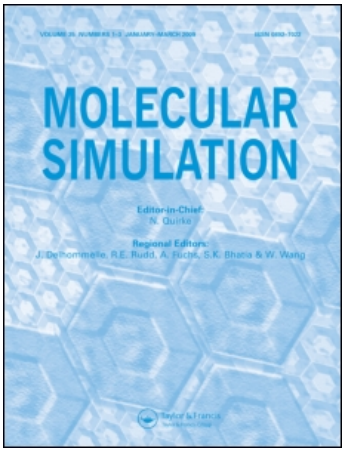

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Ab initio and dielectric studies of succinic acid and maleic acid in 1,4-dioxane

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Ab initio and dielectric studies of succinic acid and maleic acid in 1,4-dioxane

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In a continuing effort to understand the hydrogen bond through the study of dielectric and computational conformal studies of dilute solutions, succinic acid and maleic acid are studied in solutions of 1,4-dioxane solvent. Dielectric studies give an account of the net dipole moment of the system under study, which is then compared with the values obtained from conformal analysis. The dielectric measurements were made at 303 K at a frequency of 9.83 GHz using a X-band microwave test bench in order to determine the relaxation times and the dipole moments. The static dielectric permittivity and the high frequency dielectric permittivity were measured using a LCR meter and an Abbe's refractometer, respectively. The results are inspected in comparison with the dipole moment results of *ab initio* calculations of some of the conformers in gas phase and in liquid phase. Gaussian-03 software package with 6–31G(d) basis set optimisation was used for this purpose. Onsager's reaction field model is used to study the solvation of the dicarboxylic acids in 1,4-dioxane. The results are interpreted in terms of the intermolecular and intramolecular hydrogen bond interactions in the dilute systems.

Keywords: *Ab initio*; Dielectric spectroscopy; Dicarboxylic acids; Dioxane; Solvation

1. Introduction

It is needless to elaborate the role of hydrogen bonds in the conformation and the stability of complex molecular systems, and especially those of biological importance. In our continuing effort to understand the hydrogen bonds through dielectric studies of dilute solutions and conformational *ab initio* analysis [1,2], we present the studies undertaken for two dicarboxylic acids, namely, succinic acid and maleic acid, in dilute solutions of 1,4-dioxane.

Dicarboxylic acids are known for their ability to form intramolecular hydrogen bonds leading to complex stabilized structures. Enhancement of the net dipole moment of the system is a measure of the association of the molecules in the given system [3]. The enhancement of the dipole moment has been attributed to various factors such as polarization effect, partial or complete proton transfer and reaction field effects. If there is a complete charge transfer, the increment in the dipole moment is seen to be the order of 10 D [4] and reaction field effects are predominant when the complex formation in the system is in the presence of a polar solvent.

Conformations of succinic acid [5] and maleic acid [5,6] have been studied previously. Conformational preference of succinic acid is not understood well because the presence of intermolecular and intramolecular hydrogen bonds in this system leading to many possible conformations. The presence of large carboxylic groups on either end of the molecule suggests the stability of the trans conformer from a purely steric hindrance point of view. The preference for the gauche conformer arises from the fact that this conformation supports intramolecular hydrogen bonding and these intramolecular hydrogen bonds give stability to the system. The presence of two competing conformers is easily seen.

Solid succinic acid is seen to undergo fast polymorphous transitions that are observed in the optical spectra [7,8,9]. Further, it has been shown by Ponomarenko *et al.* [9] that up to a temperature of 160°C succinic acid is a dielectric, based on conductivity studies, hence ruling out any ionic contribution to the net dipole moment. Sloth *et al.* [10] have studies the influence of the orientation of a succinic acid molecule with respect to the surface of a particle, with a view to understand aerosol action.

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Maleic acid (*cis*-butenedionic acid) too has four carbon atoms, but the presence of a C=C makes the molecule rigid in terms of group rotations about the C–C axis. This double bond inhibits the rotation of the COOH groups about the C–C bond, hence hindering some of the molecular motions. This in turn alters the nature of intramolecular hydrogen bonding that is possible, although maleic acid retains the ability for intermolecular hydrogen bonding.

Rogers [11] has seen dioxane to be a non-ionising solvent. Molecular dynamics and Monte Carlo simulations have indicated 1,4-dioxane to have a disordered structure with an average spherical packing [12,13]. 1,4-Dioxane has three possible conformations, the chair, the bath and the twist. Of these the chair conformation has the greatest stability [14] and the bath and the twist conformers are both likely to have the lowest stability. The molecules of 1,4-dioxane tend to form a layered structure with several C–H···O bonds if the molecules are in bath conformation. Whereas the molecules with chair conformation tend to form linear chain associations with the dipole moment tending to zero. Here the dipole–dipole interactions are the leading interactions [15].

The gauche and trans conformers of succinic acid are taken up for the present study. Moravetz *et al.* [16] have found the gauche conformer to be most probable in solutions. The chair conformation of 1,4-dioxane was seen to be the most stable conformer and hence taken up for the present study. We present here the dielectric studies of dilute solutions of succinic acid and maleic acid in 1,4-dioxane and some *ab initio* studies to support the experimental observations.

2. Experimental and computational details

Solutions of succinic acid and maleic acid in 1,4-dioxane were prepared in the concentration range of 0.01–0.05 weight fractions. All the chemicals used were of Analar grade (purity >99.5%) and were used directly, without further purification. The static dielectric permittivity was measured using a LCR meter, ε' and ε'' were determined at X-band frequency (9.7 GHz) using a microwave test bench plunger method and ε_∞ was determined from refractometry studies with sodium-D source using an Abbe's refractometer. The measurement accuracies of ε' and ε'' are ± 1 and $\pm 5\%$, respectively.

The dielectric relaxation times have been analysed using Higasi's [13] formulation wherein, ε_0, ε', ε'' and ε_∞ are assumed to vary linearly with the weight fraction of the solute. This linearity is seen from the data presented in tables 1 and 2. Two relaxation times are associated with the relaxation of molecules in the liquid state. One relaxation time namely τ_1 corresponds to the overall relaxation of the molecule that is, an end-to-end rotation of the system, and hence a longer relaxation time. The second relaxation time τ_2 corresponds to the shorter relaxation of the side-chains or segments of the molecule. Since this model corresponds to an ideal situation of two rotational motions, an average relaxation time, $\tau_0 = [\tau_1\tau_2]^{0.5}$ is defined. τ_0 is called the mean relaxation time. The details of the relevant equations are the same as mentioned by Malathi *et al.* [17].

The bistable model of Eyring [18] is assumed here wherein the mean relaxation time is related to the thermodynamic parameters through equation (1)

$$\tau = \left[\frac{h}{kT}\right] \exp\left[\frac{\Delta F}{RT}\right] \tag{1}$$

where k is the boltzmann constant, R is the real gas constant and T is the temperature in Kelvin. Bauer *et al.* [19] have suggested that the activation energy is nearly equal to the energy necessary to break the hydrogen bonds. Hence the activation energies are calculated for the dilute systems to get a comparison of the activation

Table 1. Dielectric permittivity and relaxation times for succinic acid in 1,4-dioxane.

Weight fraction	ε_o	ε_∞	ε'	ε''	τ_1 *(ps)*	τ_2 *(ps)*	τ_0 *(ps)*	*Activation energy* $(kJ\,mol)^{-1}$	μ *(D)*
0.01	2.61	2.131	2.53	0.14	12.98	9.22	10.94	12.53	3.493
0.02	2.79	2.158	2.63	0.21	13.72	12.18	12.98	12.10	3.512
0.03	2.98	2.179	2.74	0.31	14.88	12.49	13.64	11.98	3.529
0.04	3.23	2.221	2.89	0.43	15.28	12.76	13.96	11.92	3.537
0.05	3.41	2.223	2.96	0.49	15.44	14.82	15.44	11.72	3.541

Table 2. Dielectric permittivity and relaxation times for maleic acid in 1,4-dioxane.

Weight fraction	ε_o	ε_∞	ε'	ε''	τ_1 *(ps)*	τ_2 *(ps)*	τ_0 *(ps)*	*Activation energy* $(kJ\,mol)^{-1}$	μ *(D)*
0.01	2.74	2.142	2.62	0.19	12.12	10.19	11.11	12.49	3.289
0.02	2.91	2.164	2.78	0.26	10.73	8.06	9.36	12.94	3.225
0.03	3.13	2.183	2.86	0.38	13.56	11.46	12.47	12.20	3.234
0.04	3.27	2.229	2.92	0.47	16.27	12.01	13.98	11.91	3.241
0.05	3.56	2.231	3.01	0.53	15.43	16.74	16.07	11.56	3.256

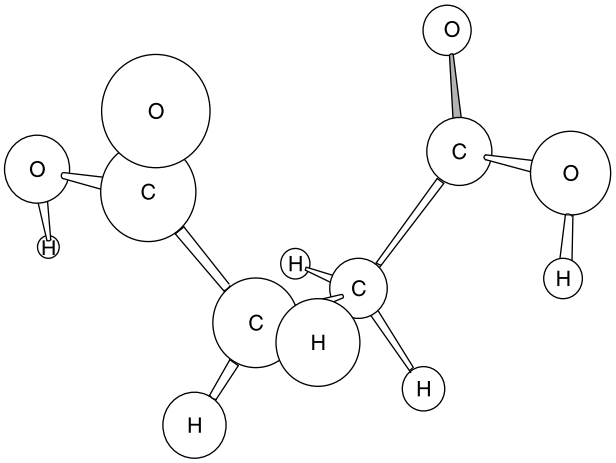

Figure 1. Trans conformation of succinic acid.

energies and to determine the concentration at which this has a minimum value. The activation energy determined from dielectric studies is not equal to the value determined from computations since the former refers to the energy required for the molecules to rotate about the mean position, assuming a bistable model in the presence of an external electric field.

It has been seen that MNDO/PM3 is appropriate for the study of hydrogen-bonded complexes [15]. Conformal analysis for the chosen systems was performed initially at the PM3 optimisation using WinMOPAC, the output of which was taken for subsequent optimisations at STO-3G and 6−31G(d) levels. The optimisations at STO-3G and 6−31G(d) were performed using Gaussian-03 on an IBM64-RS6000 machine.

For the stable conformers, the Onsager model reaction field was applied with 1,4-dioxane as the solvent. In this model it is assumed that the solute is placed in a spherical cavity in the solvent with the solvent being a homogeneous polarizable medium that has a constant dielectric permittivity. As it can be seen, this is a simple model. The dipole moment of the solute molecule polarizes the surrounding medium, which in turn polarizes

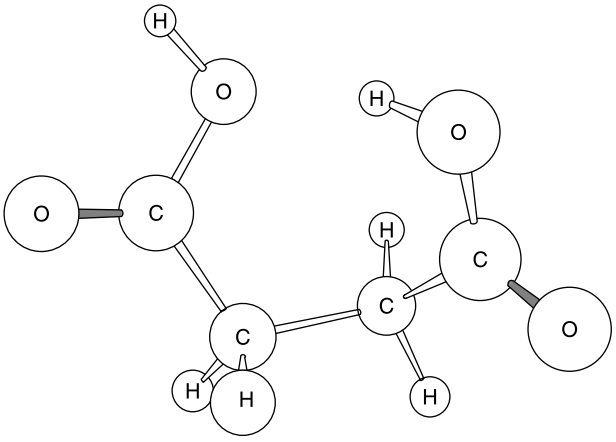

Figure 2. Gauche conformation of succinic acid.

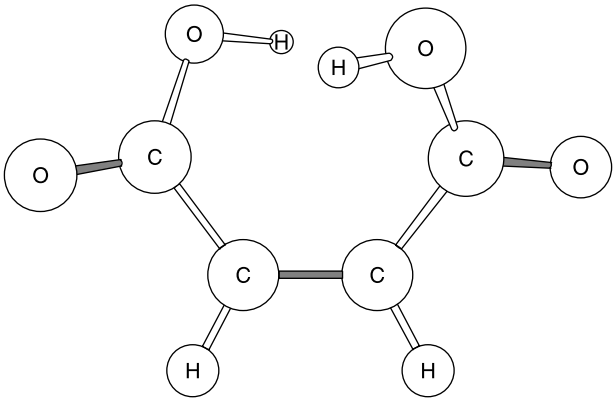

Figure 3. Minimum energy conformation of maleic acid.

the solute charge distribution. In Gaussian-03 [20], this mutual polarization is treated in a self-consistent manner. The reaction field is given by the equation (2)

$$R = \left[\frac{2\mu(\varepsilon - 1)}{V(2\varepsilon + 1)}\right] \tag{2}$$

where V is the volume of the solvent molecule.

3. Results and discussion

The experimentally observed results for the two dilute systems are reported in tables 1 and 2. It is seen from the data in these tables that the minimum value of the dipole moment for both the systems corresponds to the maximum value of the activation energy. This occurs for a concentration of 0.01 weight percent for succinic acid and 0.02 weight percent for maleic acid. The activation energy can be taken to be a measure of the strength of the hydrogen bonding of the system. Larger activation energy implies that the system requires a larger energy to be supplied to it to break the hydrogen bonds and hence

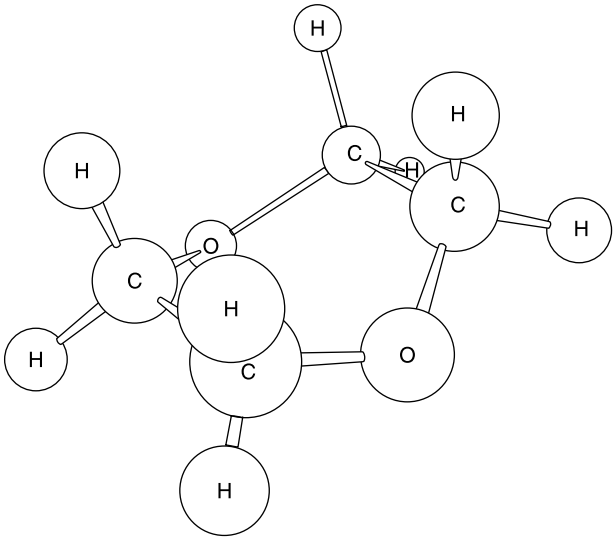

Figure 4. Minimum energy conformation of 1,4-dioxane.

Table 3. Total energy in (Hartree) and the dipole moment μ in Debye at STO-3G optimisation in gas phase and on solvation by 1,4-dioxane.

System	μ	*Total energy*	μ *on solvation*	*Total energy on solvation*
1,4-dioxane (14 D)	1.9004	−301.979797	–	–
Succinic acid—Trans	5.6105	−448.4528787	5.8418	−448.4561768
Succinic acid—Gauche	3.6181	−448.469926	4.5608	−448.469926
Maleic acid	3.2337	−447.2297874	3.7741	−447.2356307

Table 4. Total energy in Hartree and the dipole moment μ in Debye at 6–31G(d) optimisation in gas phase and on solvation by 1,4-dioxane.

System	μ	*Total energy*	μ *Solvation*	*Total energy on solvation*
1,4-dioxane	1.7221	− 305.8144629	–	–
Succinic acid—trans	6.1563	− 454.4457889	6.0959	−454.0264838
Succinic acid—gauche	6.1544	− 454.4457889	5.4503	−454.4361053
Maleic acid	6.0764	− 453.241052716	4.8249	−453.2209827

implies either a stronger hydrogen bond or the presence of a larger number of hydrogen bonds. The lowering of the dipole moment in this case where the net charge is constant can be taken to be indicative of the stronger bonding between the species. The coincidence of the activation energy maximum and the dipole moment minimum values further corroborates this premise.

It is also seen from the data that τ_1 is not equal to τ_2 for the concentrations, where the dipole moment of the system in minimum, in both the systems. Since $\tau_1 \sim \tau_2$ implies a rigid molecule, it may be concluded that for the two concentrations under consideration, the intermolecular interactions yield a flexible structure where the group rotation is different from the net molecular rotation. An apparent contradiction is seen. On one hand the decrease in dipole moment and increase in the activation energy seem to suggest a more rigid structure whereas the relaxation time indicates two distinct mechanisms, hence suggestive of a structure with more conformational degrees of freedom. One possible mechanism at work could be an enhanced solute–solvent interaction at the specific concentrations leading to a complex that has a lower dipole moment but the interactions permitting the rotation of parts of the molecule, hence leading to two distinct relaxation times.

In order to further understand these interactions, *ab initio* studies are taken up. Geometry optimisation was performed for the gauche and the trans conformations of succinic acid, maleic acid and for the chair conformation of 1,4-dioxane; the optimize conformations of the same are given in figures 1–4. The dipole moment values for the various levels of optimization are reported in table 3 and the respective energies in table 4. The gauche conformer of succinic acid is seen to possess the lower energy. The stability of this conformation is seen to be due to the presence of intermolecular O–H···O hydrogen bonding.

The dipole moments of the molecules on solvation by 1,4-dioxane as calculated by the Onsager's reaction field model at STO-3G and 6–31G(d) optimization are reported in tables 3 and 4 that the enhancement of dipole on solvation for the two dicarboxylic acids is about 0.5 D for maleic acid and 0.9 D for succinic acid. This is far greater than the variation in the dipole moment of each of the systems with concentration. For the data it seems unlikely that pure solvation effects are responsible for the stabilization. It is seen that there are two contributions to the variation of dipole moment—the difference in the conformation of the solvent molecule and the solvation due to the solute molecule.

Table 5. Total energy in Hartree and the dipole moment μ in Debye at 6–31G(d) optimisation for the structure proposed by Ponomarenko *et al.* [9].

μ-*STO-3G*	*Total energy* − *STO-3G*	μ − *6–31G(d)*	*Total energy* − *6–31G(d)*
$\mu = 8.4237$	−1052.4484266	7.1812	−1066.1100606

Until now we have considered only a single molecule of succinic/maleic acid solvated by a continuum of 1,4-dioxane. But in the liquid state, it is possible for both the solute and the solvent molecules to form clusters of two or more molecules. The dipole moment of two molecules of succinic acid optimised at the 6–31G(d) level is found to be 7.3198 D. The energy minimization of the interaction of one molecule of 1,4-dioxane with one molecule of succinic acid yields a dipole moment of 5.6930 D. These values are much larger than the present observations and hence were not pursued further.

Ponomarenko *et al.* [9] have determined the dielectric permittivity of succinic acid in 1,4-dioxane to be 2.4 D from refractometry studies. Since ε_∞ does not take into account the orientational polarization of the system, the dipole moment is lower than what is determined in the present case ($\sim$3.5 D). In the same paper, they quote a reference where the dipole moment of succinic acid in gas phase is determined to be 2.15 D. Succinic acid has a large number of conformations [5] and hence it is likely that 2.15 D corresponds to one of the conformers in gas phase. On solvation, the interaction of the solute molecule with the solvent molecule may stabilize a few conformers. Ponomarenko *et al.* have further indicated one possible interaction of succinic acid with 1,4-dioxane, as shown in

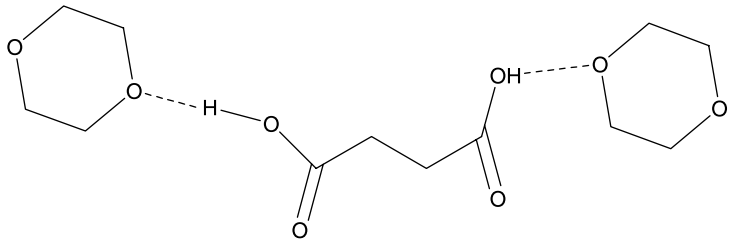

Figure 5. The possible interaction suggested by Ponomarenko *et al.* [9] for succinic acid in 1,4-dioxane.

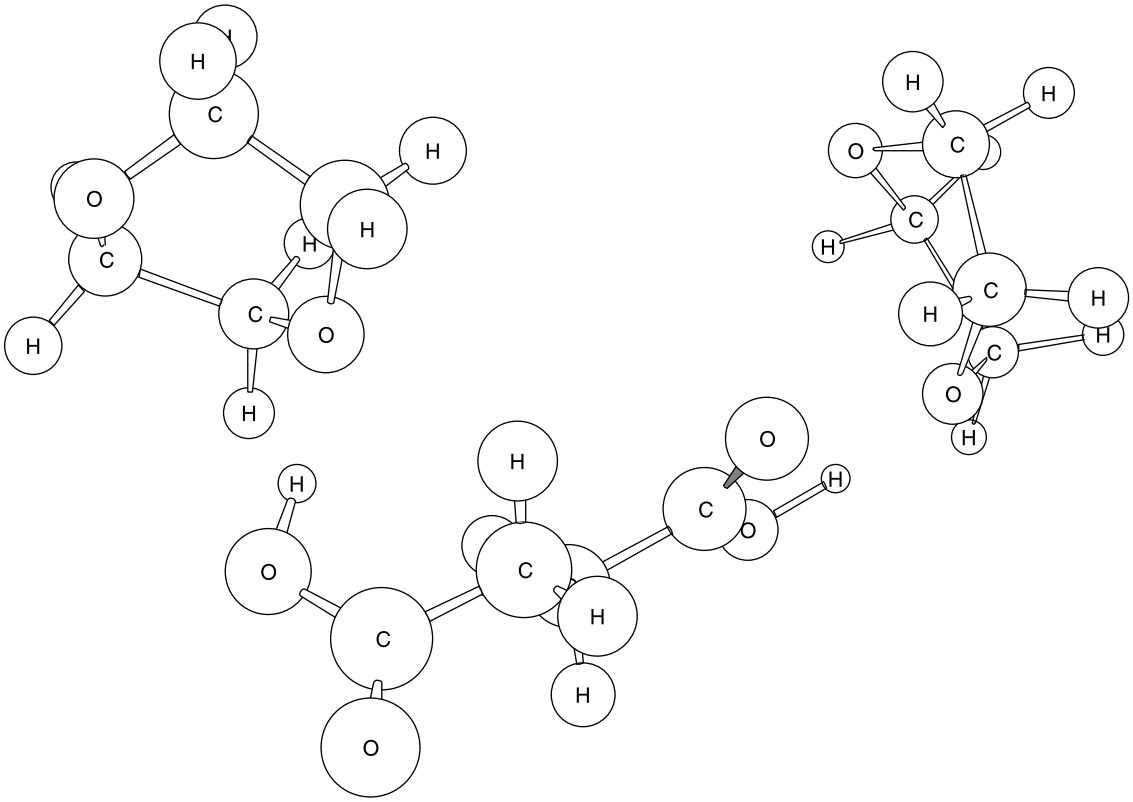

Figure 6. Conformation of the structure proposed in figure 5, optimised at the STO-3G basis.

figure 5 with $\Delta\mu = 0.3$ D. This conformation was taken up for study. The final conformation optimized at the STO-3G is with a total energy of and the final conformation is shown in figure 6. Given the high value of the resultant dipole moment for this system, such an interaction of one molecule of succinic acid with two molecules of 1,4-dioxane as suggested by Ponomarenko *et al.* [9] seems unlikely (table 5) (figure 7).

4. Conclusions

The dielectric properties of two dicarboxylic acids namely succinic acid and maleic acid were studied in dilute solutions of 1,4-dioxane. Previous reports indicate 1,4-dioxane to be a non-polarizing solvent and for the gauche conformer of succinic acid to be stable in solutions. Our present studies indicate the preference of gauche conformation in the solution state. On performing a concentration variation of succinic/maleic acid solute in 1,4-dioxane solvent from 0.01 to 0.05 weight percent, it is seen that succinic acid–dioxane system shows the formation of a stable configuration for 0.01 weight percent and maleic acid at 0.02 weight percent.

Ab initio conformational analysis of succinic acid indicate the presence of intramolecular hydrogen bonding. Solvation of succinic acid by dioxane using Onsager's reaction field model indicates the enhancement of the dipole moment of the system by 0.5 and by 0.9 D in the case of maleic acid in dioxane. This is in agreement with previous observations that succinic acid is a dielectric at room temperature. Large charge transfer will give enhancement in dipole moment to the order of 10 D. Conformational analysis of a structure previously proposed for the solvation of succinic acid in 1,4-dioxane is found to be insufficient to predict the experimental observation. Compared to some specific interactions between succinic/maleic acids considered, Onsager's

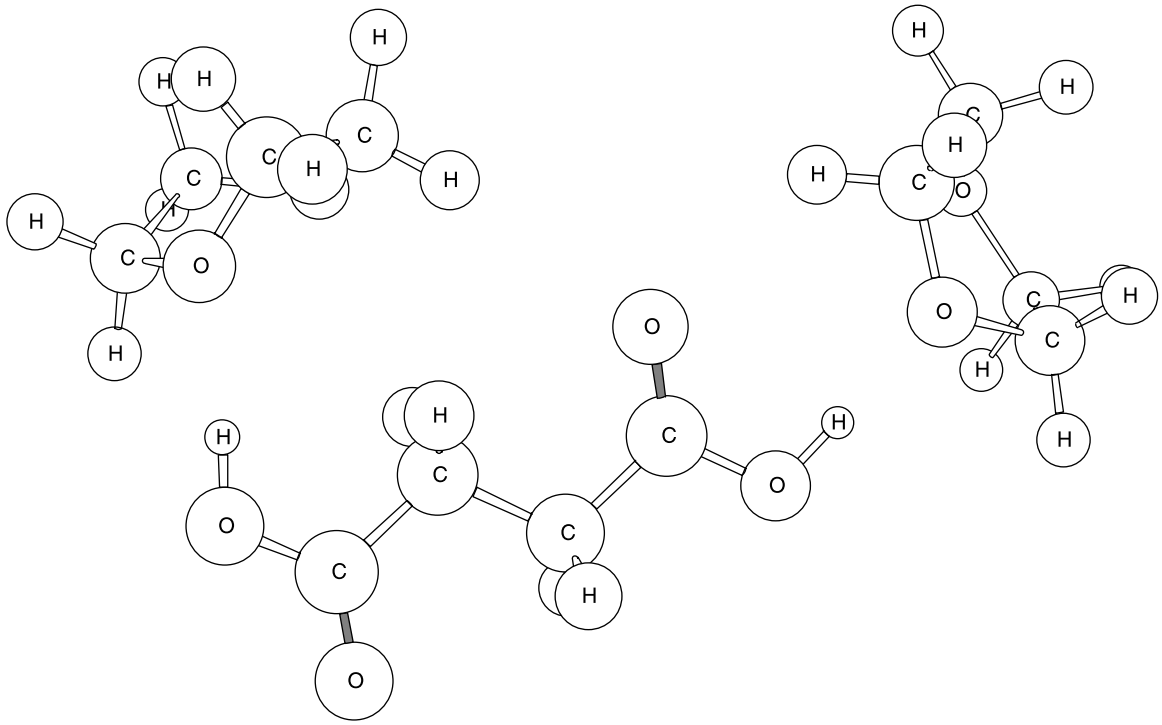

Figure 7. Conformation of the structure proposed in figure 5, optimised at the 6−31G(d) basis.

solvation model is seen to give results that are closer to the experimental observations. We conclude that unlike in the case of solvation of simple molecules or binary systems of simple molecules that do not show a marked preference for intramolecular hydrogen bonding, dicarboxylic acids in 1,4-dioxane are best represented by the Onsager's reaction field model wherein solvent is treated as a continuum. This implies the absence of specific solute–solvent interactions in these systems.

The present measurements are important since biological activity is closely related to the transfer of electron/proton in the given system and dipole moment is a measure of the charge transfer in the system. These observations, especially the comparison of the experimental dipole moment with that obtained from conformational analysis gains further importance since many biological interactions and their reactivity are measured from the dissociation constant pK_a and fluorescence spectra, that are in turn directly related to the dipole moment of the system.

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