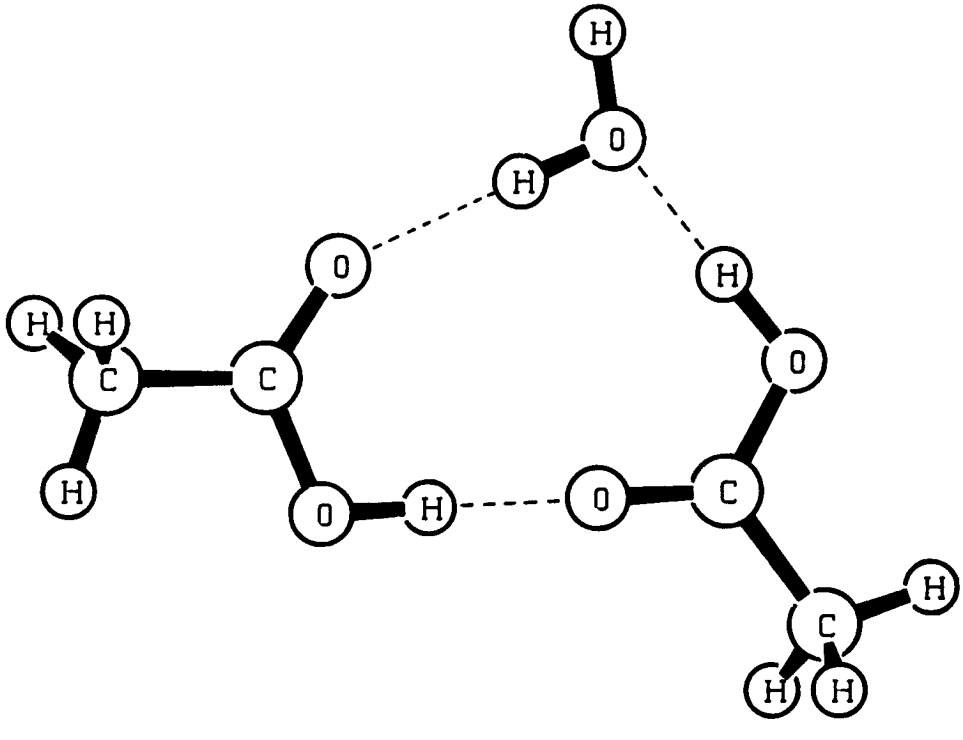


Fig. 1 Most stable position of six water molecules around acetic acid and definition of the rotation angle.

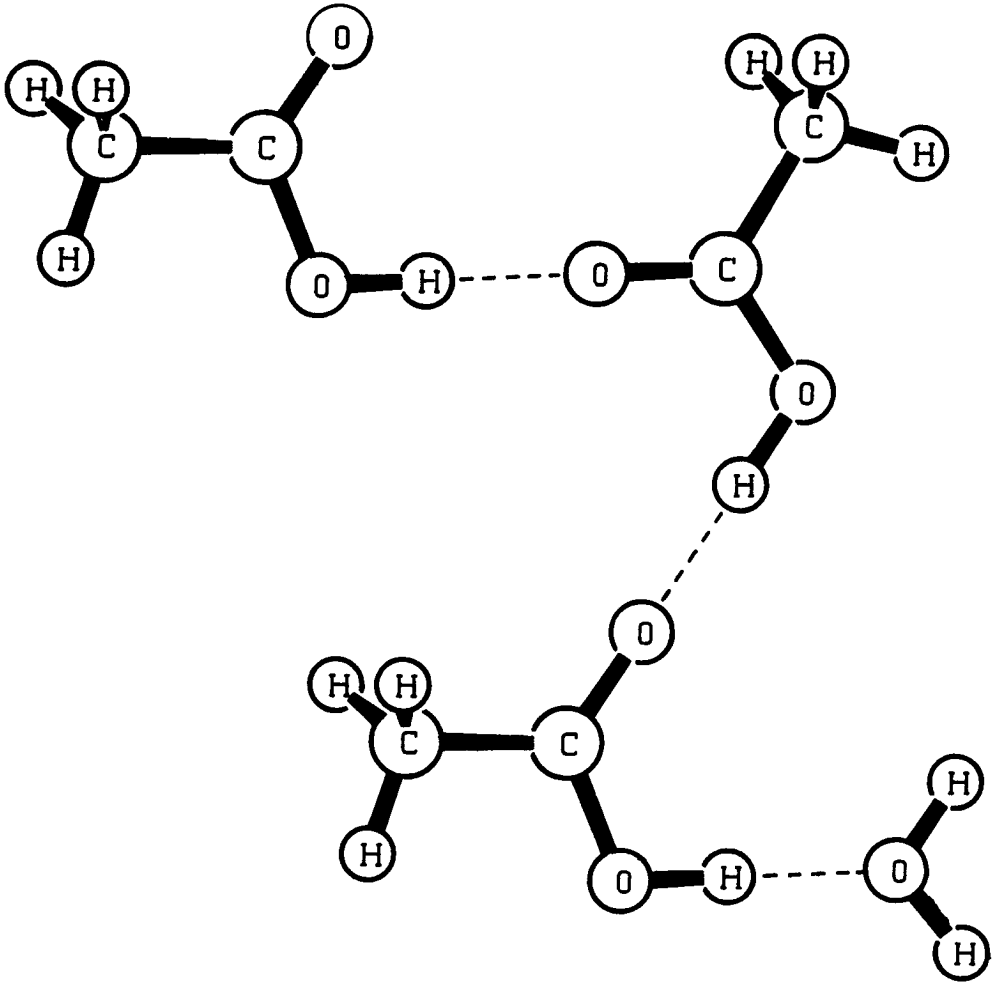


(a)



(b)

Fig. 2 Hydration model of (a) monomer (b) linear dimer and (c) linear trimer.



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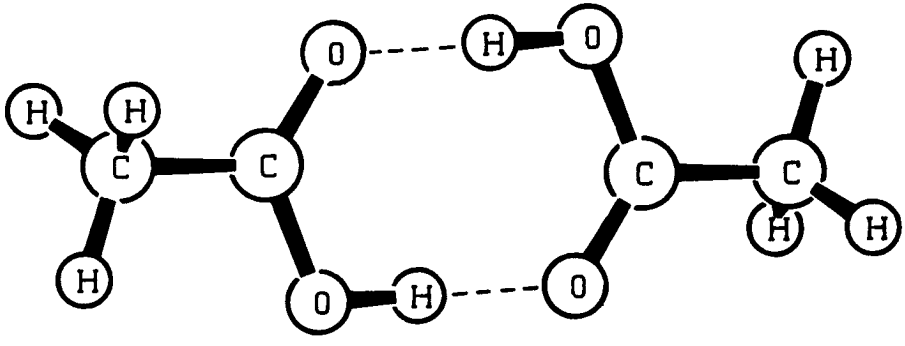

Fig. 3 Optimized structure of cyclic dimer.