Computational Study of the Stability of Tautomers and equilibrium constants of Cyanuric acid (CA) in Different solvents.

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ABSTRACT

In the present investigation, the tautomeric and equilibrium of Cyanuricacid has been studied using Hartree Fock (HF) method in the gas phase and different solvents using the PCM model. The relative energies of these tautomers have been calculated at the HF level of theory using 6-311++ G(d,p) basis set. Energetics and relative stabilities of the tautomers were compared and analyzed in both the gaseous and different solvents. The results indicate that the keto tautomer (CA1) is the most stable form in the gas phase and other solvents. The order of stability of isomers was found to be CA1 > CA3> CA11> CA2> CA6> CA10> CA7> CA4> CA5> CA9>CA8. Having the largest dipole moment the CA8 tautomer is expected to have the strongest interaction with polar solvents.The HF method calculated tautomeric equilibrium constants with respect to the most stable tautomer CA1 of Cyanuric acid both in the gas and in different solvents. The pK_T of the equilibrium constants calculated starting from the general outline of interconversion.

Key words: Cyanuric acid; Hartree Fock method; Relative stabilities; Equilibrium constantsand solvent effects.

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INTRODUCTION

Studies of tautomerism phenomena have been valuable in many areas of chemistry as demonstrated by several reviews of experimental and theoretical studies in chemistry and biochemistry [1-5].The experimental studies on tautomerism 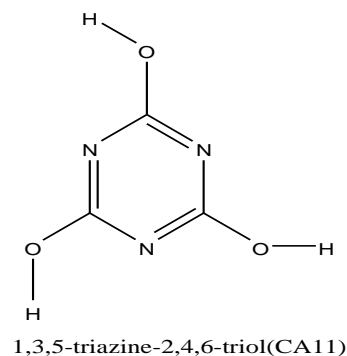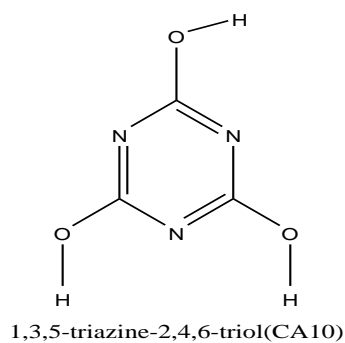are still a challenging problem in chemistry and molecular biology. Most tautomers are not observed in the experimental studies because of their low concentration. A detailed analysis of the structure and changes in geometrical and energetic parameters caused by the migration of hydrogen atom would enable us to understand the different properties of tautomers. Knowledge of the relative stabilities of tautomeric forms of heterocycles as well as the conversion from one tautomeric form to another is important from the point of view of structural chemistry.

Cyanuric acid has a diverse role to play in chemistry, particular with regard to commercial or industrial use, for many years. It has featured in products ranging from flame retardants and plant growth feed to a catalyst for NO_X removal from exhaust and lavatory cleaning blocks[6].CA1exists in equilibrium with its tautomer CA10 or CA11(Refer the figure1)and has the attributes of high symmetry and planarity, coupled with three hydrogen bond donors and three acceptors. It is a middy acidic compound with pK_a values of 6.85, 10.91 and >12[7]. Cyanuric acid is only slightly water soluble and is thermally unstable. At high temperatures, it decomposes to form toxic cyanic acid[8]. Cyanuric acid exists preferentially as the oxo tautomer (CA1) rather than the hydroxy form (CA10 or CA11)[9] (sheme1)Commercial applications of Cyanuric acid include stabilizers of swimming pooldisinfectants, household bleach, industrials cleaners, dishwasher detergents, and generalsanitizers. Cyanuric acid has been found to naturally occur in nature insoil humus[8]. Melamine combination with Cyanuric acid or the analogues, including ammeline and ammelide, appear to cause crystallization in renal tubules[10]. Most of the infants were asymptomatic, and a few suffered from stoneinduced urinary obstruction resulting in acute renal failure[11].

1,3,5-triazinane-2,4,6-trione(CA1)

6-hydroxy-1,3,5-triazine-2,4(1*H*,3*H*)-dione(CA2)

6-hydroxy-1,3,5-triazine-2,4(1*H*,3*H*)-dione(CA3)

4,6-dihydroxy-1,3,5-triazin-2(1*H*)-one(CA4)

4,6-dihydroxy-1,3,5-triazin-2(1*H*)-one(CA5)

4,6-dihydroxy-1,3,5-triazin-2(1*H*)-one(CA6)

4,6-dihydroxy-1,3,5-triazin-2(1*H*)-one(CA7)

4,6-dihydroxy-1,3,5-triazin-2(5*H*)-one (CA8)

4,6-dihydroxy-1,3,5-triazin-2(5*H*)-one(CA9)

1,3,5-triazine-2,4,6-triol(CA10)

1,3,5-triazine-2,4,6-triol(CA11)

Scheme 1. The selected tautomer structures of cyanuric acid (tautomer CA1(1,3,5-triazinane-2,4,6-trione);CA2 and CA3 (6-hydroxy-1,3,5-triazine-2,4(1H,3H)-dione);CA4,CA5, CA6, and CA7(4,6-dihydroxy-1,3,5-triazin-2(1H)-one);CA8 and CA9 (4,6-dihydroxy-1,3,5-triazin-2(5H)-one);CA10 and CA11 (1,3,5-triazine-2,4,6-triol).
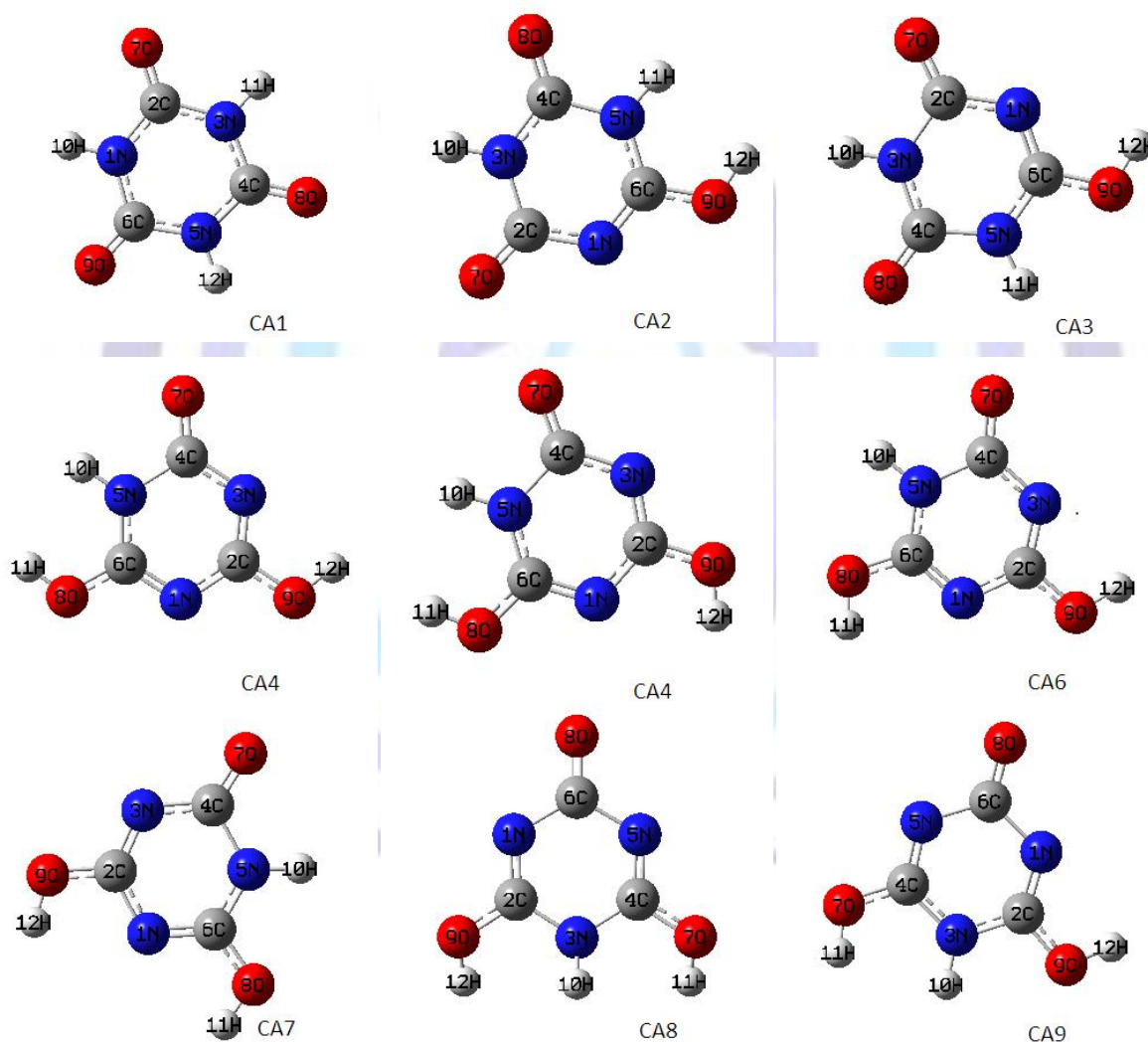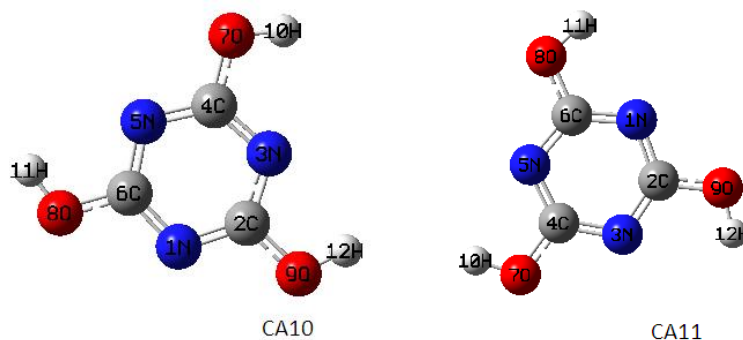

CA1

CA2

CA3

CA4

CA4

CA6

CA7

CA8

CA9

Figure 1. Leven structural isomers of C3N3O3H3 comprising Cyanuric acid (1,3,5-triazinane-2,4,6-trione) (labeled (1)), 6-hydroxy-1,3,5-triazine-2,4(1H,3H)- dione ((2) and (3)), 4,6-dihydroxy-1,3,5-triazin-2(1H)-one ((4), (5),(6) (7),(8)and (9)), and 1,3,5-triazine-2,4,6-triol ((10) and (11)) in gas phase. Each atom is colored and numbered. Grey is carbon, blue is nitrogen, red is oxygen and white is hydrogen.

In this research article we calculates various parameters to determine, the theoretical possible tautomers of Cyanuric acid. Tautomeric equlibria are important and it is impossible to correctly interpret the detail mechanism of reactions of tautomeric heterocycles without knowing the dominant tautomeric structure. Equally, it is impossible to correctly interpret the biological activity and function of potentially tautomeric heterocycles without representing them in correct structure. Also, understanding of the relative stabilities of heterocyclic tautomers and any subsequent conversions between tautomeric forms is very vital for both structural chemists and biologists [12]. Along this line, relative stabilities of various tautomeric structures of five-, six- and seven-membered heterocyclic rings were investigated using both theoretical and experimental tools [13].Tautomerism interconversion has been investigated by chemists during last decades. Recently, study of tautomerism received renewed attention due to its importance on determination of compounds' properties and their area of applications. The importance of tautomerism is revealed more since in recent years the investigation about tautomerism has been the major topic in theoretical chemistry.

COMPUTATIONAL SECTION

Molecular geometries of tautomeric forms of Cyanuricacid were fully optimized by using the Gaussian quantum chemistry software package Gaussian 09w [14]. Programs at the HF level of theory, using the 6-311++G(d,p) basis sets[14]. Initial geometry generated from standard geometrical parameters minimized without any constraint in the potential energy surface at HF level, adopting the standard 6-311++G(d,p) basis set. Following the geometry optimizations, analytical frequency calculations were proceeded at the HF/6-311++G (d,p) level, following standard procedures, to obtain the thermochemical properties. In addition the effects of solvents on the tautomeric structure properties were studied by means of the self-consistent reaction-field (SCRF) method based on PCM developed by Tomasi and coworkers [15]. It is one of the most widely used approaches. In this model, a solute is considered inside a cavity and the solvent as a structureless medium characterized by some parameters such as its dielectric constant, molar volume and Polarizability. This consideration can substantially improve the simulation results for the electronic or vibrational spectroscopy of real molecular systems[16,17].The solvents chose for this studies are polar protic solvents namely water (ε = 74.80) andethanol (ε = 24.55) and polar aprotic solvents liketetrahydrofuran(THF) (ε = 7.50) and dimethylformamide (ε = 38.00).

In the present paper, we report the relative stability, Gibbs free energy, enthalpy and entropy, tautomeric equilibrium constants and dipole moments for the Cyanuric acid 298.15 K. After having predicted the relative stability of tautomers, we have found the tautomeric equilibrium constants with respect to the more stabletautomer in the gas phase and indifferent solvents.

RESULTS AND DISCUSSION

RELATIVE STABILITY

Cyanuric acid exhibits eleven theoretical possible tautomers and eleven structural isomers of $C_3N_3O_3H_3$ comprising; Cyanuric acid (1,3,5-triazinane-2,4,6-trione) (labeled (CA1)), 6-hydroxy-1,3,5-triazine-2,4(1H,3H)- dione ((CA2) and (CA3)), 4,6-dihydroxy-1,3,5-triazin-2(1H)-one ((CA4), (CA5),(CA6) (CA7),(CA8) and (CA9)), and 1,3,5-triazine-2,4,6-triol ((CA10) and (CA11)) are in scheme 1. The structures correspond to cyanuric acid species labeled (CA2) and (CA3) are monohydroxytautomers, six are dihydroxytautomers (CA4,CA5,CA6,CA7,CA8 and CA9) and the structures of (CA10 and CA11) aretrihydroxytautomers, these differ in the mono proton,di proton and tri proton transfer and orientation of the hydroxyl group. The optimized geometrics are shown in Figure 2 in gas phase.Each atom is colored and numbered. Grey is carbon, blue is nitrogen, red is oxygen and white is hydrogen.
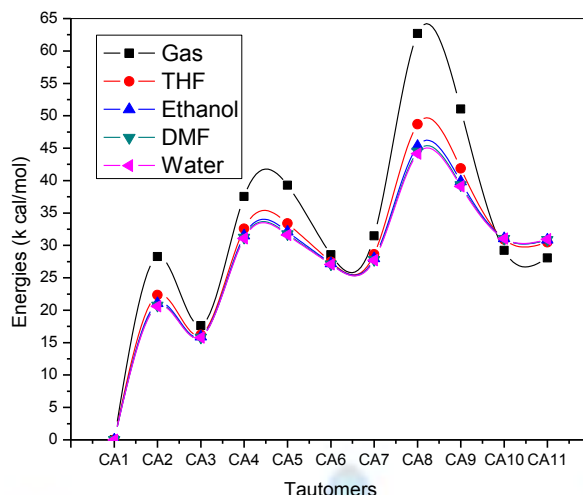
Figure 2. The Relative energies for Tautomers in different solvents

In TableI, results are presented for the absolute and relative electronic energy in gas and different (aqueous, ethanol, THF and DMF) solution phase, respectively, evaluated at the HF levels of theory in conjunction with 6-311++G** basis set. The calculations at the HF levels of theory suggest that the Cyanuric acid form, CA1, is the most stable isomer in both gas phase and different solutions. The order of stability of isomers was found to be CA1>CA3>CA11>CA2> CA6>CA10>CA7>CA4>CA5>CA9>CA8. Based on the HF calculations in the gas phase, the energy of CA3,CA11,CA2, CA6, CA10,CA7,CA4,CA5,CA9 and CA8 isomers are 17.62,28.05,28.28,28.55,29.22,31.48,37.27,39.27,51.04 and 62.69 kcal/mol higher than CA1 isomer, respectively.Solvent effects are relevant to tautomer stability phenomena, since polarity differences among tautomers can induce significant changes in their relative energies in solutions. For this purpose, the PCM calculations were employed to analyze the solvent effects on tautomerism of Cyanuric acid. The results obtained for different solutions have been reported in Table 1 and compared with those obtained from the gas phase calculations. It is evident that the electronic energies of tautomers decrease in comparison with gas phase. As the dielectric constant of solvent increases the tautomer energy is decreases.The order of stability of tautomers was found in the different solvents to be CA1 > CA3 > CA2 > CA6 > CA7 > CA11 > CA10 > CA4 > CA5 > CA9 > CA8 in aqueous phase; CA1 > CA3 > CA2 > CA6 > CA7> CA11 > CA4 > CA10 > CA5 > CA9 > CA8 in ethanol phase; and CA1 > CA3 > CA2 > CA6 > CA7 > CA11 > CA10 > CA4 > CA5 > CA9 > CA8 in both THF and DMF phase. In all phases the tautomer CA1 is morestable.Figure 3 shows the effect of various solvents on the stability of each isomer. The instability of each isomer has been plotted versus its dipole moment which depends on the kind of the selected solvent. It is evident that the CA8 isomer is considerably affected by solvent.
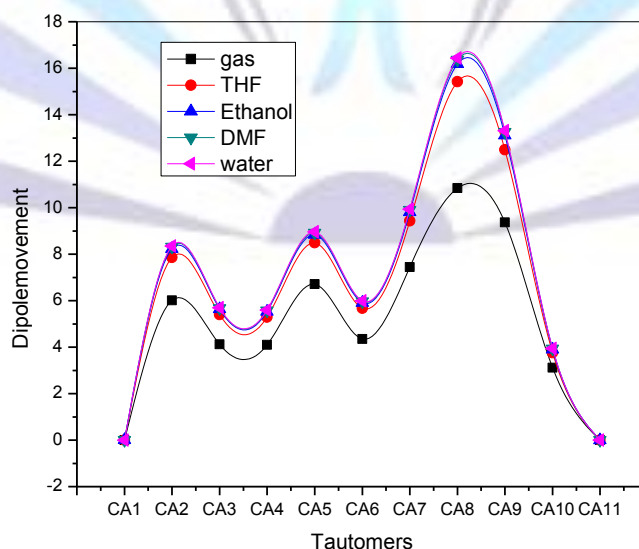

Figure 3. Dipole movements for Tautomers in different solvents

Table 1. The energies of tautomers(a.u) at HF/6-311++G(d,p) level in different media and the relative energies compared to the most stable isomer CA1.The relative energies in brackets in kcal mol-1.

Tautomer	gas (ε = 1.00)	THF(ε = 7.50)	ethanol(ε = 1.00)	DMF(ε = 24.55)	water(ε = 78.50)
CA1	-503.5295806(0.00)	-503.5295806 (0.00)	-503.549091930 (0.00)	-503.549628574(0.00)	-503.549904703 (0.00)
CA2	-503.4845165 (28.28)	-503.4845165 (22.34)	-503.515499106 (21.08)	-503.516562962(20.75)	-503.517057789 (20.61)
CA3	-503.5015004 (17.62)	-503.5015004 (16.19)	-503.523730220 (15.91)	-503.524448503(15.80)	-503.524780719 (15.77)
CA4	-503.4697602 (37.54)	-503.4697602 (32.57)	-503.498896899 (31.50)	-503.499893327(31.21)	-503.500356596 (31.09)
CA5	-503.4669966 (39.27)	-503.4669966 (33.38)	-503.497937766 (32.10)	-503.499009109(31.76)	-503.499507532 (31.62)
CA6	-503.4840763 (28.55)	-503.4840763 (27.44)	-503.505751459 (27.20)	-503.506454752(27.09)	-503.506780968 (27.06)
CA7	-503.4794190 (31.48)	-503.4794190 (28.64)	-503.504489135 (27.99)	-503.505342321(27.79)	-503.505739083 (27.71)
CA8	-503. 4296812 (62.69)	-503.42968120 (48.69)	-503.476857997 (45.33)	-503.478680666 (44.52)	-503.479531705 (44.16)
CA9	-503.4482400 (51.04)	-503.44824004 (41.89)	-503.485600800 (39.84)	-503.486951562 (39.33)	-503.487581455 (39.11)
CA10	-503.4830177 (29.22)	-503.4830177 (30.89)	-503.499581117 (31.07)	503.500143827(31.05)	-503.500405407 (31.06)
CA11	- 503.4848776(28.05)	-503.4848776 (30.47)	-503.499877294 (30.88)	503.500430658(30.87)	-503.500592144 (30.94)

DIPOLE MOMENT

As we can see from Table 2, the calculated dipole moments are changed on moving from thegas phase (ε = 1) to solvents [THF(ε = 7.80);ethanol (ε = 24.55); DMF (ε = 38.00) and water (ε = 78.4) and the dipole moments are sensitive to the polarity of the medium. The calculated dipole moments are substantially higher in a medium of high relative permittivity, mainly due to major charge redistribution in the molecule, and also by changes in the distances between the charge separations. The magnitude of the influence of the solvent reaction field on electronic structure is different in different tautomers. This may also explain the great variation of the calculated dipole moments of the tautomers.

The CA8 tautomer has the largest dipole moment and the CA11 has the smallest dipole moment in all phases. Having the largest dipole moment the CA8 tautomer is expected to have the strongest interaction with polar molecules of water in biological environment. The structure of a tautomer obviously affects the magnitude and orientation of a dipole moment. For example, a transition from an keto- to a enol- form usually leads to an increase of the dipole moment, and upon a transition from one enol form of CA11 and tautomer to the keto form of CA1 form we observe 0.0002 and 0.0013D dipole moment change respectively. However, the position of hydrogen attached to O in the ring of cyanuric acid has much greater influence on the dipole moment. Not only does it affect the magnitude of the dipole moment but it even changes its orientation. This is indicated by the fact that the orientation of dipole moments in the CA2 and CA3, tautomers of cynuric acid with H attached to the O atom is almost opposite, and the similar effect to absevered in all cynuric acid tautomers.The calculated dipole moments for the studied tautomers at the HF/6-311++G (d,p) level in solution are given in Table 2. The order of the dipole moment of tautomers in gas phase is CA11 > CA1 > CA10 > CA4 > CA3 > CA6 > CA2 > CA5 > CA7 > CA9 > CA8. The figure 3shows the effect of solvents on dipole movements for tautomers of cynuric acid. The two tautomers CA8 and CA9have large magnitude in total energy differences in gas phase and large dipole moments (Table 2). This leads to the inversion of their order of stability in polar solvent.

Table.2. The zero dipole moments (μ) in Debye units,Polarizability(α) and Mean Polarizability $\langle \alpha \rangle$ for the tautomers at HF/6- 311++G(d,p) level in different solvents.

Polariza bility(α)	Gas (ε = 1.00)										
	CA1	CA2	CA3	CA4	CA5	CA6	CA7	CA8	CA9	CA10	CA11
α_{xx}	65.860	65.634	62.378	66.908	67.082	64.071	67.295	56.290	59.935	70.870	67.941
α_{yy}	65.856	70.256	72.878	70.768	71.026	73.201	70.464	83.688	78.115	65.065	67.935
α_{zz}	31.924	32.632	32.666	33.295	33.307	33.330	33.339	34.609	33.643	33.881	33.883
$\langle \alpha \rangle$	54.547	56.174	55.974	56.990	57.138	56.867	57.033	58.196	57.231	56.605	56.586
μ	0.0013	6.0137	4.1201	4.1018	6.7086	4.3529	7.4374	10.8363	9.3673	3.1097	0.0002
	THF(ε = 7.50)										
α_{xx}	78.972	78.015	74.486	79.220	79.772	76.670	79.548	68.232	71.891	84.845	82.286
α_{yy}	78.957	86.136	88.788	87.372	87.345	89.465	87.097	100.298	95.794	79.719	82.298
α_{zz}	37.232	38.287	38.313	39.313	39.321	39.323	39.338	39.530	39.576	40.211	40.221
$\langle \alpha \rangle$	65.054	67.479	67.196	68.635	68.813	68.486	68.661	69.353	69.087	68.258	68.268
μ	0.002	7.8617	5.3943	5.292	8.4879	5.6696	9.4292	15.4215	12.4961	3.7619	0.002
	ethanol(ε = 1.00)										
α_{xx}	81.259	80.138	76.678	81.380	81.978	78.989	81.797	70.828	74.285	87.299	84.935
α_{yy}	81.262	89.103	91.654	90.530	90.455	92.441	90.115	103.202	98.885	82.582	84.923
α_{zz}	38.570	39.715	39.744	40.843	40.844	40.844	40.857	41.086	41.111	41.809	35.701
$\langle \alpha \rangle$	67.030	69.652	69.359	70.918	71.092	70.758	70.923	71.705	71.427	70.563	68.520
μ	0.0066	8.232	5.6339	5.5251	8.8437	5.9109	9.8141	16.1875	13.1161	3.9005	0.0018
	DMF(ε = 24.55)										
α_{xx}	81.776	80.591	77.141	81.846	82.453	79.493	82.283	71.415	74.811	87.826	85.530
α_{yy}	81.775	89.749	92.257	91.220	91.135	93.086	90.771	103.813	99.551	83.212	85.544
α_{zz}	38.875	40.045	40.074	41.197	41.197	41.197	41.209	41.449	41.467	42.179	42.207
$\langle \alpha \rangle$	67.475	70.128	69.824	71.421	71.595	71.259	71.421	72.226	71.943	71.072	71.094
μ	0.0032	8.3138	5.6741	5.5761	8.9217	5.9634	9.8991	16.3567	13.2529	3.9314	0.0011
	water(ε = 78.50)										
α_{xx}	82.013	80.800	77.361	82.061	82.674	79.728	82.509	71.688	75.058	88.071	85.775
α_{yy}	81.998	90.050	92.544	91.540	91.451	93.386	91.077	104.094	99.858	83.506	85.786
α_{zz}	39.019	34.031	40.231	41.365	41.364	41.363	41.375	41.621	41.635	42.354	35.692
$\langle \alpha \rangle$	67.677	68.294	70.045	71.655	71.830	71.492	71.654	72.468	72.184	71.310	69.084
μ	0.0023	8.3519	5.698	5.5998	8.9582	5.9877	9.939	16.4354	13.3169	3.9459	0.0019

MOLECULAR POLARIZABILITY

The Polarizability calculations carried out for different solvents effects on cynuric acid tautomers are summarized in table 2. Here, α is a second rank tensor property called the dipole Polarizability and mean Polarizability $\langle \alpha \rangle$ are evaluated using

$$\langle \alpha \rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$ (1)

When a molecule is placed in a liquid environment, it is polarized, i.e., its electrostatic moments are changed giving rise to induced multipole moments. The amount of polarization will depend on several factors including, of course, the Polarizability of the solute and the electric field provided by the environment. As seen from the Figure 4. inthe gas phase the polarizabilities are low and in all the solvents are high values, the order of polarizabilities is Gas > THF > ethanol > DMF > water, due to increase of dielectric constant of solvents. The largest Polarizability was observed for CA8 tautomer in all phases.CA8 tautomer is more polarizable than other tautomers because of its dipole moment is high value in all solvents.
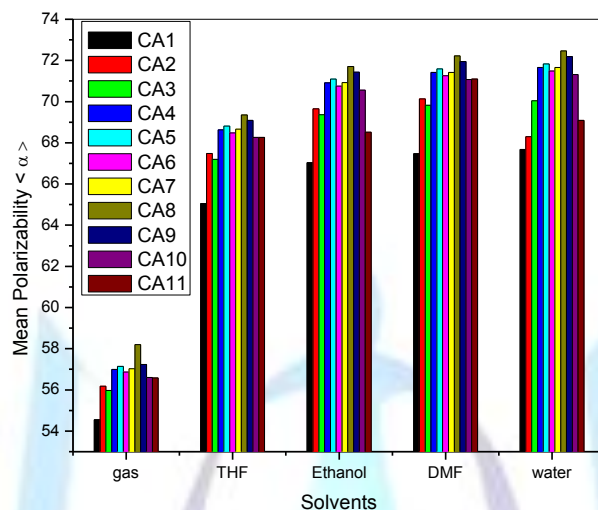

Figure 4.PolarizablitiesVs Solvents

ENERGETICS

Thermodynamic and kinetic factors are important to the understanding of tautomeric equlibria and their impact on biology.The enthalpies, entropies and Gibbs free energies for the tautomers of cynuricacid are given inTables 3.in different solvents. The change of enthalpy (ΔH) and the free energy (ΔG) changeare positivein all phases of the conversion from CA1 to other tautomersand are endothermic and non spontaneous process respectively.

Table .3.The calculated thermodynamic properties for tautomers of Cynuric acid in gas phase and different solvents by using HF/6-311++G (d,p) at 298.15 K

Tautomer	gas (ε = 1.00)			THF(ε = 7.50)			ethanol(ε = 1.00)			DMF(ε = 24.55)			water(ε = 78.50)		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
CA1↔CA2	27.78	27.32	1.554	21.45	21.83	-1.278	20.12	20.44	-1.085	19.80	20.18	-1.295	19.65	20.05	-1.324
CA1↔CA3	17.53	17.75	-0.767	16.08	16.28	-0.688	15.77	15.92	-0.497	15.68	15.89	-0.701	15.64	15.86	-0.733
CA1↔CA4	37.17	37.44	-0.888	32.34	32.58	-0.803	31.24	31.45	-0.717	30.97	31.25	-0.952	30.85	31.15	-0.993
CA1↔CA5	38.83	63.58	-0.747	33.26	33.67	-1.386	31.92	32.24	-1.084	31.59	31.97	-1.257	31.45	31.82	-1.268
CA1↔CA6	28.51	29.08	-1.893	27.30	27.75	-1.496	27.02	27.40	-1.269	26.94	27.38	-1.474	26.90	27.35	-1.502
CA1↔CA7	31.32	31.80	-1.614	28.50	28.93	-1.455	27.81	28.17	-1.227	27.63	28.06	-1.437	27.55	27.99	-1.467
CA1↔CA8	61.70	61.23	1.556	48.30	47.59	2.354	44.93	44.50	1.428	44.14	43.88	0.857	43.78	43.57	0.678
CA1↔CA9	50.31	49.48	2.793	41.36	40.63	2.449	39.34	39.18	0.561	38.87	38.83	0.118	38.65	38.65	-0.007
CA1↔CA10	29.34	30.15	-2.725	30.85	31.47	-2.083	30.99	31.53	-1.818	30.99	31.59	-2.016	31.00	31.61	-2.04
CA1↔CA11	28.22	29.06	-2.806	30.50	31.15	-2.18	30.82	31.36	-1.816	30.87	31.51	-2.146	30.88	31.49	-2.033

TAUTOMERIC EQUILIBRIA IN THE GAS PHASE AND SOLUTION

Cyanuric acid exists mainly in eleven tautomeric forms (CA1- CA11) that are in equilibrium. CA1 has a keto form and can be converted to CA2 and CA3 tautomers through a proton transfer and rotation around the C-O bond, simultaneously. The CA4 to CA9 isomers give the dihydroxy form by two protons transfer and considering the orientation of the hydroxyl

hydrogen's. CA10 and CA11 are converted try hydroxyl isomers through three proton transfer.Therefore, only eleven isomers were considered in the present study.

The HF method calculated tautomeric equilibrium constants with respect to the most stable tautomer CA1 of Cyanuric acid both in the gas and in different solution are listed in Table 3. The tautomeric equilibrium between tautomers a and b is described as

$$a \overset{K_T}{\rightleftharpoons} b \tag{2}$$

Equilibrium constants for each species were calculated by using the following equation

$$K_T = e^{-(\Delta G/RT)} \tag{3}$$

Where K_T is the tautomeric equilibrium constant between the tautomers, the gas constant R is 1.987×10^{-3} kcal/mol; and the temperature T is 298.15 K. The pK_T values of the studied molecules were calculated by means of the following equation

$$pK_T = \frac{\Delta G}{2.303 RT} \tag{4}$$

The equilibrium between the tautomers 1 and 3 of cyanuric acid values for show that the CA2 is more dominant than the CA3, both for the gas and different solvents with a pK$_T$ value of 13.0,(gas) and 11.93(THF) , 11.66 (ethanol),11.64 DMF and 13.01(water) respectively. This is confirm to thermodynamic data of CA1↔CA3, see the table 3. The remaining tautomers are not detectable amounts because of the pK_T values are very high.

From the Table 4 the pK_T values are decreasing with increase in polarity of solvents. Solvent effects have been ascribed to two major components[18], electrostatic solvent-solute interaction and hydrogen bonding. The hydrogen bonding effects cannot be estimated in a quantitative manner from the salvation model, and needs further large-scale calculations. The electrostatic solvent-solute effects, however, are readily estimated by the reaction field continuum model [19] using the dipole moments and molecular polarizabilities. Application of the reaction field continuum model leads to an explanation of the change in order of tautomeric stability on going from gas phase to solution. However, such a treatment lacks explicit consideration of base-water hydrogen bonding effects [20].

From the interconversiondiagram, to evaluate in a more realistic way theconstants of equilibriums as represented in Figure. 5. Table 5 contained the pK_T of the equilibrium constants calculated starting from the general outline of interconversion. Some pK_T were positive and the other negative; that determinate the privileged direction of equilibrium.

If the pK_T was positive, equilibrium moved from right towards the left and when it was negative, equilibrium moved from left towards the right. By taking account of all these directions of displacement, we obtained.

Table 4. HF/6-31++ G(d,p) predicted tautomeric equilibrium constants (pK_T) with respect to the most stable tautomer of CA1in the gas phase and different solvents at 298.15 K

Tautomer	gas (ε = 1.00)		THF(ε = 7.50)		ethanol(ε = 1.00)		DMF(ε = 24.55)		water(ε = 78.50)	
	к	pK_T	к	pK_T	к	pK_T	к	pK_T	к	pK_T
CA1↔CA2	9.4148×10^{-21}	20.0262	9.9565×10^{-17}	16.0019	1.0399×10^{-25}	14.9830	1.6128×10^{-15}	14.7924	2.0085×10^{-15}	14.6971
CA1↔CA3	9.7463×10^{-14}	13.0112	1.1651×10^{-12}	11.9336	2.1393×10^{-12}	11.6697	2.2504×10^{-12}	11.6477	2.3673×10^{-12}	11.6257
CA1↔CA4	3.5943×10^{-28}	27.4444	1.3125×10^{-24}	23.8819	8.8390×10^{-24}	23.0536	1.2388×10^{-23}	22.9070	1.4666×10^{-23}	22.8337
CA1↔CA5	2.4797×10^{-47}	46.6056	2.0850×10^{-25}	24.6809	2.3299×10^{-24}	23.6327	3.6749×10^{-24}	23.4347	4.7337×10^{-24}	23.3248
CA1↔CA6	4.8271×10^{-22}	21.3163	4.5563×10^{-21}	20.3414	8.2256×10^{-21}	20.0848	8.5080×10^{-21}	20.0702	8.9499×10^{-21}	20.0482
CA1↔CA7	4.8963×10^{-24}	23.3101	6.2179×10^{-22}	21.2064	2.2425×10^{-21}	20.6493	2.7000×10^{-21}	20.5686	3.0387×10^{-21}	20.5173
CA1↔CA8	1.3091×10^{-45}	44.8830	$1.3044 \times 10^{}$	34.8846	$2.4014 \times 10^{-}$	32.6195	$6.8383 \times 10^{-}$	32.1650	$1.1539 \times 10^{-}$	31.9378

			0^{-35}		33		33		32	
CA1↔CA9	5.3706×10^{-37}	36.2700	1.6492×10^{-30}	29.7827	1.9061×10^{-29}	28.7198	3.4412×10^{-29}	28.4633	4.6629×10^{-29}	28.3313
CA1↔CA10	7.9315×10^{-23}	22.1006	8.5460×10^{-24}	23.0682	7.7230×10^{-24}	23.1122	6.9791×10^{-24}	23.1562	6.7475×10^{-24}	23.1709
CA1↔CA11	4.9929×10^{-22}	21.3016	1.4666×10^{-23}	22.8337	1.0289×10^{-23}	22.9876	7.9881×10^{-24}	23.0976	8.2624×10^{-24}	23.0829

Table .5..HF/6-311++G(d,p) predicted tautomeric equilibrium constants (pK_T) with respect to the most stable tautomer of CA1in the gas phase and different solvents from the interconversion diagram at 298.15 K

Tautomer	gas (ε = 1.00) K	pK_T	THF(ε = 7.50) K	pK_T	ethanol(ε = 1.00) K	pK_T	DMF(ε = 24.55) K	pK_T	water(ε = 78.50) K	pK_T
CA2↔CA3	1.0178×10^{7}	-7.0077	1.1702×10^{4}	-4.0683	2.0921×10^{3}	-3.3206	1.3953×10^{3}	-3.1447	1.1588×10^{3}	-3.0640
CA2↔CA4	3.8177×10^{-8}	7.4182	1.3182×10^{-8}	7.8800	8.4999×10^{-9}	8.0706	7.6813×10^{-9}	8.1146	7.3020×10^{-9}	8.1366
CA2↔CA5	2.5897×10^{27}	26.5867	2.0941×10^{-9}	8.6790	2.2404×10^{-9}	8.6497	7.6813×10^{-9}	8.1146	2.3173×10^{-9}	8.6350
CA2↔CA6	5.1271×10^{-2}	1.2901	4.5761×10^{-5}	4.3395	7.9097×10^{-6}	5.1018	5.3649×10^{-6}	5.2704	4.4558×10^{-6}	5.3511
CA2↔CA8	1.3672×10^{-25}	24.8641	1.3101×10^{-19}	18.8827	2.3485×10^{-18}	17.6292	4.2399×10^{-18}	17.3726	5.6489×10^{-18}	17.2480
CA2↔CA10	8.2835×10^{-3}	2.0818	8.5833×10^{-8}	7.0663	7.4263×10^{-9}	8.1292	4.3272×10^{-9}	8.3638	3.3593×10^{-9}	8.4737
CA3↔CA4	3.7506×10^{-15}	14.4259	1.1264×10^{-12}	11.9483	4.0627×10^{-12}	11.3912	5.5051×10^{-12}	11.2592	6.3009×10^{-12}	11.2006
CA3↔CA6	5.0370×10^{-9}	8.2978	3.9104×10^{-9}	8.4078	3.8450×10^{-9}	8.4151	3.7806×10^{-9}	8.4224	3.7806×10^{-9}	8.4224
CA3↔CA5	2.5442×10^{-34}	33.5944	1.7895×10^{-13}	12.7473	1.0708×10^{-12}	11.9703	5.5051×10^{-12}	11.2592	3.7806×10^{-9}	8.4224
CA3↔CA7	5.1092×10^{-11}	10.2916	5.3365×10^{-10}	9.2727	1.0307×10^{-9}	8.9869	1.1998×10^{-9}	8.9209	1.2836×10^{-9}	8.8916
CA3↔CA9	5.5103×10^{-24}	23.2588	1.4154×10^{-18}	17.8491	8.9101×10^{-18}	17.0501	1.5291×10^{-17}	16.8155	1.9697×10^{-17}	16.7056
CA3↔CA11	5.2100×10^{-9}	8.2832	1.2587×10^{-11}	10.9001	4.8097×10^{-12}	11.3179	3.5496×10^{-12}	11.4498	3.4902×10^{-12}	11.4571
CA4↔CA6	1.3429×10^{6}	-6.1281	3.4713×10^{3}	-3.5405	9.3055×10^{2}	-2.9687	6.9843×10^{2}	-2.8441	6.1022×10^{2}	-2.7855
CA4↔CA10	2.1697×10^{5}	-5.3364	6.4021	-0.8063	8.7369×10^{-1}	0.0586	5.6334×10^{-1}	0.2492	4.6005×10^{-1}	0.3372
CA4↔CA8	3.5814×10^{-18}	17.4459	9.7722×10^{-12}	11.0100	2.7167×10^{-10}	9.5659	5.5197×10^{-10}	9.2581	7.7361×10^{-10}	9.1115
CA5↔CA6	1.9798×10^{25}	-25.2966	2.2224×10^{4}	-4.3468	3.5304×10^{3}	-3.5478	6.9843×10^{2}	-2.8441	1.8906×10^{3}	-3.2766
CA5↔CA9	22026932448	-10.3430	8.0443×10^{-6}	5.0945	8.3205×10^{-6}	5.0798	2.7777×10^{-6}	5.5563	9.8503×10^{-6}	5.0065
CA5↔CA11	2.0477×10^{25}	-25.3113	7.0342×10^{1}	-1.8472	4.4914	-0.6524	6.4478×10^{-1}	0.1906	1.7751	-0.2492
CA6↔CA7	1.0143×10^{-2}	1.9938	1.3418×10^{-1}	0.8723	2.7262×10^{-1}	0.5644	3.1735×10^{-1}	0.4985	3.3951×10^{-1}	0.4691

| Tautomer	gas (ε = 1.00)		THF(ε = 7.50)		ethanol(ε = 1.00)		DMF(ε = 24.55)		water(ε = 78.50)	
	K	pK_T	K	pK_T	K	pK_T	K	pK_T	K	pK_T
CA6↔CA10	1.6156×10^{-1}	0.7917	1.8442×10^{-3}	2.7342	9.3889×10^{-4}	3.0274	8.0657×10^{-4}	3.0934	7.5391×10^{-4}	3.1227
CA6↔CA11	1.0343	-0.0147	3.2190×10^{-3}	2.4923	1.2509×10^{-3}	2.9028	9.2317×10^{-4}	3.0347	9.2317×10^{-4}	3.0347
CA6↔CA8	2.6667×10^{-24}	23.5740	2.8151×10^{-15}	14.5505	2.9194×10^{-13}	12.5347	7.9029×10^{-13}	12.1022	1.2893×10^{-12}	11.8896
CA7↔CA7	1.0968×10^{-13}	12.9598	2.6975×10^{-9}	8.5690	8.6446×10^{-9}	8.0633	1.2745×10^{-8}	7.8947	1.5345×10^{-8}	7.8140
CA7↔CA11	1.0197×10^{2}	-2.0085	2.3587×10^{-2}	1.6273	4.6664×10^{-3}	2.3310	2.9584×10^{-3}	2.5289	2.7190×10^{-3}	2.5656
CA8↔CA9	4.1720×10^{8}	-8.6204	1.2857×10^{5}	-5.1092	7.9374×10^{3}	-3.8997	5.0322×10^{3}	-3.7018	4.0408×10^{3}	-3.6065
CA8↔CA10	6.0583×10^{22}	-22.7824	6.5513×10^{11}	-11.8163	3.2159×10^{9}	-9.5073	1.0205×10^{9}	-9.0089	5.9468×10^{7}	-8.7743
CA8↔CA11	3.8786×10^{23}	-23.5887	1.1243×10^{12}	-12.0509	4.2847×10^{9}	-9.6319	1.1681×10^{9}	-9.0675	7.2819×10^{8}	-8.8622
CA9↔CA10	1.4768×10^{14}	-14.1693	5.0951×10^{6}	-6.7072	4.0515×10^{5}	-5.6076	2.0280×10^{5}	-5.3071	1.4716×10^{5}	-5.1678
CA9↔CA11	9.2967×10^{14}	-14.9683	8.8931×10^{6}	-6.9491	5.3980×10^{5}	-5.7322	2.3212×10^{5}	-5.3657	1.8020×10^{5}	-5.2558
CA10↔CA11	6.4021	-0.8063	1.7161	-0.2346	1.3323	-0.1246	1.1445	-0.0586	1.2245	-0.0880
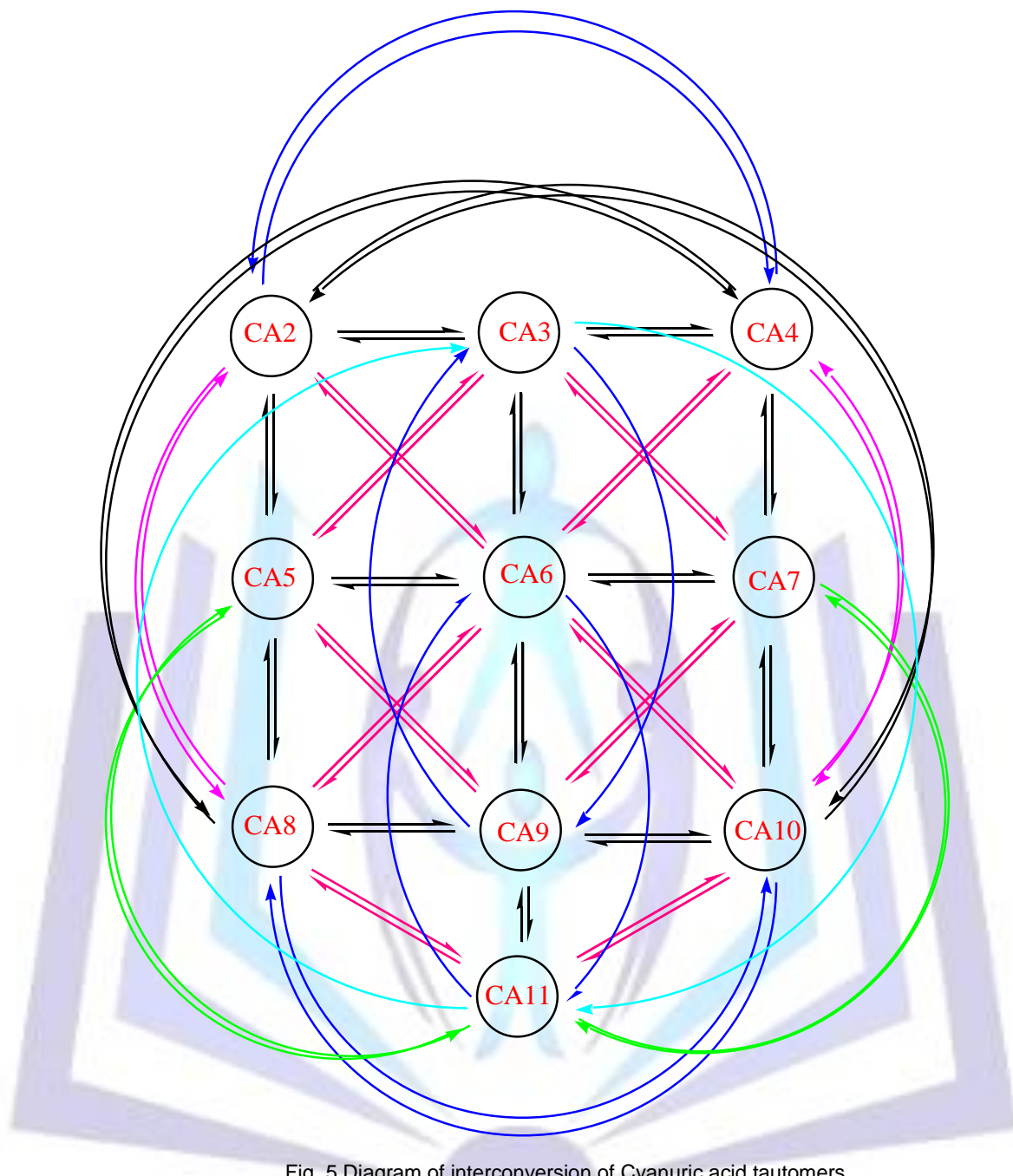
Fig .5.Diagram of interconversion of Cyanuric acid tautomers.

CONCLUSION

Tautomers of Cyanuric acid acid have been studied by using HF methods in the gas phase and in different solvents (IPCM). The following conclusions have been drawn from the present study:All the optimized tautomers present at the stationary points are corresponding to local minima in the potential energy surface. The keto form **CA1** was found to be the most stable form over than all enol forms in the gas phase and different solvents. The influence of the polar environment substantially enhanced the dipole moment for all the tautomers in going from the gaseous to aqueous phase, which indicates that there is an increase in stability of the molecular system due to the solvent-molecule interaction and redistribution of the charge. The pK_T values are decreasing to increase the polarity of solvents. Solvent effects have been ascribed to two major components, electrostatic solvent-solute interaction and hydrogen bonding.

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