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NONLINEAR OPTICAL PROPERTIES (NLO) OF 1, 3, 5-TRIAMINO-2, 4, 6-TRINITROBENZENE (TATB) USING QUANTUM CHEMICAL METHODS

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Abstract: Vibrational and nonlinear optical properties of 1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB) have been investigated using quantum chemical methods. The Finite-Field approach has been used to obtain the static first and second hyperpolarizability components (β and γ) by applying field either in X, Y or Z direction. The geometries of TATB are optimized using quantum chemical methods with different exchange and correlation. The geometrical parameters and vibrational frequencies obtained at B3LP/6-311++G** level are in excellent agreement with the experimental determinations.

Keywords: TATB, nonlinear optical properties, finite field method, Quantum chemical methods,

1. INTRODUCTION

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) is an important molecular crystal widely used in high-performance energetic applications. Nonlinear optical (NLO) materials have attracted much interest because of their potential applications in optoelectronic technology. In particular organic molecules are very suitable in this field owing to their fast electronic responses to external stimuli, ease and flexibility of chemical design, lightweighting materials, good processability in devices, etc.[1] In this context, two-dimensional (2D) octopolar molecules, with 1,3,5-triamino2,4,6-trinitrobenzene (TATB) being the prototypical example, are shown to exhibit second-order NLO features similar to those of their one-dimensional (1D) D-π-A dipolar homologues, overcoming their intrinsic limitations.[2]

Several efforts have been made to understand the NLO properties of organic molecules for the last two decades [3-12]. NLO properties are important for the development of photonic devices, optically based computers, optically based telecommunication systems, and other applications such as optical processing and storage of data/images etc. Several studies have been performed on donor-acceptor type molecules with conjugated chain in between and their NLO properties [13-19]. Theoretical methods such as quantum chemical methods play an important role for the prediction of NLO properties of a material and its suitability for photonic applications.

TATB, a 1,3,5-triamino-2,4,6-trinitro substituted benzene, is a high energy material and has attracted substantial interest recently due to its stability under thermal, impact or shock initiation conditions and may have high NLO properties [27-42]. Due to various competing effects such as electron transfer between amino and nitro group, hydrogen bonding between these groups and sterric effect, it is difficult to determine the structure of TATB [34-36,43]. Both planar as well as nonplanar structures of TATB are suggested. Planar structure of TATB, predicted by X-ray crystallographic study, has been confirmed using Hartree-Fock and Local density functional methods [43,44]. Voigt-Martin et. al. have reinvestigated the structure of TATB using electron diffraction, high resolution imaging, simulation of electron patterns and images and packing energy calculations [30]. Several theoretical studies have also been performed which have focused largely on push-pull and/or steric effects to determine the molecular structure of TATB [34,36,43]. Roszak et. al. have studied the molecular structure of TATB monomer and dimer using MP2 and Density Functional Theory (DFT) method with different exchange and correlation functionals and various basis sets [32]. Gee et. al. have presented all-atom force field for TATB using high level ab initio single point energy calculations of TATB dimmers [45].

The aim of this work is to study TATB molecule at various levels to obtain vibrations and nonlinear

optical properties at different level of theory.

2. Computational details

Geometry optimizations were carried out using *Gaussian* suit of program [22]. The geometries of TATB molecule have optimized using quantum chemical methods with different basis set. DFT with B3LYP, B3PW91 and PBEPBE exchange and correlation functionals have been used for the geometry optimization of TATB molecule. Using these calculations we decided the level of theory at which TATB molecule show the lowest energy and the minimum energy structure. These minimum energy structures are then used to calculate NLO properties of TATB at various levels of theory.

3. RESULTS AND DISCUSSION

We first optimized the geometries of TATB molecule at different levels to obtain the lowest energy structure. We have used DFT method with different exchange and correlation functionals. It is found that the TATB molecule shows the lowest energy at B3LYP/6-311++G****** level among different levels of theories used here. Table I represents bond lengths and angles for TATB at different levels used here alongwith the experimental determinations [17].

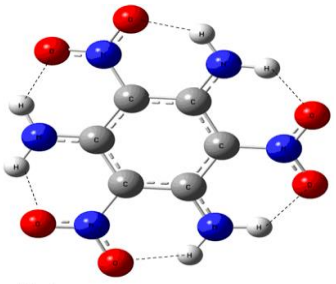

Fig. 1.

Table 1. Geometrical parameters for TATB obtained using different methods with 6-311++G****** basis set alongwith experimental values. Bond lengths in Å and angles in degree.

Bond length/angle	B3LYP	B3PW91	PBEPBE	HF	Expt.*
C-C	1.395	1.392	1.400	1.386	1.397[a]
C-H	1.084	1.085	1.092	1.075	1.102[a]
C-N (C-NH_2)	1.327	1.323	1.333	1.325	1.314
C-N (C-NO_2)	1.436	1.430	1.439	1.440	1.419
N-O	1.242	1.237	1.256	1.194	1.243
<C-C-C	120	120	120	120	----
<C-C-H	120	120	120	120	----

We have also used here various basis sets viz. 6-311G, 6-311+G, 6-311+G*, 6-311++G*, 6-311++G** with different methods to obtain NLO properties of TATB. We have applied Finite-Field of different strength either in X, Y or Z direction for the TATB molecule to decide the suitable field strength in order to obtain the numerical stable hyperporizabilities. The geometries of TATB optimized at B3LYP/6-311++G****** level have been used here since at this level of theory TATB molecule shows the lowest energy among different levels used here. Once the suitable field strength is decided to prevent the numerical instability, we then obtained hyperporizabilities of TATB using different methods and basis sets. Figure 2(a) and 2(b) shows the variation of β and γ respectively of TATB with field strengths applied either in X, Y or Z direction using the Finite-Field method. In Fig. 2, the hyperpolarizability values after certain field strength are the large negative values which are not shown in Fig. 2. We have shown only positive values in Fig. 1. Figure 2 shows that the necessity of applying different field strengths in order to avoid the numerical instability. From Figure 2, it can be said that TATB molecule shows numerical stable hyperporizabilities at a certain range of field strength applied either in X, Y or Z direction. Therefore we have chosen field strength of 0.008 a.u. to calculate the hyperporizabilities of TATB using different methods and basis sets. We have obtained hyperporizabilities using different levels of theory in addition to B3LYP/6-311++G****** level with field strength of 0.008 a.u. applied either in X, Y or Z direction. We can consider hyperporizabilities obtained at B3LYP/6-311++G** level as the reference since at this level of theory the TATB molecule show the lowest energy, geometrical parameters and vibrational frequencies are in excellent agreement with the experimental determinations.

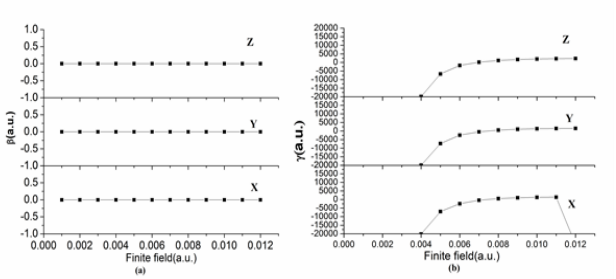

Fig. 2 Variation of β and γ for TATB with field strength at B3LYP/6-311++G****** level.

The β values are zero irrespective of the level of theory and direction in the applied field. However γ values are nonzero for TATB as can be seen from Fig. 3. Figure 3 shows the variation of γ of TATB obtained using different methods and basis sets with field strength of 0.008 a.u. applied either in X, Y or Z direction.

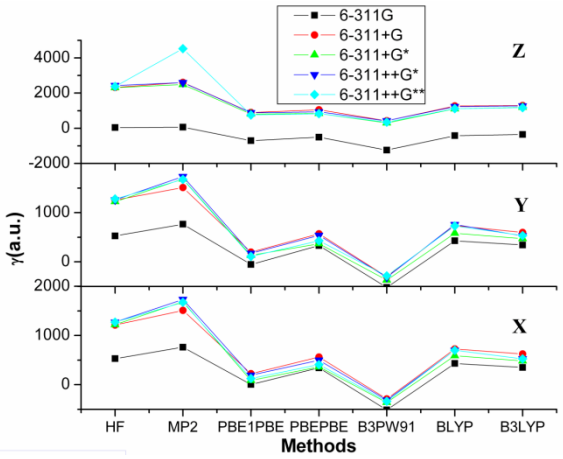

Fig. 3 Variation in γ for TATB obtained using various methods and basis sets using field strength of 0.008 a.u..

4. CONCLUSIONS

NLO properties of TATB molecule are studied systematically. The field is applied either in X, Y or Z direction. TATB shows zero β values irrespective of the applied field direction. There is no large change in β values of TATB. However a significant increase in β values is obtained for the field applied in X direction. Large γ values are also obtained for the TATB. Among different levels of theory used here for obtaining the hyperpolarizabilities, MP2 level shows higher β and γ values than the DFT method with different exchange and correlation functionals. The optimized geometries obtained at B3LYP/6-311++G** level of theory are in excellent agreement with the experimental determinations.

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