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3-D Representation of Young's, Shear and Linear Moduli of Six Sulfonamide based Compounds using GULP

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Abstract

Molecular dynamic study of six sulfonamide based compounds was carried out to compute several properties like Bulk (K), Young's (E), Shear (G) modulus, Linear compressibility, Poisson's ratio, s- and p-wave velocities, Heat capacity, Zero point energy, Lattice energy, static dielectric constant and refractive index tensor components. Relation between physical properties and number of carbon atoms in a compound have been established in this paper. All these calculations were performed using GULP program and reported single crystal data.

Keywords: *GULP; sulfonamide based single crystals; Young's, Bulk, shear moduli, poison's ration; Heat capacity, dielectric constant.*

INTRODUCTION

In order to prevent and cure bacterial infections in human beings, Benene sulfonamide based compounds were used initially [1]. They exhibit antibacterial, antifungal, anti inflammatory, antitumor, anticancer, anti-HIV and antitubercular properties [2-9]. Since Benzene sulfonamide based compounds offer so much in drug synthesis, we have made an attempt to study structure- property relation by carrying out molecular modeling. Further to simulate physical properties like elastic constant tensor components in 3-dimension along with other parameters of these materials, a

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program, General Utility Lattice Program (GULP), a freely available software is used. Six single crystal data of benzene sulfonamide based compounds reported earlier were used in the following investigation [10-14]. With experimental single crystal data reported earlier, we have published the structure-property relation by simulating Phonon density of states, atomic electric potential, refractive index and dielectric constant of Prop-2-en-1-one based compounds. For validation of the computed elastic constants in these compounds, we have referred to "Second and Higher Order Elastic Constants" by A. G. Every, A. K. McCurdy (auth.), D. F. Nelson (eds.) [16].

MATERIALS AND METHODS

Six single crystal data of benzene sulfonamide based compounds were used and they are [10-14]:

1. 2,5-Dimethoxy-N-phenyl benzene sulphonamide ($C_{14}H_{15}NO_4S$) (Monoclinic, $P2_{1/c}$)
2. 4-Bromo-N-(4-fluorophenyl) benzene sulfonamide ($C_{12}H_9BrFNO_2S$) (Orthorhombic, P_{na2_1})
3. 3,5-dichloro-N-(2,3-dimethylphenyl) benzene sulfonamide ($C_{14}H_{13}Cl_2NO_2S$) (Monoclinic, $P2_{1/n}$)
4. 3,5-dichloro-N-(2,6-dimethylphenyl) benzene sulfonamide ($C_{14}H_{13}Cl_2NO_2S$) (Triclinic, P1)
5. 3,5-dichloro-N-(3,5-dimethylphenyl) benzene sulfonamide ($C_{14}H_{13}Cl_2NO_2S$) (Monoclinic, $P2_{1/c}$)
6. 4-Bromo-N-(4-bromophenyl) benzene sulfonamide ($C_{12}H_9Br_2NO_2S$) (Monoclinic, $P2_{1/n}$)

The non-availability of physical parameters of said single crystals have led way to predict elastic constants and mechanical properties theoretically; this further leads to avail holistic view of structure-property relation. With ideal crystal structure information as input data, molecular dynamic simulation using GULP program [10-14] is carried out to investigate physical parameters and its dependence on the chemical structure and corresponding variations. Present study focus on predicting elastic constants, such as Bulk (K), Young's (E), Shear (G) modulus and Poisson's ratio, while evaluating s- and p-wave velocities, static dielectric constant tensor using molecular dynamics simulation. Said computational analyses were carried out using reported single crystal data of all six crystals (in IUCr journal). Further, the concern of this study is to understand stability of a single

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crystal, and the parameters responsible for the same. Influence of zero point energy on the stability of single crystals is also evaluated in the study. Reported theoretical approaches are used empirically to find out inter atomic potentials and thereby to predict surface related properties and morphology [15]. This theoretical prediction is challenging computationally but is reliable and crucial in this study. Some physical parameters such as elastic tensor, bulk modulus (K), dielectric constant are related to second derivatives of the energy with respect to strain and can be easily derived using X-ray data of a good single crystal. With considerations from Hooke's law, elastic constants are calculated performing suitable symmetry operations. The possible realisation of elastic planar displacement of molecules and their critical nature in the form of 3-dimensional representation of linear, bulk (K), shear (G) and young's (E) moduli is discussed. We also provide a validation of these predicted parameters with an experimental data of related samples.

RESULTS AND DISCUSSION

Mechanical properties

As discussed earlier, our focus is on stability parameters of single crystals. There are several examples, those draw our interests and one amongst is the hydrogen bonded molecular crystalline systems, that are less stable [14]. The contribution of the zero point energy on the stability of single crystal is calculated in the study. Out of various theoretical approaches, most reliable method is followed to minimise lattice energy and thereby to predict surface properties and morphology [15]. Elastic constant tensor (in GPa) is calculated by minimisation of the lattice energy and obtained results are presented in Table 1. Conceptual explanation of experimental elastic constants are provided when the direct validation of elastic constants is not available, using similar compounds bearing same number of carbon atoms. We know that, the structures of all organic compounds are formed by carbon and major contribution to elasticity is due to this atomic network. With this rudimental idea, the experimental values of elastic constant is compared with the compound containing nearest number of carbon atoms in order to justify our predicted values [16-24]. The variations in results can be ascertained to the additional ions, which cause imperfection in crystals, and also variation of elastic constant.

From these tensor components, we have computed bulk (K), Young's (E), shear (G)

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modulus and Poisson's ratio (P) of all the compounds using $E = \frac{\dot{\gamma}}{\epsilon}; \dot{G} = \frac{\bar{E}}{2(1+\nu)}; \dot{K} = \frac{\dot{E}}{3(1-2\nu)}$ and they are shown in Table 2.

Here it is noteworthy that, only for the compounds which are elastically stable, one could obtain 3D representations using ELATE software [http://progs.coudert.name/elate] and thus we were able to plot for the compounds 1 and 3. The Figures (2(a) and 2(b)) represent the directional variations of moduli for compounds 1 and 3. These figures present the changes in the various moduli in regard to displacement of maximum value corresponding to lattice constants along x, y and z-axes. The critical values of moduli and their changes near the maximum displacement are represented by these figure boundaries (as given by Frank limitations [25-29]). Bulk modulus versus unit cell volume shows a maximum for compound -6 with a value of 0.0521 GPa as predicted from Figure 2. Bulk (K), shear (G) and young's (E) moduli along with Poisson's ratio is computed using Voigt averaging method is given in Table 2 for all the six compounds.

Table 1: Computed elastic constant tensor components

Compo-nent	$C_{14}H_{15}NO_4S$	$C_{12}H_9BrFNO_2S$	$C_{14}H_{13}Cl_2NO_2S$	$C_{14}H_{13}Cl_2NO_2S$	$C_{14}H_{13}Cl_2NO_2S$	$C_{12}H_9Br_2NO_2S$	$C_{16}F_{34}$ Exp.result	$C_{12}H_{10}$ in(GPa)	$C_{14}H_{12}N_2$	$C_{12}H_4Br_2NO_2S$
C11	0.051	0.033	0.162	0.039	0.028	0.132	5.3	5.05	14.3	7.36
C22	0.043	0.022	0.213	0.026	0.001	0.015	-	6.97	7.99	18.35
C33	0.034	0.013	0.051	0.049	0.063	0.177	6.63	16.6	6.36	20.2
C44	0.012	0.010	0.024	0.008	-0.006	0.023	-0.038	1.83	2.40	3.70
C55	0.012	0.004	0.044	0.014	-0.012	0.012	-	2.26	1.06	5.82
C66	0.008	0.008	0.060	0.010	0.003	0.037	-	4.11	3.24	3.55
C12	0.016	0.004	-0.082	0.014	0.002	0.028	-	4.05	5.11	3.55
C13	0.018	0.008	0.003	0.017	0.016	0.023	1.032	2.88	3.37	6.77
C15	0.006	-	0.011	0.003	0.009	-0.005	-	6.11	-	-0.049
C25	0.002	-	0.019	-	0.002	-0.004	-	0.94	-	-0.81
C53	-0.006	-	-0.002	0.002	-0.012	0.018	-	-	-	-
C46	0.004	-	-0.007	0.005	0.006	-0.007	-	-0.84	-	0.82

Table 2: Obtained physical parameters

Moduli(GPA)	$C_{14}H_{15}NO_4S$	$C_{12}H_9BrFNO_2S$	$C_{14}H_{13}Cl_2NO_2S$	$C_{14}H_{13}Cl_2NO_2S$	$C_{14}H_{13}Cl_2NO_2S$	$C_{12}H_4Br_2NO_2S$
$/V^3 in \mathring{A}^3$	1384.7	1245.8	1488.6	747.1	1465.7	1332.2
Bulk	0.027	0.011	0.018	0.024	0.012	0.052

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Young's	0.029	0.019	0.087	0.027	0.033	0.078
Shear	0.011	0.008	0.063	0.011	0.005	0.031
Poisson						
ratio	0.315	0.221	-0.308	0.306	0.-0.029	0.250
s-wave(km/s)	0.0720	0.489	1.687	0.348	0.715	0.898
p-wave(km/s)	1.312	0.0.824	2.147	0.857	0.996	1.557
Lattice						
energy(eV)	-4.68	-11.27	-2.24	-1.73	-3.13	-0.380
Dielectric constant	2.45	3.04	0.035	2.125	-5.565	0.735
refractive						
index	1.634	1.744	1.821	2.021	2.483	1.662
zero-point						
energy(eV)	0.158	0.134	0.188	0.058	0.104	0.512
Entropy(eV/K)	0.083	0.076	0.036	0.045	0.043	0.029
Heat Capacity						
constant vol(eV/K)	0.020	-0.017	0.009	0.010	0.010	0.007

Elastic wave velocities

The elastic wave components, s-wave and p-wave velocities are computed using the equations [16-25]$vl = (3B + 4G/3\rho)$ and $vt = (G/\rho)$; where vl and vt represents the longitudinal and transverse velocities. B and G represents the bulk and shear moduli, and ρ gives the density of material. The predicted velocities are high in compound 3 wherein it posses the maximum unit cell volume when compared to rest. Reported velocity values for lithium fluoride is nearly 2.4km/s [30-31]. The variation in elastic wave velocity is due to the considered molecules; which are relatively lengthy, the overlapping of elastic fields occur by compensating elastic stress with signs reversed which results in abrupt values.

Piezoelectric constant, refractive indices and dielectric constant

Piezoelectric constant relates the applied electric field and strain in non-centrosymmetric materials which is obtained by deriving induced polarisation. These calculated values are given in Table 2. Lattice energy is used to determine static dielectric constant [19] and the square root of dielectric constant gives refractive indicex. It is evident from Table 3 that the components of refractive index and dielectric constant increase with an increase in number of atoms in a chemical structure. It can be observed that, all these molecules are centrosymmetric and thus the piezo electric strain matrix is zero.

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Lattice energy and Zero point energy

Determination of lattice energy is always accompanied with interactions of all molecules within a unit cell and other potentials from short and long range in a crystal. Using GULP the lattice energy and zero point energy of all compounds under study are calculated and given in Table 2. Zero point energy with an additional atom, is maximum for Br (compound-6) and is minimum along chlorine (compound-4). Entropy and heat capacity values are on broader scale remain same in all compounds.

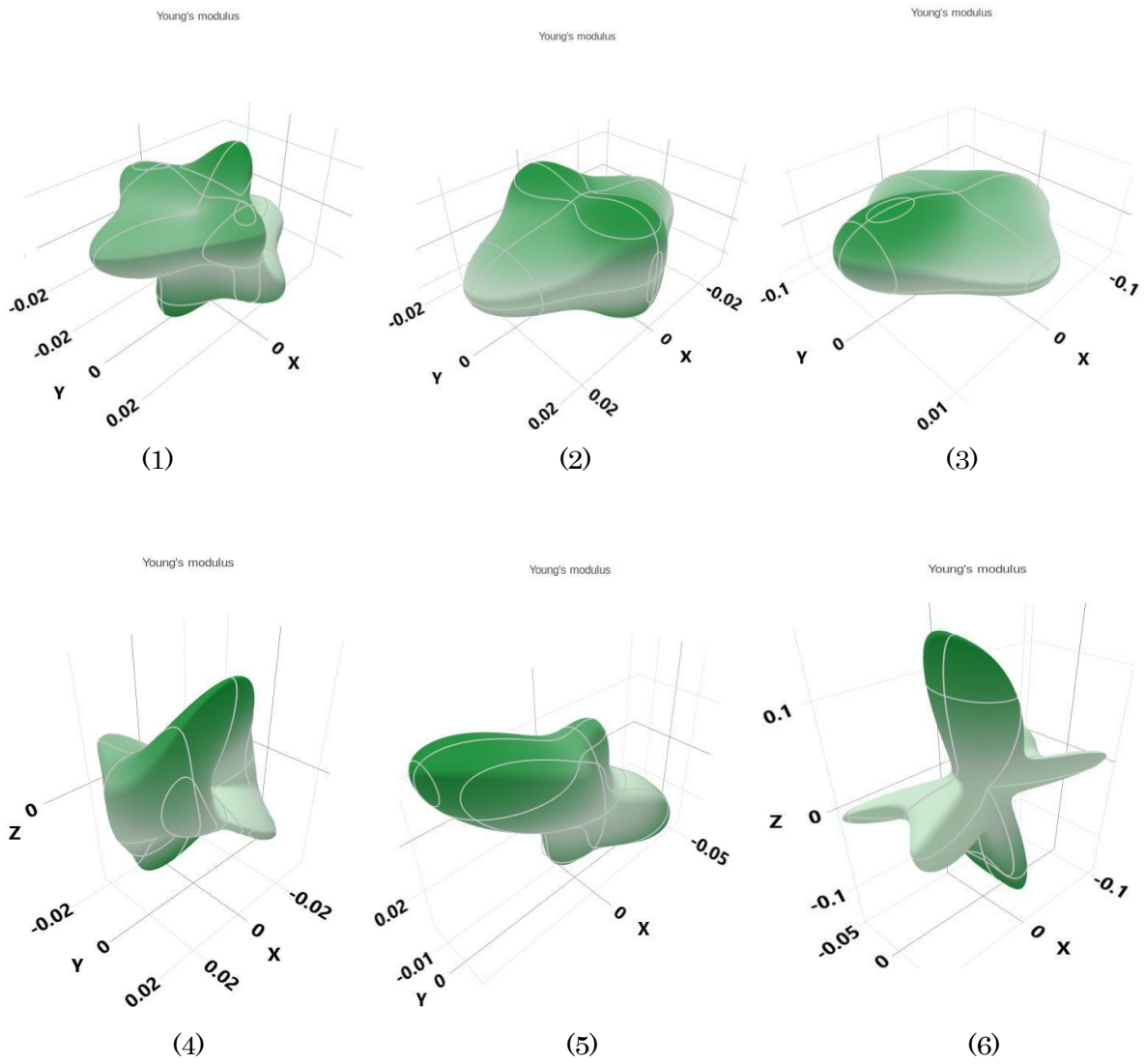


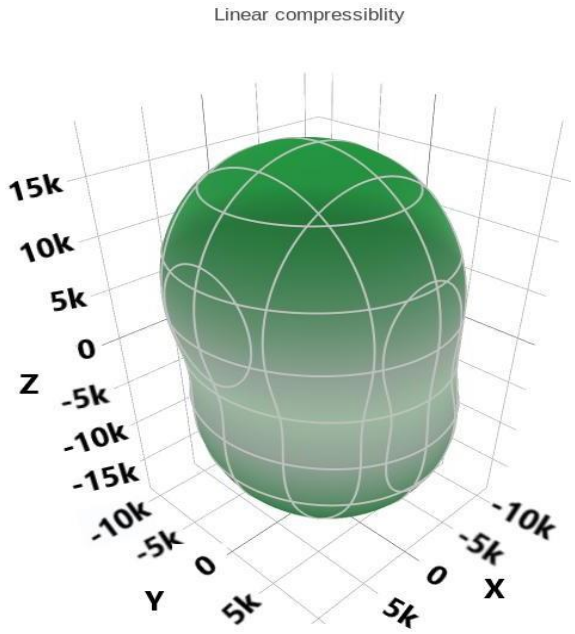
Figure 1: 3 - dimensional variation of Youngs's modulus in the order from compound 1 to 6.

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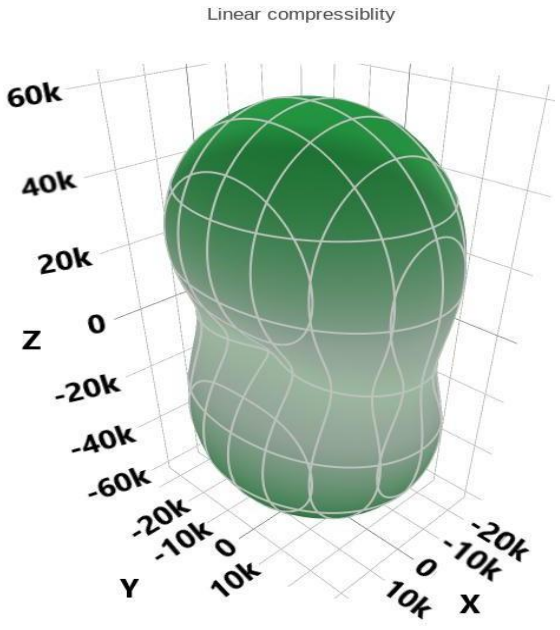
Functional analysis

We have compared various physical parameters with six sulfonamide base compounds and we attempt to draw correlation between parameters and six compounds, if any. For this, we make use of well established procedure along with statistics package FPCA. Here the depicted behaviour of θ, representing a physical parameter, as function of t for the ith sample (here 'i' varies from compound 1 to 6) is written as $\hat{\theta}_i(t) = \hat{\mu}$ $),_K$ is the infinite sum which is been truncated to an appropriate finite constant K.

The step wise procedure to estimate FPC Eigen functions and Eigen values are technically brief and detailed in our earlier paper Urs et al [32] supported with Yao et all [33]. Here't' refers to unit cell volume of compounds 1 to 6. Computations were performed employing FPCA package available in MATLAB (The Math Works Inc., Natick MA, USA). Figure 3 shows the correlation between the bulk modulus and the unit cell volume of the six samples under study. Functional analysis carried out presents a correlation among samples over a stretch of the unit cell volume and this study presents a functional mean value of bulk (K) modulus and a maximum observed. This procedure enables one to predict values in and beyond the sample region, using statistical extrapolation.



(1)



(2)

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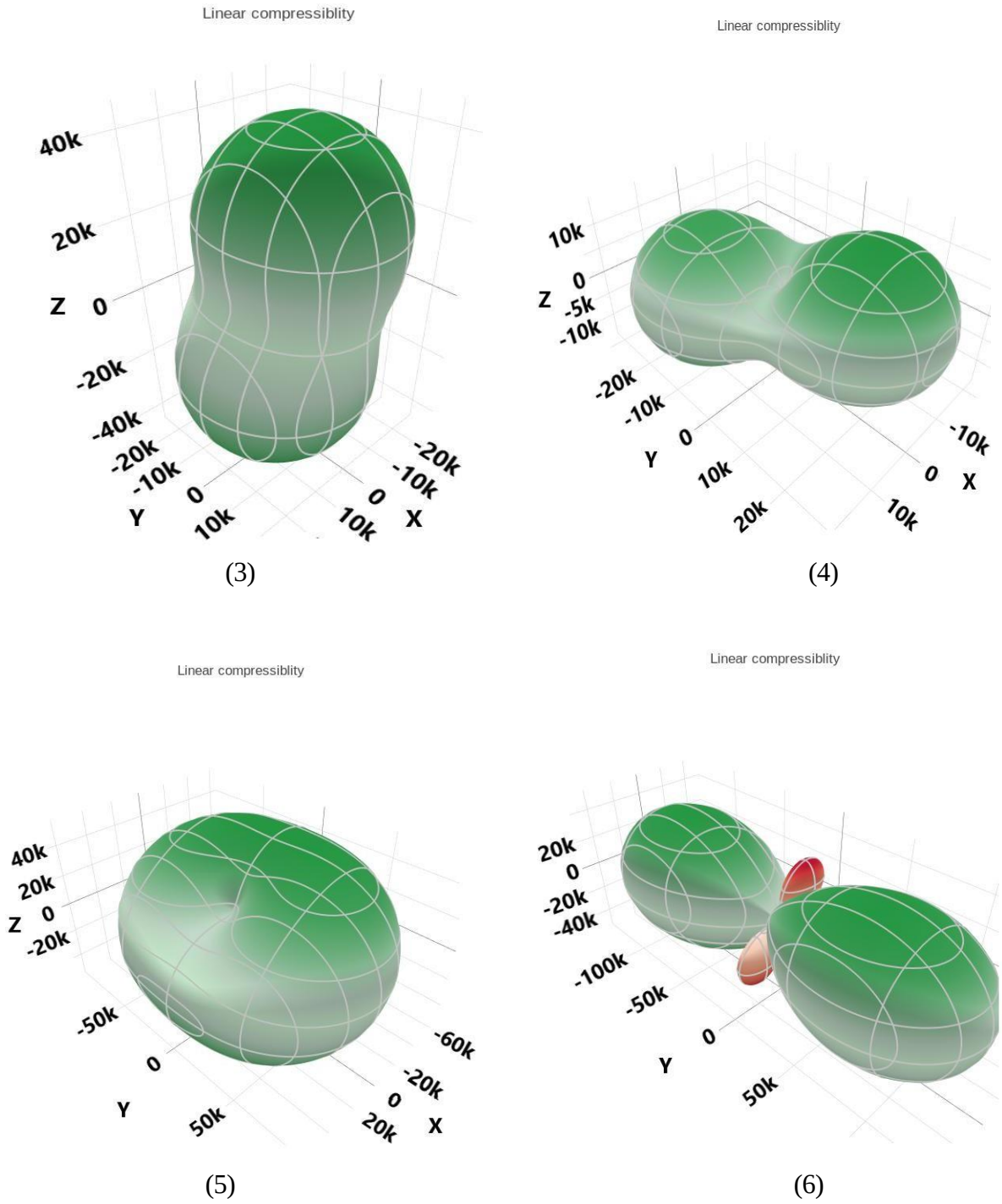


Figure 2: 3 - dimensional variation of linear modulus for compound 1 to compound 6.

CONCLUSIONS

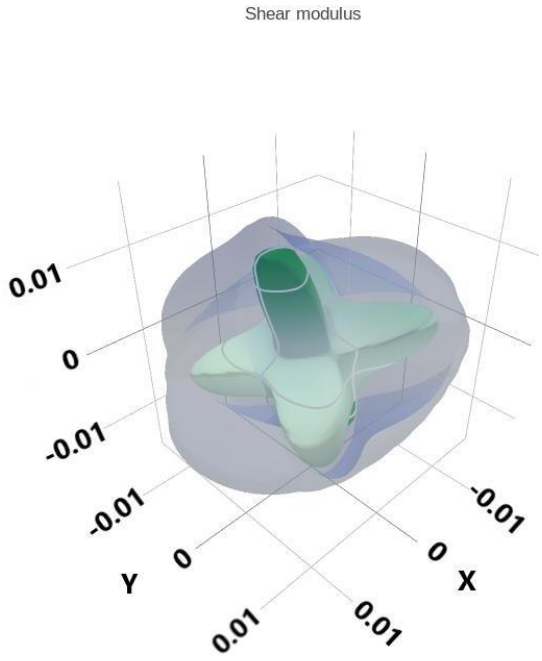
Single crystal data reported for six sulfonamide compounds have been used to compute the elastic tensor components and other physical parameters using molecular mechanics technique. The following observations drawn from our study

1. Elastic components computed are compared with experimental data of compounds containing same number of

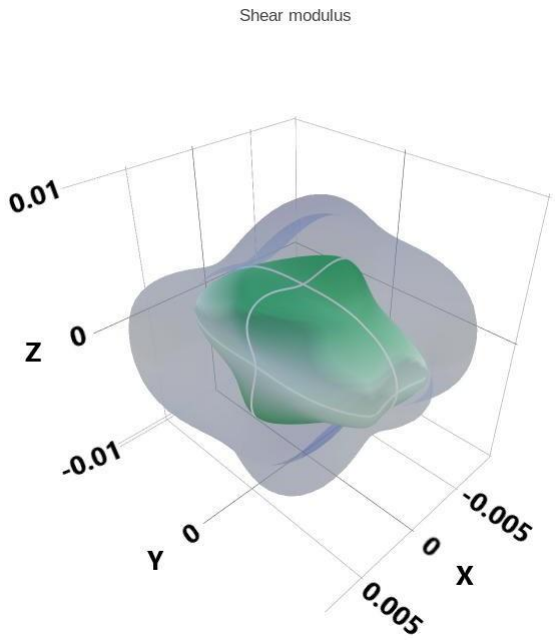
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carbon atoms in order to have fair comparison and obtained results are in agreement with the earlier methods.

2. All compounds studies here are elastically stable, else it is impossible to obtain 3-D presentation of different moduli.
3. Bulk modulus shows a maximum value for compound-6 and a minimum for compound-5.
4. S-wave and p-wave velocities are maximum for compound -3 with high unit cell volume.
5. Changes in dielectric constant, refractive index, lattice energy, zero point energy, heat capacity and entropy are due to the number of carbon atoms and the size of unit cell, which affects the propagation of light.
6. Correlation between the predicted physical parameter with unit cell volume is effectively drawn using functional data analysis.

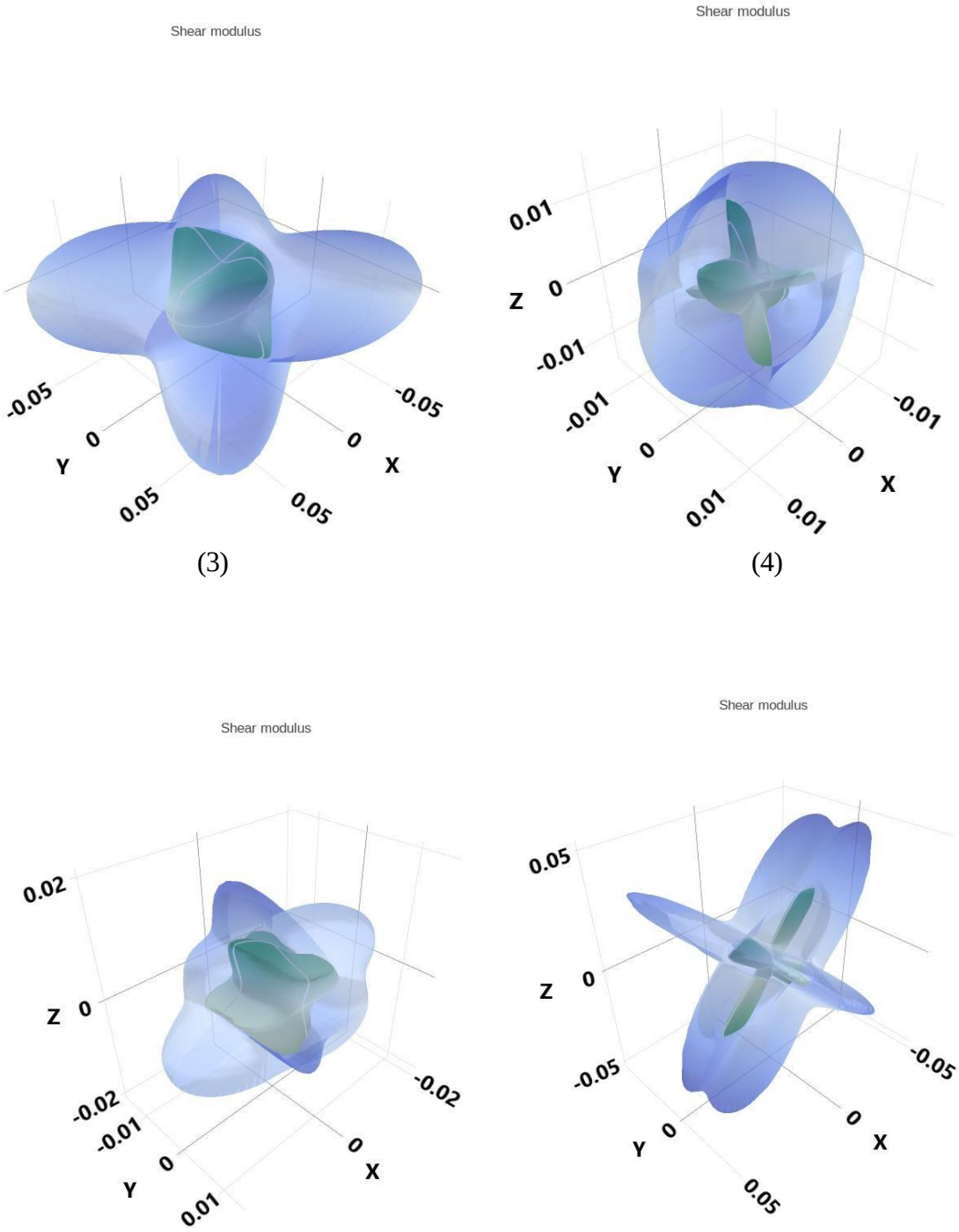


(1)



(2)

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(3) (4)

(5) (6)

Figure 3: Variation of shear modulus for the compound 1 to 6.

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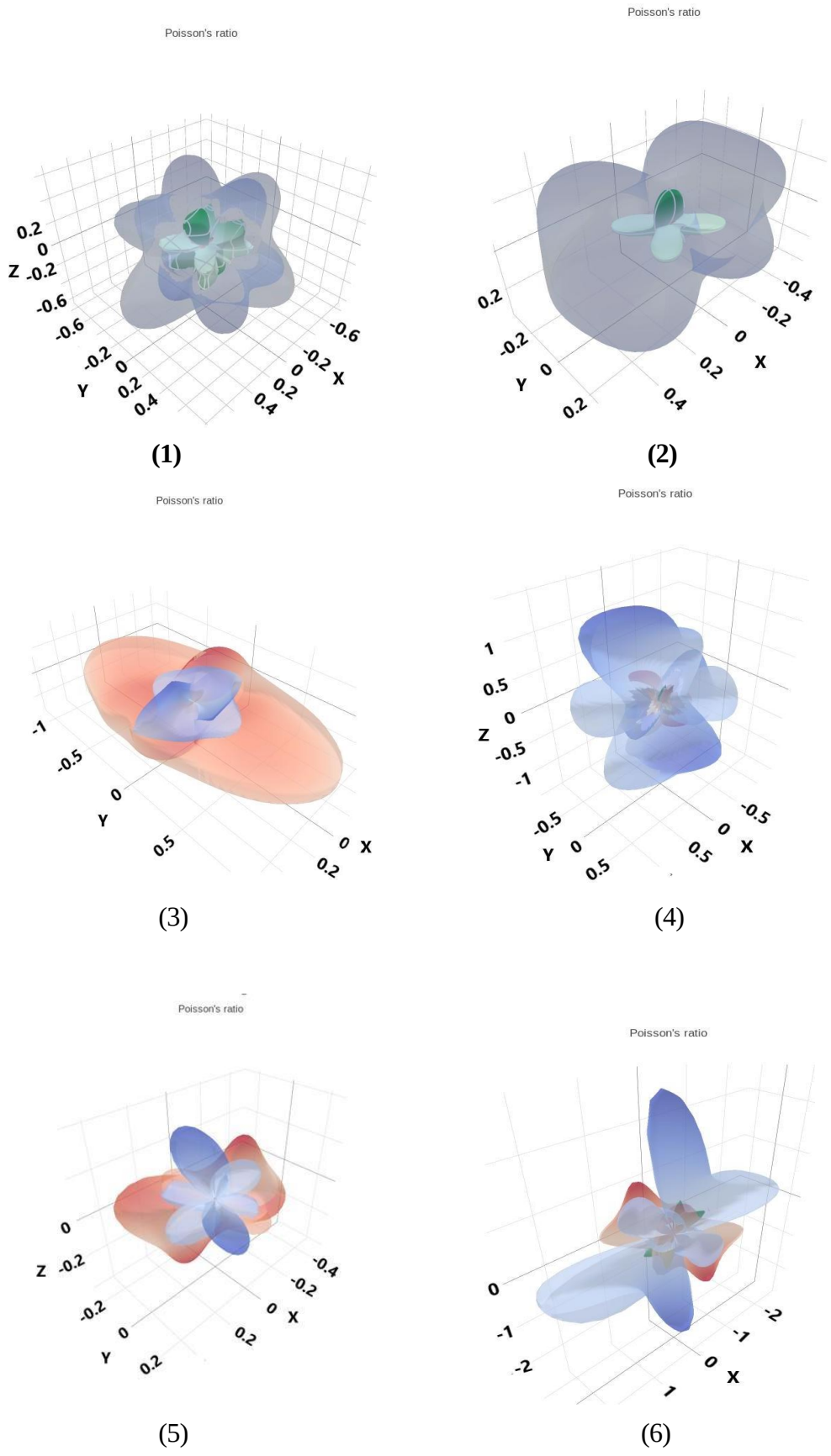


Figure 4: Variation of Poisson ratio in the order of compound 1 to compound 6.

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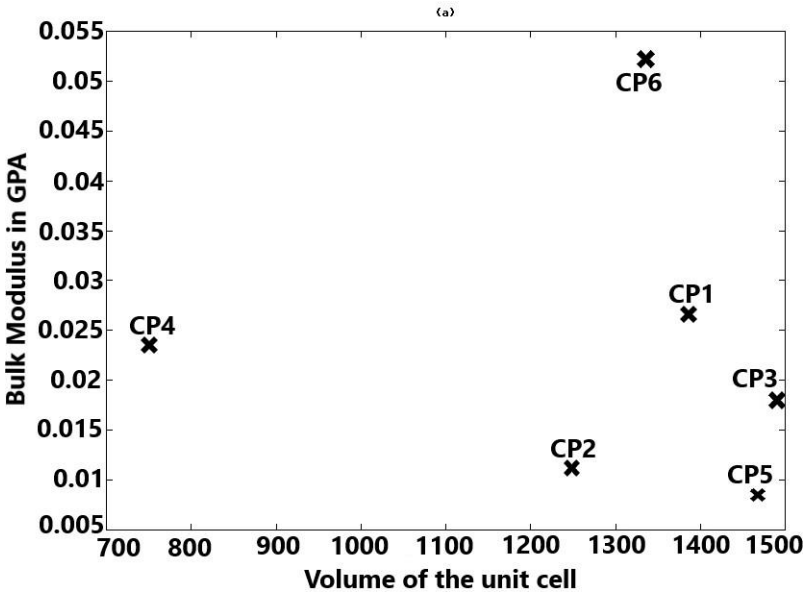


Figure 5: Variation of Bulk modulus with unit cell volume

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