Different Planer Conformers of Polyacrylic Acid in The Glass Ionomer Cements

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Abstract:

Glass ionomer cements are dental restorative materials used for filling teeth and for luting cements. The materials are derived from the reaction of silicate glass powders and polyalkenoic acids such as homo- and co-polymers of polyacrylic acid. Co- polymers and homopolymer of polyacrylic acids play an important role in the formation of GICs. The functional groups of homo-polymer acid are more regularly arranged than the copolymeric acid. Therefore, that reduces H-bonding between acid molecules, reduces the degree of gelling, decrease the viscosity and improves storage cements. To achieve an improved understanding of the *physical and chemical properties of the cement, the structure and relative energetic of different conformers of the acrylic acid monomer were initially investigated using state-of-the-art quantum mechanical calculations. The results indicated a strong hydrogen bond stabilization for the sin- H-O-C=O dihedral angle, whereas the sin- and anti- C=C-C=O conformers both exhibited similar energies.*

Key words: *glass ionomer cements, Co-polymer polyacryclic acid (PAA), Monomer acrylic acid, State-of -the- art quantum mechanical.*

1.Introduction

A Glass Ionomer Cement (GIC) is a class of dental restorative materials used for filling teeth and within luting cements (a thick, viscous, glue-like material placed between the tooth and a prosthesis, that hardens and forms a strong “bond” via chemical reactions between the tooth and prosthesis) [1]. As such, the adhesion of restorative materials is one of the key aspects of restorative dental science. The materials must be flexible enough to cover the whole of the tooth (its “nooks and crannies” and jagged edges). The materials are derived from the reaction of silicate glass powders and polyalkenoic acids such as homo- and co-polymers of polyacrylic acid [2].

during setting reaction, the polyalkenoic acid and glass powder are mixed, the glass outer surface is attacked by the carboxyl group of acid and that causing Ca^{2+} F^{-} and Al^{3+} ions release. In this phase of setting reaction (primary stage) of setting, the ions of Ca^{2+} are released more quickly and are mainly responsible for reacting with the polyacid to produce akin. While Al^{3+} an ion are released more slowly than Ca^{2+} ions and becomes comprised in setting at a later stage (secondary reaction stage). The set material consists of untreated glass cores surrounded by cross-linked polyacid matrix. The primary setting reaction between the powder and the liquid is mainly an ionic acid-base reaction. Figure1.1 shows the setting reaction of glass ionomer cements [3].

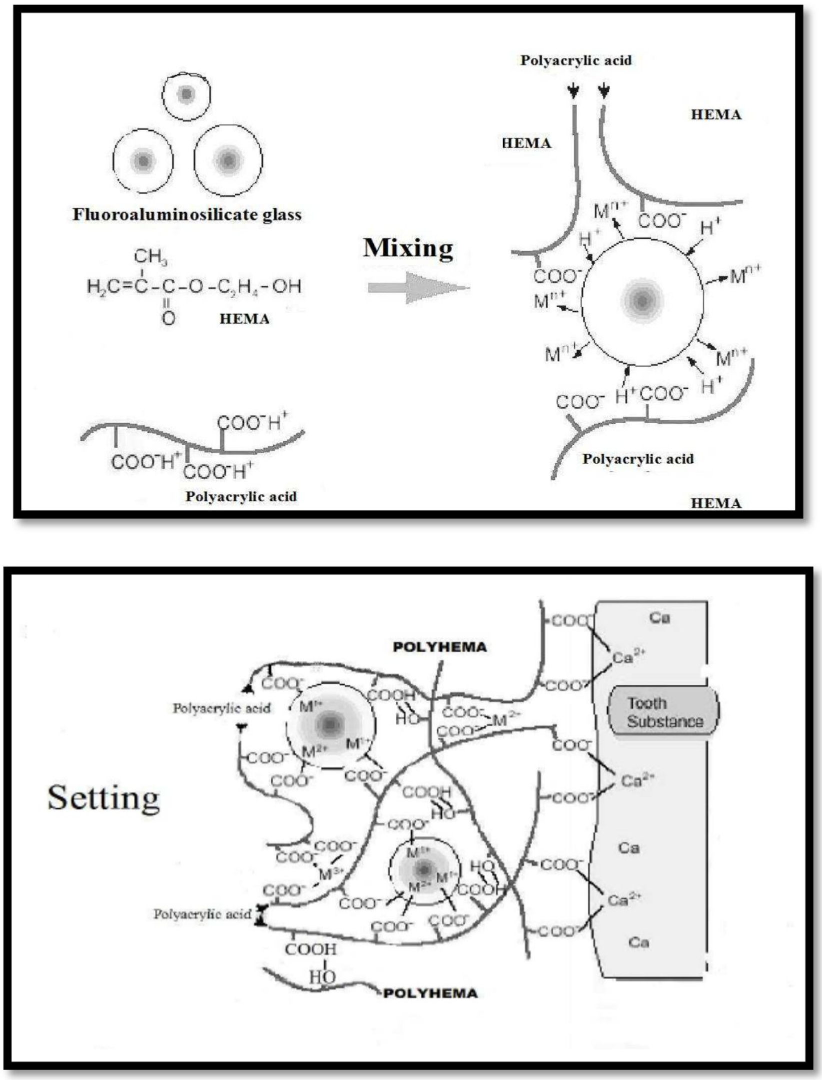


Figure 1.2 Schematic the setting reaction of glass ionomer cements.

In accordance with Brønsted-Lowry acid-base theory, the powder acts as a proton acceptor and the liquid as a proton donor. Due to the iconic nature of the setting method, toxic monomers, initiators or activators are eradicated from the setting reaction [3, 4]. The set glass ionomer cement consists of amorphous, glass-like matrix of ceramic particles within an ion-cross-linked polymer or ionomer. These materials are based on the reaction of a silicate glass powder with polyacids. For decades the polymeric materials used for GIC are based on poly (acrylic acid), poly (acrylic acid co-itaconic acid) or poly (acrylic acid co-Maleic acid)., the polymer material has been chemically modified so it has double bonds polymerize- able by free radicals; the aqueous formulation also contains a monomer with methacrylate groups [5].

However, the importance of the formation reactions of polyacrylic acid for the construction of the cement and the technology is the importance of their production. Therefore, an improved understanding of the physical and chemical properties of the cement will be using performed functional density calculations to obtain a detailed look at these reactions and identify possible reaction methods; this study aims to investigate the mechanism of setting reaction of GICs theoretically.

Since Aluminum chelation and tracking structural changes using Si, Al,\and O as 'probes' that there should be matching results of the geometric and electronic structure of these materials, with 'atomic resolution'. Theory and computation introduce a cost-effective means of doing this; however, not one theoretical or computational study exists on these materials [6.7]. Additionally, there is a serious lack of understanding of the local atomic structure and how they correspond to the NMR trends observed. An exemplary spectrum, generated at differing times after initiation of setting, is shown in Figure 1.2 for a sample of LG26Sr, a commercial GIC.

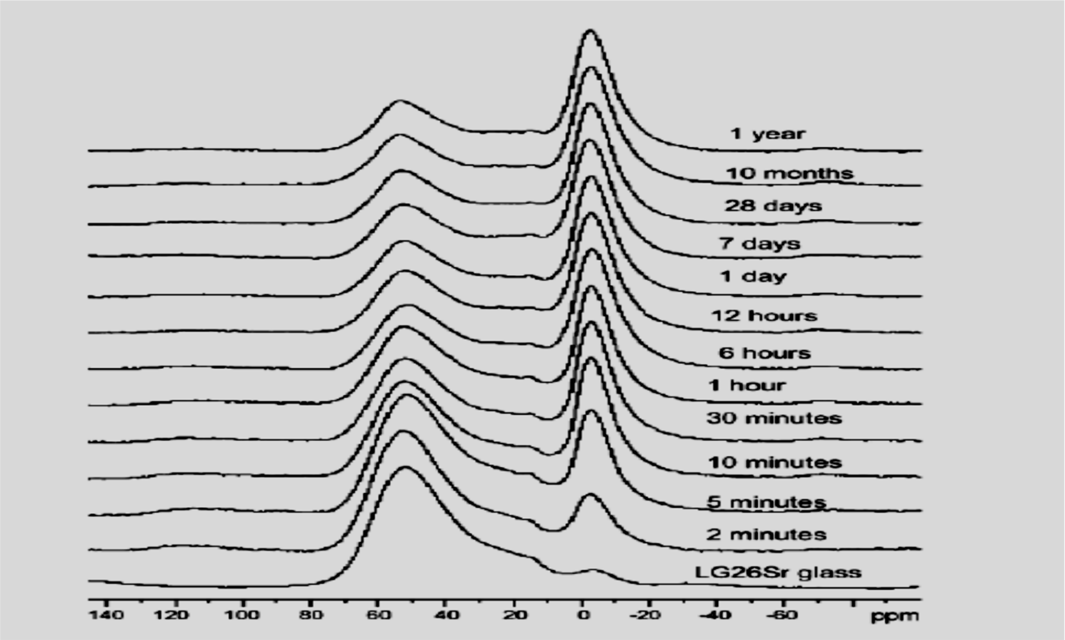


Figure 1.2 - 27Al-NMR spectrum (1M AlCl3•6H2O as standard) sampled over a 1 year period for LG26Sr GIC, a commercial composition containing Sr; deconvolution shows peaks at ~53, 30, 12 and 2 ppm, with a shoulder extending over ~35-50 ppm

Computation provides a cost-effective means to deriving exact information about the local environment around the Al. This would be especially helpful in answering fundamental questions, while providing a means to quantitatively tracking the influence/effect of P, F, Na, Ca additions As a first step, all topologically possible neutral Al-coordinated acid-polymer structures were modeled towards uncovering the topologically probably (energetically stable) set and their respective chemical shifts relative to the commonly used AlC13•6H2O standard.

In order to gain an improved understanding of glass ionomer cements it is necessary to probe the molecular geometry of the polymeric species (and other constituents) involved within the complex setting reaction. The polymeric species within glass ionomer cements are either homopolymers of acrylic acid, *i.e.* poly (acrylic acid), or copolymers of acrylic acid with α,β unsaturated polycarboxylic acids, *e.g.* itaconic acid or maleic acid. As the potential energy surface describing the overall relative energies for each conformation of poly (acrylic acid) is complex, a simpler, initial model was constructed using the acrylic acid monomer itself.

2. Computational Details

All molecules studied in this paper have closed shells (no unpaired electrons), so a Restricted Hartree-Fock (RHF) approach (two electrons in each molecular orbital) is used. A guesstimate of the molecular wave function undergoes successive refinement until the electronic energies (and wave function) do not vary using a Self-Consistent Field (SCF) approach [8]. The coordinates of the nuclei under the Born-Oppenheimer approximation are varied using standard minimization approaches until the maximum and root-mean-square (RMS) gradients, displacement (forces) become lower than a certain threshold value, *i.e.*a stationary point is located. A vibration frequency analysis is performed upon all stationary points to identify whether a minimum (all positive frequencies) or nth -order transition state (n imaginary frequencies) has been obtained.

Relative energies (noted in kJ mol^{-1} for convenience) were calculated for a series of conformers by tabulating the Restricted Hartree-Fock energy (*RHFE*) obtained either in Hartrees (HF/3-21G, HF/6-31G (d)) or kcal mol^{-1} (AM1, PM3) relative to the minimum energy for the series. Conversion factors of 1 kcal mol^{-1} 4.1840 kJ mol^{-1} and 1 Hartee (a.u.) _ 627.51 kcal mol^{-1} 2625.50 kJ mol^{-1} were employed.

Simple model structures were first drawn-out on paper then subsequently constructed for input into geometry-optimisations, followed by frequency analyses to ensure the tructures resided at minima on their respective potential energy hypersurfaces (PEHSs). With this certainty in mind, their NMR shifts relative to that of the AlCl3•6H2O standard were determined.

3. Results and Discussion

3.1 monomer- acrylic acid

Electron diffraction studies on acrylic acid and its hydrogen-bonded dimer confirmed the asymmetry of the C-O and C=O bond lengths, i.e. the system is not resonance stabilized. The C-O bond in the acrylic acid dimer is 0.07 Å shorter than the C-O bond in the monomer, whereas the C=O bonds for both monomer and dimer are identical [9].

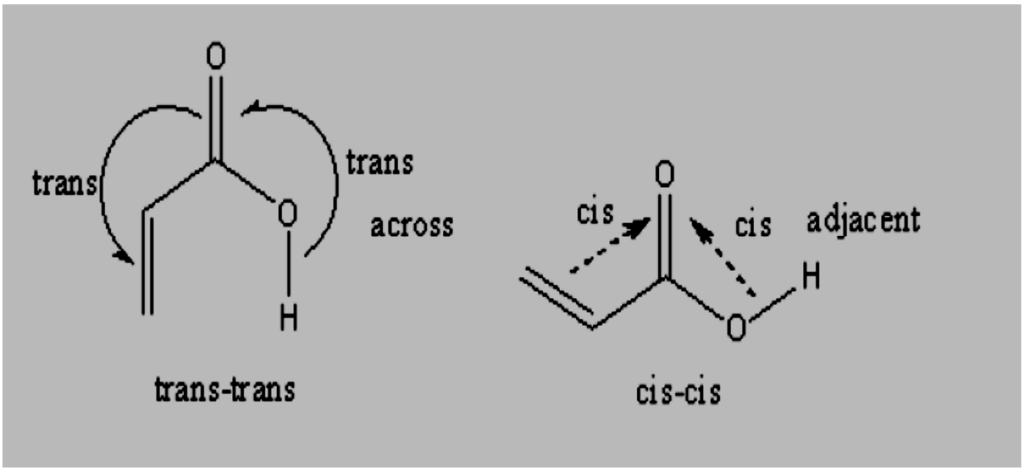


Figure3.1 Diagram for the shape cis and trans isomer

The shape of the acrylic acid monomer should be directly incorporated into the polymer, assuming that (steric) non-bonding or hydrogen-bonding effects within the polymer are neglected. A preference for planar configurations was assumed due to hydrogen bonding (H-O-C=O dihedral) and conjugation (C=C-C=O dihedral) effects. Identification of two clear dihedral angles as noted above allows the formation of four possible conformers, namely: **cis-cis, trans-cis, cis-trans, trans-trans** as depicted in Figure 3.2 below.

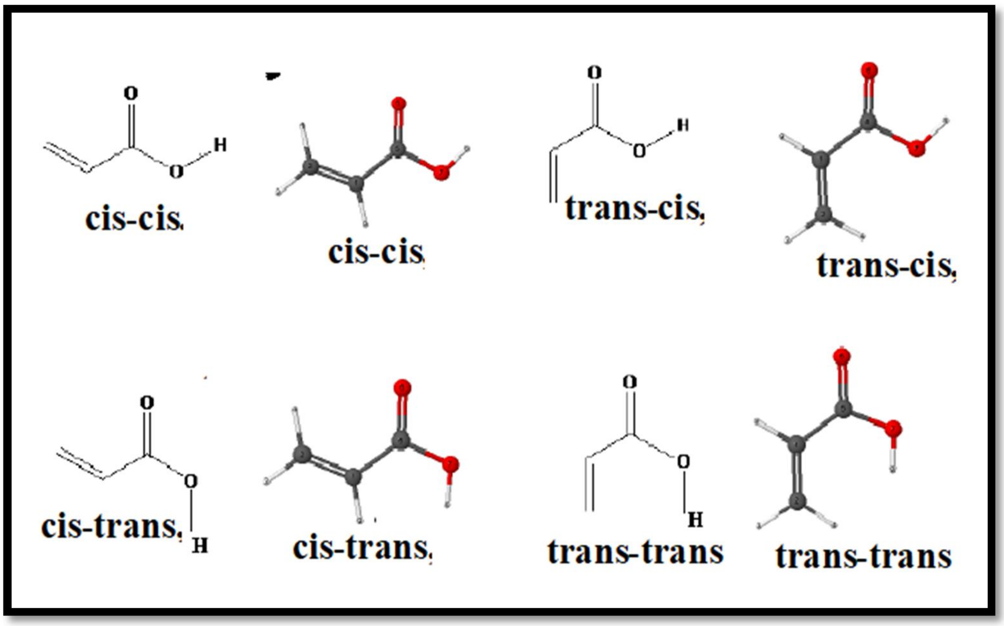
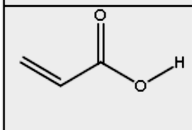
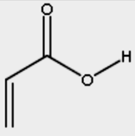
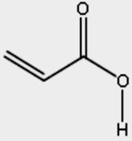
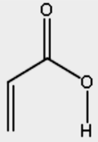


Figure 3.2 The four planar conformations of acrylic acid. The first and second dihedral angles are C=C-C=O and H-O-C=O respectively.

Conformational analysis of the acrylic acid monomer was performed using variety of quantum-mechanical methods (Semi-Empirical, HF) utilising different basis sets, the results of which are tabulated in Table 3.1. All conformers produced stationary points upon geometry optimization. Infra-red (IR) vibrational spectra for each stationary point were calculated to check whether a minimum (all positive frequencies), *n*th-order transition state (*n* negative frequencies) or maximum (all negative frequencies) were obtained. The frequency of the first normal mode (excluding any low-frequency rotations/translations) for each conformation is included in Table 3.1.

Table 3.1 Semi-empirical and Hartree-Fock conformational analysis of acrylic acid.

Initial Conformer	AM1		PM3		3-21G		6-31G(*d*)	
	ΔE^a	ν_1 cm^{-1}	ΔE	ν_1 cm^{-1}	ΔE	ν_1 cm^{-1}	ΔE	ν_1 cm^{-1}
 (1)cis-cis	0	+80	0	+52	0	+157	0	+121
 (2) trans-cis	1.7	+60	3.8	+58	2.9	+159	1.8	+123
 (3) cis-trans	22.6	+61	9.6	+76	35.4	+136	31.0	+99
 (4) trans-trans	27.2	-72	11.7	+41	47.8	-136	37.8	-115

Δ^{α}-kcal mol^{-1}(kJ mol^{-1} in parentheses) relative to lowest energy conformer The AM1 semi-empirical method produced a 1^{st} -order transition state (v_1= -72 cm^{-1}) for the *trans-trans* conformer **(4)**, whilst the related PM3 semi-empirical method produced a minimum structure for the same conformer. The molecular geometry and its relative energetics are strongly dependent upon the conformation of the O-H group – with the hydrogen atoms of the O-H group preferring (+22.6 kJ mol^{-1}) to be located on the same side as the carbonyl oxygen (C=O). This gives rise to a conformationally locked *cis*- (0°) conformation for the second H-O-C=O dihedral angle. The resultant stability is due to a combination of intra-molecular hydrogen bonding (5-30 kJ mol-1) and other non-bonding Coulombic / van der Waals interactions. There appears to be little or no conformational preference (4 kcal mol^{-1} at most) for the freely rotating vinyl group within the acrylic acid monomer.

The energetic differences between the related PM3 conformers are less, but the same qualitative trends are observed. An identical qualitative trend in energies (albeit with larger relative energies) are observed for the Hartree-Fock based methods with *cis-cis* <*trans-cis* < *cis-trans* < *trans-trans*. Animation of the lowest vibrational normal mode (not corresponding to a translation/rotation) shows a clear rotation about the C-C=C=O dihedral, with an almost negligible contribution from the H-O=C=O dihedral.

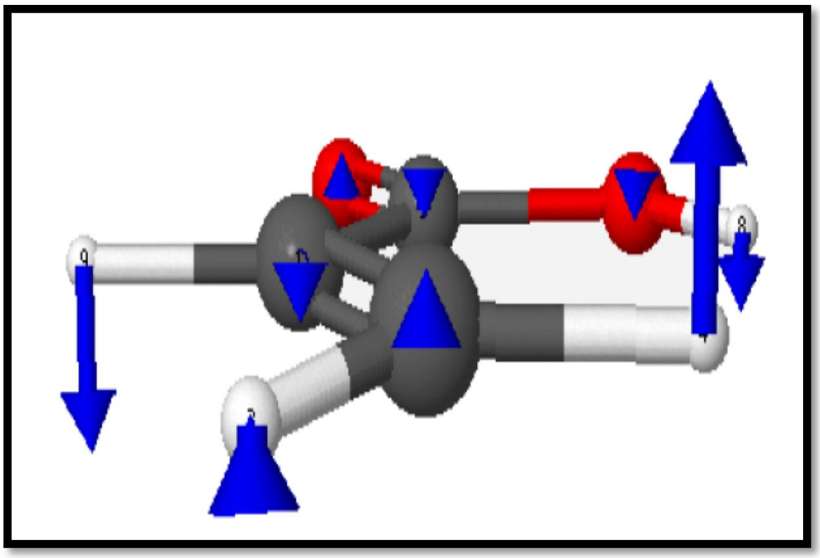


Figure3.4 Lowest vibrational frequency normal mode (non-rotation / translation) for acrylic acid.

3.1.1Potential Energy Scans

The geometry of the resultant transition states and heights of the activation barriers required to rotate each dihedral angle within the acrylic acid monomer can be inferred from the relative energies of the conformers. A higher activation energy should, for example, be observed for the rotation of the H-O=C=O dihedral, where the transition state is "late" (H-C=C=O >> 90°) in accordance with the Hammond Postulate [10]. To ascertain an improved estimatation of the barrier involved in rotation of both dihedrals, series of 1D- (rotating each bond separately) and 2D- (rotating both dihedrals simultaneously) potential energy scans were calculated as depicted below.

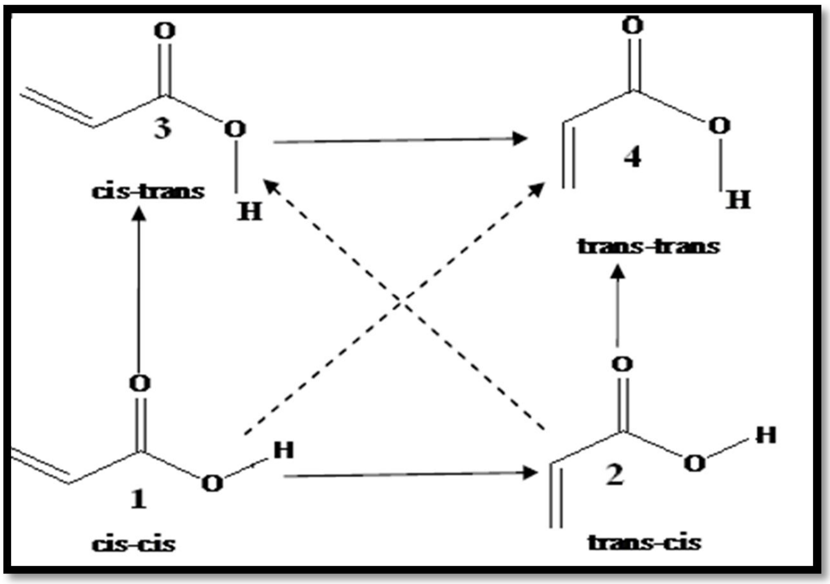


Figure3.3. Rotational conformational interconversions. 1D interconversions showed with solid arrow, whilst 2D interconversions represented by dashed arrow.

Figure 3.4 illustrates the four diagrams that is depict a slice through a multidimensional potential energy surface (PES). The semi-empirical AM1 and PM3 PESs are similar in structure with high H-O-C=O barrier heights: AM1 (*ca.* 50 kJ mol^{-1}) *vs* PM3 (*ca.* 35 kJ mol^{-1}); and low C=C-C=O barrier heights: AM1 (*ca.* 10 kJ mol^{-1}) *vs* PM3 (*ca.* 5 kJ mol^{-1}). This agrees with the previous results from figure 3.4 where the hydrogen atom of the carboxylic acid group is in an *syn*-conformation relative to the carbonylic oxygen atom, and the vinyl group appears to be freely rotating.

The *ab initio* (Hartree-Fock) based potential energy surfaces appear to be similar to each other, but are markedly different from their semi-empirical counterparts. An improved description of hydrogen bonding should be obtained for the HF/6-31G (*d*) basis set relative to the 3-21G basis. Both produce high H-O-C=O barriers (ca. 80-90 kJ mol^{-1}) and slightly lower, but not negligible, C=C-C=O barriers (*ca.* 30-40 kJ mol^{-1}), indicating a higher degree of conformational locking.

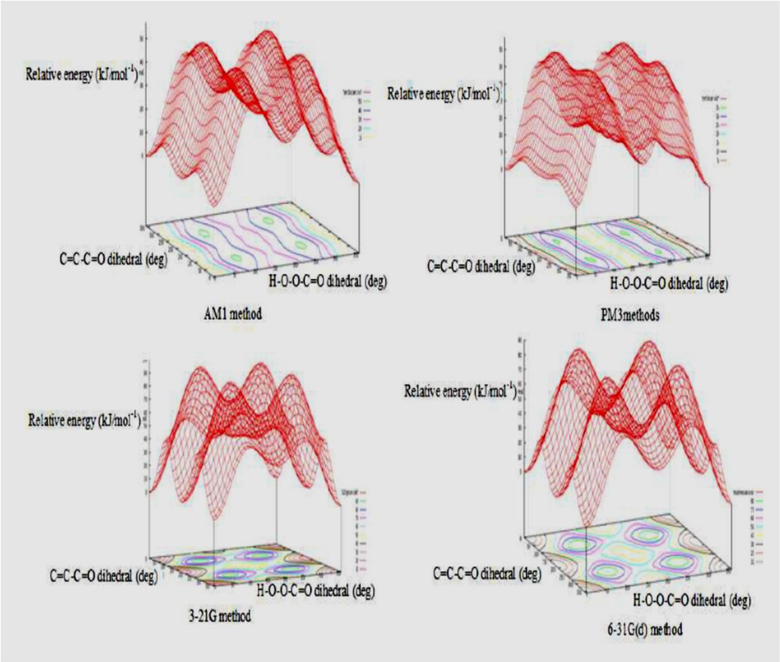


Figure3.4.The four diagrams depict a slice through a multidimensional potential energy surface (PES).

Having gleamed information regarding the global minimum conformation and relative energetic for different planer configurations of acrylic acid, it is necessary to probe the other polymeric constituents of the glass ionomer cement-monomers of unsaturated organic polyacids. The next study was investigated, in order of complexity:

i) maleic and tumaric acids
ii) itaconic acid

3.2 Maleic and fumaric acids

The central C=C bond within butenedioic acid gives rise to two different geometric isomers with significantly different physical and chemical properties: maleic (*Z*-) and fumaric (*E*-) acids. Maleic acid, for example, is thermodynamically less stable than fumaric acid – where the difference in the heat of combustion is 22.7 kJ mol-^{1} [10]. Intramolecular hydrogen bonding within maleic acid [11]. is responsible for its higher solubility in water (78 g / 100 ml at 25 ^{o}C *vs* 0.63 g / 100 ml for fumaric acid), and its lower melting point (139-140 ^{o}C for maleic, 287 ^{o}C for fumaric acid).

A systematic conformational analysis was performed by pictorial analysis of the five different dihedral angles - H-O-C=O (x2), O=C-C-H (x2) and H-C=C-H within the molecule. This gives rise to a total of 32 possible planar conformations, 16 for each molecule.

Both fumaric and maleic acids exhibit 10 non-equivalent conformations (with different energies) – tabulated in Table 3.2 below. To allow rapid evaluation of the relative energies, semi-empirical quantum mechanical methods (AM1, PM3) were used for each conformer. Relative energies (relative to the lowest fumaric acid. conformer) are tabulated in Table 3.2, together with the vibrational frequency of the first normal mode. All conformers remained in their original relative configurations.

The zzezz conformer of fumaric acid possesses the lowest energy using both AM1 and PM3, followed by zeezz and zeeez respectively. For the lowest energy conformers (where both O=C-O-H conformations are *syn* (Z), the energetic trends are identical to those observed for acrylic acid, *i.e.* the O=C-O-H prefers to be *syn*-(Z), but the C=C-C=O dihedral angle exhibits a less energetic preference.

The AM1 energies for the low energy conformers (zzezz, zeezz and zeeez) are lower than their PM3 counterparts. The opposite occurs for the higher energy conformations (one *syn*- and one *anti*- or both *anti*-HO=C=O), with the eeeee conformer being the least stable.

Irregularities are observed between the two methods in determining whether the molecule is a minimum or an *n*th order transition state. For example, the zeezz conformer is clearly a minimum when calculated using AM1, but is a 1st order transition state, whose imaginary vibrational mode (Figure3.5) is mainly comprised of a rotation of the central H-C=C-H dihedral with a small amount of the neighbouring O=C-C=C dihedrals.

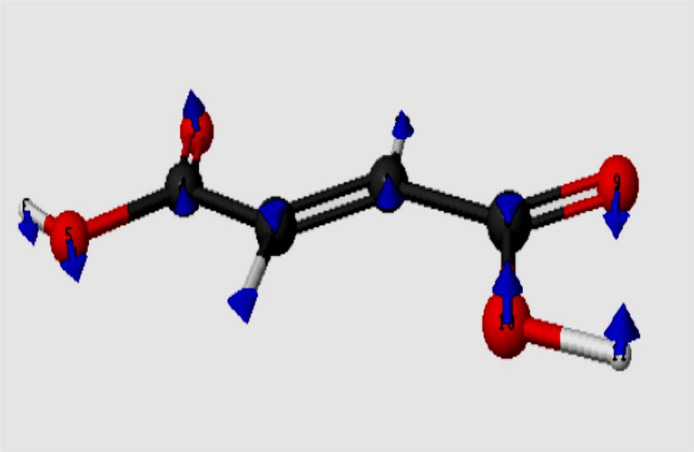
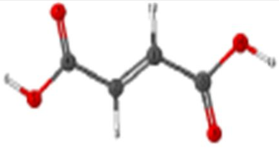
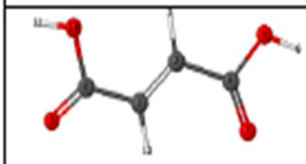
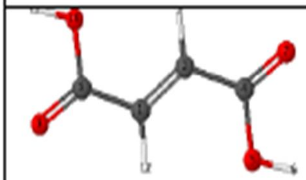
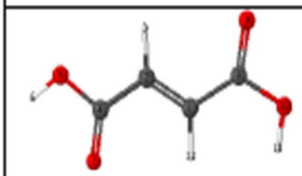
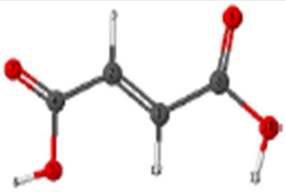
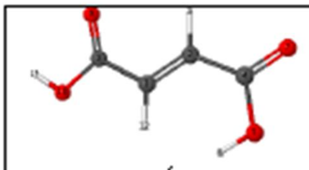
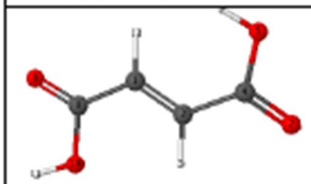
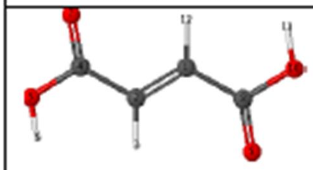
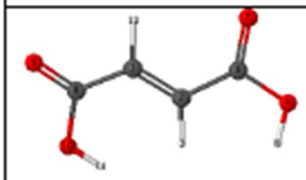
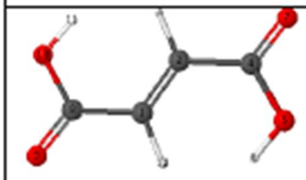


Figure 3.5 Lowest vibrational frequency normal mode (non-rotation / translation) forfumaric acid.

Table 3.2AM1 and PM3 energies for fumaric acids.

Final Conformer	AM1		PM3	
	ΔE^a ($KJ\ mol^{-1}$)	ν_1 cm^{-1}	ΔE ($KJ\ mol^{-1}$)	ν_1 cm^{-1}
 zzezz	0.0	+32	0.0	+22
 zeezz/zzeez	1.3	+26	4.0	-27
 zeeez	2.4	+24	7.7	-48
 zzeze/ezezz	22.1	+29	16.3	+20
 ezeez/zeeze	24.0	+25	14.4	-34

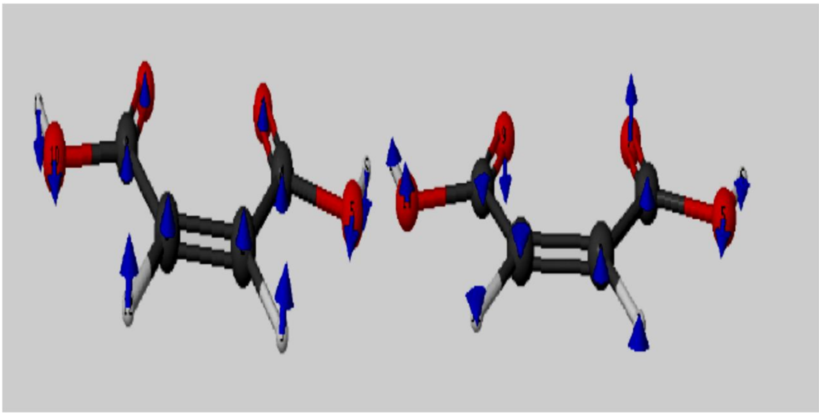
 eeezz/zzeee	28.4	-65	13.6	+27
 zeeee/eeeez	29.6	-72	16.8	-9
 ezeze	44.0	31	19.1	+23
 eeeze/ezeee	54.3	-74	26.8	+13
 eeeeee	56.9	-119	26.7	+37

ΔE^{α}-kcal mol^{-1}(kJ mol^{-1} in parentheses) relative to lowest energy conformer

The maleic acid conformers are all predicted to be 2nd order transition states (Figure 3.6). Increased steric hindrance exhibited in the middle RCH=CHR double bond is clearly shown in the higher energies of the maleic acid conformers. The excess energy is caused by the two carboxylic acids (CO_2H) moieties attempting to distance themselves from each other.

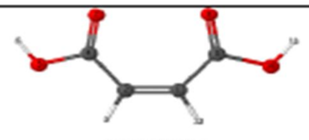
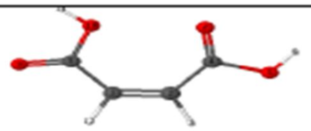
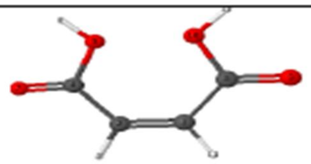
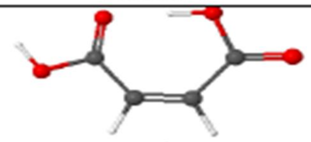
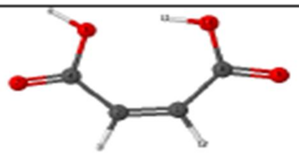
This occurs in two ways – a small increase in the O=C (carbonyl)-C (vinyl) bond angle (*e.g.* 129.4^o for zzezz-fumaric and 131.9^o for zzzzz-maleic respectively) with a larger increase in the C (carbonyl)-C (vinyl)=C (vinyl) bond angle (*e.g.* 121.0^o for zzezz fumaric and 127.5^o for zzzzz-maleic respectively).

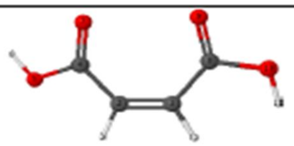
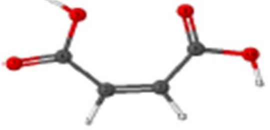
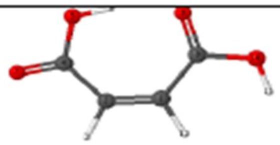
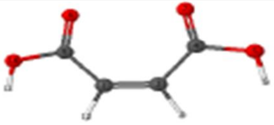
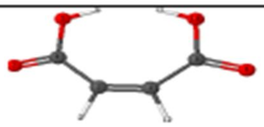
The lowest energies of the maleic acid conformers are typically 20-30 kJ mol^{-1} higher than their respective fumaric acid counterparts. Again, the lowest and highest energy conformers are predicted for pairs of *syn*- and *anti*-O=C-O-H conformations respectively.



Figures 3.6 Diagram the two pictures for both –ve modes for zzzzz maleic conformer

Table 3.3 AM1 and PM3 energies for maleic acids.

Final Conformer	AM1		PM3	
	ΔE (KJ mol^{-1})	ν_1 cm^{-1}	ΔE (KJ mol^{-1})	ν_1 cm^{-1}
 zzzzz	24.7	-54	29.5	-65
 zezzz/zzzez	24.7	-54	32.2	-66
 zezez	29.1	-65	30.6	-33
 eezzz/zzzee	32.7	-58	42.3	-66
 zezee/eezez	45.5	-107	27.12	-58

 zzzze/ezzzz	50.8	-58	42.3	-66
 ezzez/zezze	50.2	-58	44.4	-67
 eezze/ezzee	58.0	-69	23.0	-38
 ezzze	77.9	-61	56.2	-67
 eezee	114.3	-475	76.9	-325

Δe^{α}-kcal mol^{-1}(kJ mol^{-1} in parentheses) relative to lowest energy conformer

3.3 Itaconic acid:

Although itaconic acid appears to be relatively simple, a detailed study of its structure would require a guesstimated minimum of 288 conformers:

H-O-C=O (dihedral) x2 4 (2^2)
C=C-C=O x1 2 (2^1)
Dihedral x2 36 (6^2)

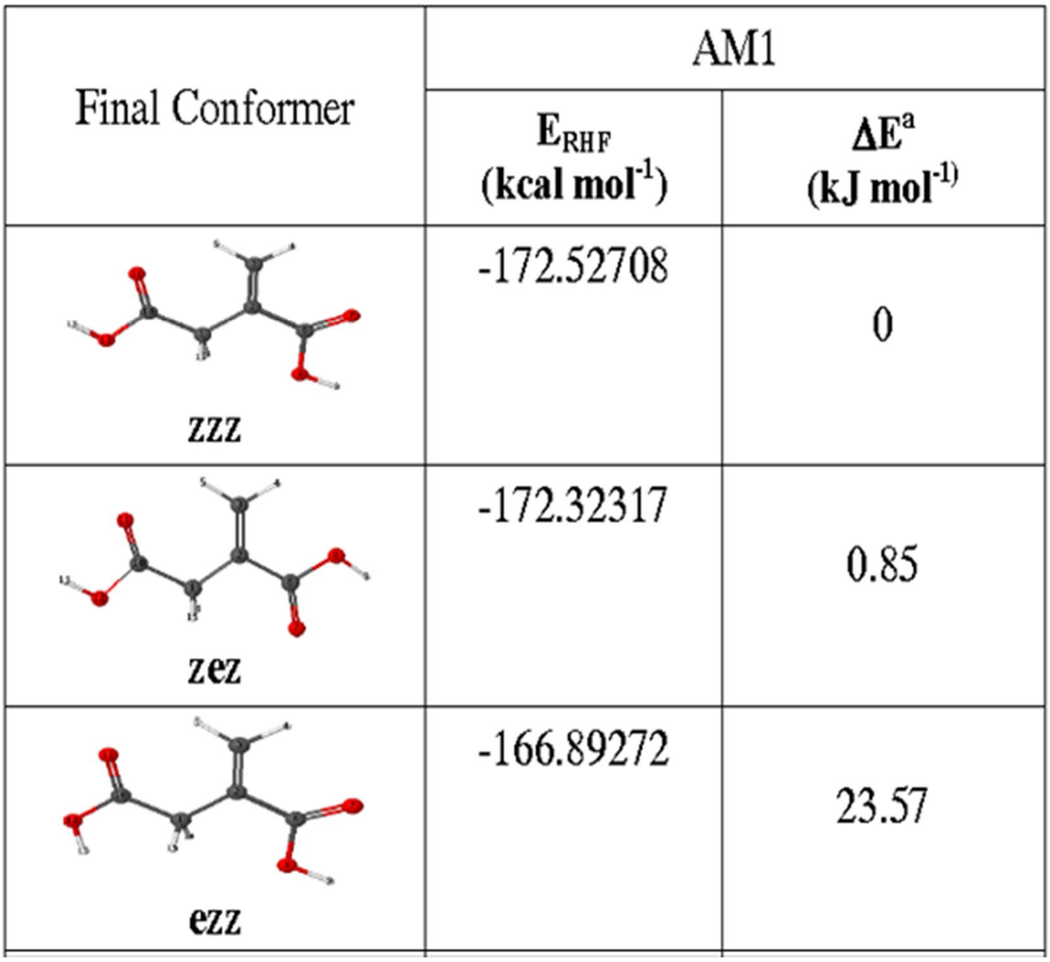
Since a detailed study of this molecule is beyond the time constraints of the paper programme, a simplified model is used whereby the (inner) dihedrals, O=C (carbonyl)-C (methylene)-C (vinyl) & C (carbonyl)-C (methylene) C (vinyl)=C (vinyl), are constrained (fixed) in a 0^{o} (*synperiplanar)* configuration. The constrained geometry optimization greatly simplifies the number of calculations (eight conformers) required (see table 3.4).

Although the numbers of conformations studied are only a fraction of the total number of conformations, initial results suggest that the zzz and zez conformations are the most stable, with the relative energy of the zez conformation being within 1 kJ mol^{-1} of the lower energy zzz conformation.

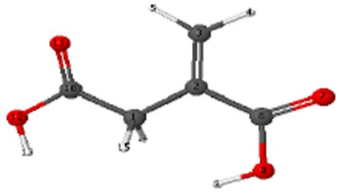
The conformation of the H-O-C=O dihedral is again conformationally locked with a preferred *syn*- configuration, whilst the conformation of the vinyl group is uncertain.

Future potential energy scans of this molecule may indicate whether or not the vinyl group is a free rotor (small activation barrier to rotation). Additional geometry optimizations where the constraints on the inner dihedral were lifted did not appear to change the conformation, indicating that the *syn*-,*syn*- conformation for the inner dihedrals is relatively stable.

Table 3.4 AM1 energies for itaconic acid.



Final Conformer	AM1	
	E_{RHF} (kcal mol^{-1})	ΔE^{a} (kJ mol$^{-1)}$
zzz	-172.52708	0
zez	-172.32317	0.85
ezz	-166.89272	23.57

 **zee**	-166.89272	23.57
 **eez**	-166.82069	23.88
 **zze**	-165.80733	28.12
 **eee**	-160.67823	49.58
 **eze**	-159.23965	55.59

Δe^{α}-kcal mol^{-1}(kJ mol^{-1} in parentheses) relative to lowest energy conformer

4. Conclusions

Semi-empirical and HF methods have been applied to study the conformations of acrylic acid monomers. A clear energetic preference for the orientation of the hydroxyl groups is observed, which is independent of the computational method. A strong hydrogen bond stabilization for the syn- H-O-C=O dihedral angle is indicated, whereas the syn- and anti- C=C-C=O conformers both exhibited similar energies. A simple model of polyacrylic acid was generated for the melaic ,furmaic and Itaconic acid. The conformers exhibited a high degree of conformational flexibility.

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