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A theoretical investigation by DFT method on CR – 39 monomer that is a plastic polymer commonly used in the manufacture of eyeglass lenses

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Abstract: In this paper, the diallyl (oxybis(ethane-2,1-diyl)) dicarbonate (CR-39 monomer) of molecular structure that is a plastic polymer commonly used in the manufacture of eyeglass lenses, has been examined theoretically. The molecular structure of CR-39 monomer was optimized by Density Functional Theory (DFT) using B3LYP method with STO-3G basis set without specifying any symmetry for the title molecule. The non-linear optical properties were calculated at the same level and the title compound showed a good second order non-linear optical property. Besides, the frontier molecular orbital (HOMO and LUMO) energies and related molecular properties of CR – 39 monomer were investigated by theoretical calculation results.

Keywords: CR-39 Monomer, Eyeglass Lenses, Density Functional Theory (DFT), Non-Linear Optical Effects

1. Introduction

The allyl diglycol carbonate (ADC) or CR–39 is a plastic polymer used to make lenses for eyeglasses (Fig. 1). The abbreviation stands for "Columbia Resin #39" because it was the 39th formula of a thermosetting plastic developed by the Columbia Resins project in 1940. The first commercial use of CR–39 monomer was to help create glass-reinforced plastic fuel tanks for the B-17 bomber aircraft in World War II, reducing weight and increasing range of the bomber. After the War, the Armorlite Lens Company in California is credited with manufacturing the first CR–39 eyeglass lenses in 1947 [1].

Figure 1. *Eyeglass Lens.*

Performance Patented CR–39 monomer combines the optics of glass with the durability of a thermoset material. The benefits are clear. Lenses made from CR-39 monomer: (a) stand up to scratches, heat and household chemicals, (b) have less chromatic aberration than polycarbonate lenses, (c) are lightweight and less prone to shattering than glass [2].

The recent advances in computer & software technology have allowed us to compute several important chemical and physical properties of chemical systems in a predictive manner using various computational techniques [3, 4]. To the best of our knowledge, no detailed a theoretical investigation has been made on the CR – 39 monomer.

In this study, we have presented results of investigation on the molecular structure of CR–39 monomer by using DFT quantum chemical method. The molecular structure was optimized by Density Functional Theory (DFT) using B3LYP method with STO-3G as basis set without specifying any symmetry for the CR – 39 monomer. The molecular geometry, non-linear optical properties and frontier molecular orbitals were investigated from optimized molecular structure using same method.

2. Theoretical Methods

The molecular structure of the CR – 39 monomer in the ground state (in vacuo) was optimized and structural characteristics were investigated using density functional theory DFT (B3LYP) method with the STO-3G basis set. All the calculations were performed without specifying any symmetry for the CR–39 monomer by using Gauss View molecular visualization program [5] and Gaussian 03 program package [6]. The mean linear polarizability and mean first hyperpolarizability properties of the CR–39 monomer were obtained using molecular polarizabilities based on theoretical calculations. Besides, the frontier orbital energies and related molecular properties of CR–39 monomer were investigated by theoretical calculation results.

3. Results and Discussion

3.1. Molecular Geometry and Potential Energy Surface (PES)

The bond lengths of the molecular structure of the CR–39 monomer optimized by B3LYP/STO-3G basis set, were given in Table 1. The structure of the molecule with numbering scheme for the atoms is presented in Fig. 2. The values of some parameters such as total energy, zero point vibrational energy (ZPVE), entropy of the molecule have been calculated at DFT/B3LYP level using STO-3G basis set and the results are presented in Table 2.

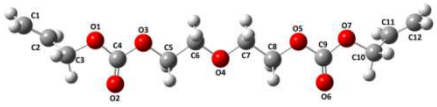

Figure 2. *CR-39 monomer.*

Table 1. *Optimized bond lengths of CR – 39 monomer (Å).*

C1 – C2	**1.337**
C2 – C3	1.5353
C3 – O1	1.4941
O1 – C4	1.4314
C4 – O2	1.252
C4 – O3	1.4298
O3 – C5	1.4856
C5 – C6	1.5647
C6 – O4	1.4739
O4 – C7	1.4739
C7 – C8	1.5647
C8 – O5	1.4856
O5 – C9	1.4298
C9 – O6	1.2521
C9 – O7	1.4314
O7 – C10	1.4943
C10 – C11	1.5353
C11 – C12	1.337

Table 2. *The calculated some parameters of CR – 39 monomer.*

Structural parameters	
Total energy (a.u.)	-981.63857639
Zero point vibrational energy (kcal/mol)	197.557
Entropy (cal/mol-K)	176.296

The potential energy surface (PES) scan with the B3LYP/STO-3G method level of theoretical approximations was performed for the title molecule by varying the dihedral angle T_1(O1—C4—O3—C5) and T_2(O7—C9—O5—C8) in steps of 0, 20, 40,..., , 340, 360 and the resultant minimum energy curve as function of dihedral angle is shown in Fig. 3.

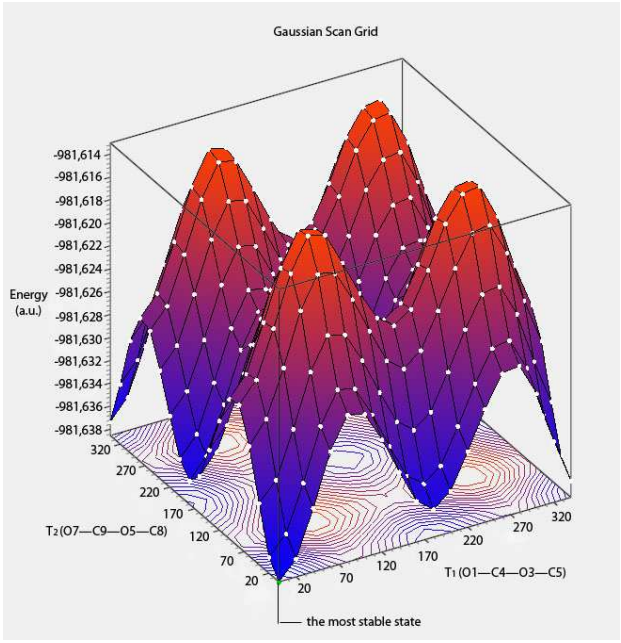

Figure 3. *PES scan for the selected degree for T1(O1—C4—O3—C5) and T2(O7—C9—O5—C8) simultaneously for CR – 39 monomer.*

The potential energy surface showed four hills. There are three points in each of these hills have the same energy. These energies are the highest energies in potential energy surface. Also, there is a point of the lowest energy. These energies are 918.613 and 918.639 a.u., respectively.

3.2. Non-Linear Optical Effects

Non-linear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields[7]. NLO is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in area such as telecommunications, signal processing, and optical interconnections [8-11].

The non-linear optical response of an isolated molecule in an electric field $E_i(\omega)$ can be represented as a Taylor series expansion of the total dipole moment, μ_{tot}, induced by the field:

$$\mu_{tot} = \mu_0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \cdots$$

where μ_0 the permanent dipole moment,$\alpha_{ij}$is the linear polarizability, and β_{ijk} is the first hyperpolarizability

tensor components. The isotropic (or average) linear polarizability is defined as [12]:

$$\alpha_{tot} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

First hyperpolarizability is a third rank tensor that can be described by 3 x 3 x 3 matrix. The 27 components of 3D matrix can be reduced to 10 components due to the Kleinman symmetry [13] (β_{xyy} , β_{yxy} , β_{yyx} , β_{yyz} , β_{yzy},β_{zyy},… Likewise other permutations also take same value). The output from Gaussian03 provides 10 components of this matrix as β_{xxx}, β_{xxy}, β_{xyy}, β_{yyy}, β_{xxz}, β_{xyz}, β_{yyz}, β_{xzz}, β_{zzz}, respectively. The components of the first hyperpolarizability can be calculated using the following equation [12]:

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{i \neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji})$$

Using the x, y and z components of β, the magnitude of the first hyperpolarizability tensor can be calculated by:

$$\beta_{tot} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$$

The complete equation for calculating the magnitude of β from Gaussian 03 output is given a follows:

$$\beta_{tot} = \sqrt{(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2}$$

The values of the polarizability α and the first hyperpolarizability β of Gaussian 03 output are reported in atomic units (a.u.), so the calculated values have been converted into electrostatic units (esu) (α: 1 a.u. = 0.1482×10^{-24} esu; β: 1 a.u. = 8.6393×10^{-33} esu.)

The calculations of the total molecular dipole moment (μ), linear polarizability (α) and first-order hyperpolarizability (β) from the Gaussian output have been explained in detail previously [14], and DFT has been extensively used as an effective method to investigate the organic NLO materials [15-19]. It is well known that from the literature, the B3LYP approach provides fairly reliable values in electric hyperpolarizability calculations when compared with accuracies of traditional ab initio methods and this predictive capability of widely used B3LYP method is of interest to a wide audience of computational scientists [20, 21]. In addition, taking into account reliability and the computational time required [22, 23], the basis set B3LYP/STO-3G was chosen for the calculations of the hyperpolarizability in this study.

Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore it was used frequently as a threshold value for comparative purposes. The components of the dipole moments, the average polarizability (or linearpolarizability), and the first hyperpolarizability components of CR–39 monomer can be seen in Table 3. Theoretically, the first-order hyperpolarizability of the optimized structure is 2.17 times magnitude calculated at the same level of urea. According to these results, the CR–39 compound is a good candidate of NLO material.

Table 3. *The molecular electric dipole moment μ (Debye), polarizability α(×10^{-24}esu) and hyper polarizability β(10^{-33}esu) values of CR – 39 monomer and Urea.*

	Calculated (B3LYP/STO-3G)
Parameters	CR – 39 monomer
Dipole moment	
μ_x	-0.0004
μ_y	-0.5928
μ_z	-0.1735
μ	0.6177
Polarizability	
α_{xx}	79.6
α_{xy}	34.8
α_{yy}	160.3
α_{xz}	4.21
α_{yz}	-1.4
α_{zz}	62.63
α	100.8
Hyper polarizability	
β_{xxx}	-5.18
β_{xxy}	9.01
β_{xyy}	4.9
β_{yyy}	-9.92
β_{xxz}	21.97
β_{xyz}	27.54
β_{yyz}	85.86
β_{xzz}	3.59
β_{yzz}	-0.97
β_{zzz}	-1.7
β	106.19

3.3. Frontier Molecular Orbitals (FMOs) Analysis and Related Molecular Properties

The highest occupied molecular orbital (HOMO) and the lowest lying unoccupied molecular orbital (LUMO) are named as frontier molecular orbitals (FMOs).The frontier molecular orbitals play an important role in the electric and optical properties, as well as in UV–vis spectra and chemical reactions [24]. The energy levels of the HOMO and LUMO orbitals computed at the B3LYP/STO-3G level for CR–39 monomer. The calculations indicate that the molecule has 73 occupied molecular orbitals. The HOMO and LUMO energies, the energy gap (ΔE), the ionization potential (I), the electronaffinity (A), the absolute electronegativity (χ), the absolute hardness (η) and softness (S), chemical potential (μ) and global electrophilicity(ω) for molecule have been calculated at the same level and the results are given in Table 4**.** By using HOMO and LUMO energy values for a molecule, ΔE, *I, A,* χ, η, S, μ and ω can be calculated as follows:

$$\Delta E = E_{HOMO} - E_{LUMO}$$
$$I = -E_{HOMO}$$

$$A = -E_{LUMO}$$
$$\chi = \frac{I + A}{2}$$
$$\eta = \frac{I - A}{2}$$
$$S = \frac{1}{\eta}$$
$$\mu = -(\frac{I + A}{2})$$
$$\omega = \frac{\mu^2}{2n}$$

Table 4. *The calculated frontier orbital energies and related molecular properties of CR–39 monomer.*

E_{HOMO} (eV)	**-4.27**
E_{LUMO} (eV)	2.7
$\Delta E(eV)$	6.97
I (eV)	4.27
A (eV)	-2.7
χ (eV)	0.78
η (eV)	3.48
S (eV^{-1})	0.28
μ	-0.78
ω	0.08

The value of the energy gap between the HOMO and LUMO are 6.97 eV for B3LYP/STO-3G. This large energy gap indicates that the title structure is quite stable.

4. Conclusions

In this study, molecular structure of CR-39 monomer that is a plastic polymer commonly used in the manufacture of eyeglass lenses, has been examined theoretically. Structural characteristics of molecule were calculated and potential energy surface was obtained. The nonlinear optical properties are also addressed theoretically. The predicted NLO properties of molecule are much greater than ones of urea. CR–39 monomer is a good candidate as second-order NLO material. The frontier orbital energies (E_{HOMO} and E_{LUMO}) and related molecular properties (ionization potential, electron affinity, absolute elctronegativity, absolute hardness, softness, chemical potential, global electrophilicity) of molecule were investigated by theoretical calculation results.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this article.

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