



Computational studies of third-order nonlinear optical properties of pyridine derivative 2-aminopyridinium p-toluenesulphonate crystal

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Abstract. We have reported a theoretical investigation on nonlinear optical behaviour, electronic and optical properties and other molecular properties of the organic nonlinear optical crystal 2-aminopyridinium p-toluenesulphonate (APPTS). The computation has been done using density functional theory (DFT) method employing 6-31G(d) basis set and Becke's three-parameter hybrid functional (B3LYP). Calculated values of static hyperpolarizability confirm the good nonlinear behaviour of the molecule. Electronic behaviour and global reactivity descriptor parameters are calculated and analysed using HOMO–LUMO analysis. Energy band gap and simulated UV–visible spectrum show good agreement with experimental results. Other important molecular properties like rotational constant, zero-point vibrational energy, total energy at room temperature and pressure have also been calculated in the ground state.

Keywords. Nonlinear optical crystal; hyperpolarizability; density functional theory; UV–visible spectrum.

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1. Introduction

Nonlinear optical (NLO) properties of materials have become a key field of multidisciplinary research after the discovery of laser. The nonlinear optical materials play important roles in photonics and optoelectronics and have potential applications in areas like optical signal processing, optical limiting, optical logic gates, laser radiation protection, etc. [1–3]. Along with linear and quadratic effects there has been growing interest in third-order optical nonlinearity [4–6]. Third-order materials have a crucial role in many applications of nonlinear optics. The third-order response leads to processes such as third harmonic generation, two-photon absorption and optical Kerr effect, i.e. intensity-dependent refractive index. Most of the nonlinear optical switching devices work on the concept of intensity-dependent refractive index.

Owing to the ease of design and processability compared to inorganic materials, the organic conjugated molecules offer great potential for use in third-order NLO devices [1], thus stimulating the research of compounds possessing sufficiently high nonlinearity,

stability and transparency. The strong delocalization of π electrons in the organic back bone determines a high molecular polarizability, and the resulting third-order optical nonlinearity. In general, large hyperpolarizabilities are the result of an optimum combination of various factors such as π delocalization length, donor–acceptor groups, dimensionality and orientation for a given molecular structure [4]. Pyridine derivatives and sulphur-rich organic materials of this class show very good nonlinearity because of their donor–acceptor arrangement with π -conjugated bond and has been synthesized extensively in recent years [7,8]. A new organic crystal 2-aminopyridinium p-toluenesulphonate (APPTS) for third-order nonlinear optical applications has been reported, which is a Donor- π -Acceptor- π -Acceptor (D- π -A- π -A) type nonlinear optical material and crystallizes in monoclinic crystal system with space group P21/n [4].

Theoretical calculations offer a quick and inexpensive way of predicting the properties of the materials, and are very useful to the experimentalist in further development of useful materials and devices. In the present communication, we report theoretically evaluated NLO

response of the title molecule using DFT [9] with B3LYP functionals using 6-31G(d) basis set with the help of Gaussian 09W package [10]. In addition to NLO properties, UV–visible spectra, HOMO–LUMO energies and thermodynamic properties are also calculated.

2. Computational details

The geometry of APPTS was optimized using the Gaussian 09 program package [10] employing 6-31G(d) basis set and Beckes three-parameter (local, nonlocal, Hartree–Fock) hybrid exchange functionals with Lee–Yang–Parr correlation functionals (B3LYP) [11]. The optimized structural parameters and wavenumbers calculated at 6-31G(d) produced best matching with experimental data [4]. Therefore, we have used geometry optimized at B3LYP/6-31G(d), shown in figure 1, for further calculations of hyperpolarizability, HOMO–LUMO, UV–visible spectra etc.

3. Result and discussion

3.1 Nonlinear optical behaviour

Nonlinear optical behaviour of NLO molecules can be easily interpreted and understood using theoretical calculations. The hyperpolarizability and intramolecular charge transfer play very important roles to explain the contribution of molecular structure in nonlinear optical properties of NLO molecules. Therefore, a theoretical correlation between molecular structure and NLO properties may suggest the possibilities of design and synthesis of new NLO materials.

The electron cloud has the ability to interact with an external electric field and hence increases the asymmetric electronic distribution in either or both the ground

and excited states, which increases optical nonlinearity [12] of the system. First hyperpolarizability (β) is a third-rank tensor that can be described by $3 \times 3 \times 3$ matrices. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [13]. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes

$$E = E^0 - \mu F - \frac{1}{2}\alpha F^2 - \frac{1}{6}\beta F^3 - \frac{1}{24}\gamma F^4 - \dots, \quad (1)$$

where E^0 is the energy of the unperturbed molecule, F is the field at the origin, μ , α , β and γ are the dipole moment, polarizability, first hyperpolarizability and the second hyperpolarizability, respectively. The second hyperpolarizability is a fourth-rank tensor and known as third-order NLO coefficient. The total static dipole moment (μ), the average polarizability (α), anisotropy of polarizability ($\Delta\alpha$) and first hyperpolarizability (β_{tot}) are defined using the x , y , z components as [14]

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (2)$$

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

$$\Delta\alpha = \sqrt{\frac{[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2)]}{2}} \quad (4)$$

$$\beta_{\text{tot}} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2}. \quad (5)$$

The vector component (β_μ), aligned along the μ direction and average second-order hyperpolarizability ($\langle\gamma\rangle$), are generally found from electronic field-induced second harmonic generation (EFISH) experiments and

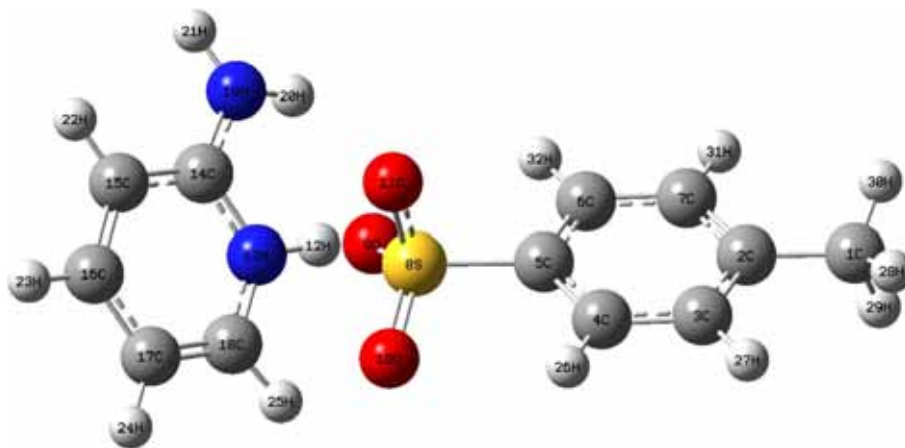


Figure 1. The molecular geometry of APPTS optimized at B3LYP/6-31G(d) level.

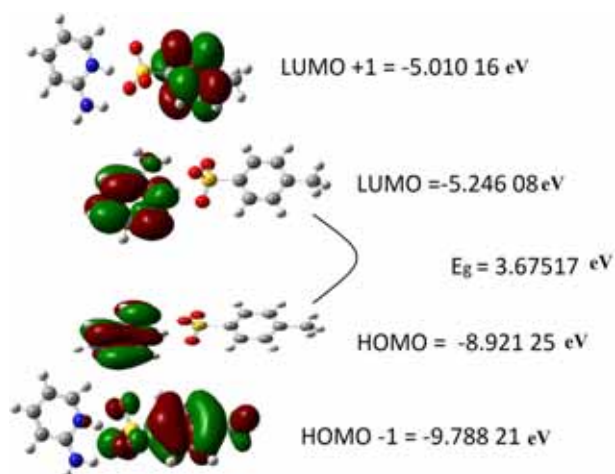


Figure 2. The molecular orbitals of APPTS at the B3LYP/6-31G(d) level.

unoccupied orbital (LUMO). The HOMO and LUMO are the main orbitals having important contribution in stability [16]. The HOMO–LUMO transitions can be easily understood from the visualization of orbital charge distribution over the molecule, which is shown in figure 2. From the figure, it is visible that HOMO is located over the pyridine ring, while HOMO-1 is located over the methyl group, sulphonate group and the benzene ring. On the other hand, LUMO shows a charge distribution over the pyridine ring and LUMO+1 is located over the benzene ring. The HOMO–LUMO transition suggests a redistribution of electron density over the aromatic part of π -conjugated system. The HOMO–LUMO energies and HOMO–LUMO gap of APPTS, which reflect the molecular stability and chemical reactivity of the molecule, were calculated using hybrid functional B3LYP and 6-31G(d) basis set,

$$\begin{aligned} \text{HOMO energy (B3LYP)} &= -8.92125 \text{ eV} \\ \text{LUMO energy (B3LYP)} &= -5.24608 \text{ eV} \\ \text{Energy gap (HOMO–LUMO)} &= 3.67517 \text{ eV.} \end{aligned}$$

In order to find the information about the chemical reactivity of APPTS molecule, global reactivity descriptors [17] such as the energies of frontier molecular orbitals ($\varepsilon_{\text{HOMO}}$, $\varepsilon_{\text{LUMO}}$), energy band gap ($\varepsilon_{\text{HOMO}} - \varepsilon_{\text{LUMO}}$), electronegativity (χ), chemical potential (μ), global hardness (η), global softness (s) and global electrophilicity index (ω) have been calculated with the help of HOMO–LUMO energies, which reflects the electrophilic behaviour of APPTS molecule, shown below. On the basis of $\varepsilon_{\text{HOMO}}$, $\varepsilon_{\text{LUMO}}$ these are determined by using eqs (7)–(11) given below:

$$\chi = -\frac{1}{2}(\varepsilon_{\text{LUMO}} + \varepsilon_{\text{HOMO}}) = 7.08367 \text{ eV} \quad (8)$$

$$\mu = -\chi = -7.08367 \text{ eV} \quad (9)$$

$$\eta = \frac{1}{2}(\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}) = 1.83759 \text{ eV} \quad (10)$$

$$s = \frac{1}{2\eta} = 0.27209 (\text{eV})^{-1} \quad (11)$$

$$\omega = \frac{\mu^2}{2\eta} = 13.65331 \text{ eV.} \quad (12)$$

Electrophilic charge transfer (ECT) is defined as the difference between ΔN_{max} values of the interacting molecules. For two molecules A and B approaching each other (i) if $\text{ECT} > 0$, charge flows from B to A and (ii) if $\text{ECT} < 0$, charge flows from A to B. ECT is calculated using eq. (12):

$$\text{ECT} = (\Delta N_{\text{max}})_{\text{A}} - (\Delta N_{\text{max}})_{\text{B}}, \quad (13)$$

$$\text{where } (\Delta N_{\text{max}})_{\text{A}} = -\mu_{\text{A}}/\eta_{\text{A}} \text{ and } (\Delta N_{\text{max}})_{\text{B}} = -\mu_{\text{B}}/\eta_{\text{B}}.$$

3.3 UV–visible spectrum

The strong π – π^* or σ – σ^* transitions are exhibited by all molecular structures in the UV–visible region with high extinction coefficient. NBO analysis shows that the molecular orbitals of APPTS molecule are mainly composed of π atomic orbitals. So, electronic spectrum predominantly contains π – π^* transitions. UV–visible spectrum of the title molecule has been calculated by employing TD-DFT/B3LYP/6-31G(d) level of theory in gas phase with the help of optimized ground-state structure of APPTS.

The calculated UV–visible spectrum of APPTS in gas phase is shown in figure 3a and is compared with experimental spectrum, which is shown in figure 3b. According to Frank–Condon principle, in a UV–visible spectrum the maximum absorption peaks are found to correspond to vertical excitation. Table 2 gives the calculated vertical excitation energies, oscillator strength (f) and wavelength.

For the gas phase, calculated UV–visible spectrum shows electronic transitions at 353.28 nm with oscillator strength $f = 0.0013$ having an excitation energy of 3.5095 eV corresponding to the HOMO–LUMO transition. The other transitions, summarized in table 2, are found at 371.98, 312.27, 288.88, 282.16 nm. The calculated HOMO–LUMO transition energy 3.5095 eV is in good agreement with the experimental value of energy band gap (3.6 eV) [4].

3.4 Thermodynamic properties

Thermodynamical properties of any molecule of a system are very useful to study that system. Thermodynamical parameters like rotational constant, zero-point

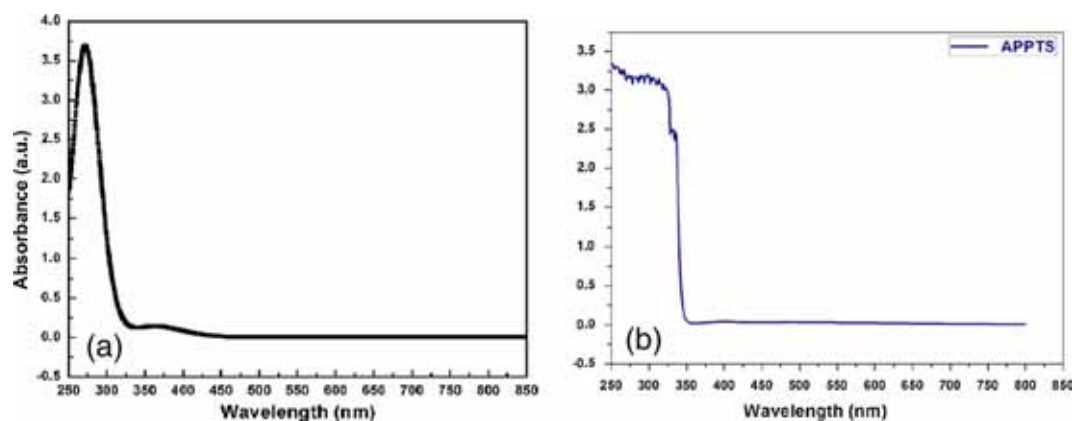


Figure 3. (a) Simulated and (b) experimental [4] absorbance spectrum of APPTS.

Table 2. Calculated absorption wavelengths, energies and oscillator strengths of APPTS using TDDFT method.

Transition type	λ (nm)		Transition energy E (eV)	Oscillator strength (f)	Assignment
	Exp.	Cal.			
H \rightarrow L	348	353.28	3.5095	0.0013	$\pi \rightarrow \pi^*$
H-1 \rightarrow L		371.98	3.3330	0.0023	$\pi \rightarrow \pi^*$
H-2 \rightarrow L		312.27	3.9705	0.0000	$\pi \rightarrow \pi^*$
H-3 \rightarrow L		288.88	4.2919	0.0005	$\sigma \rightarrow \pi^*$
H-4 \rightarrow L		282.16	4.3942	0.0026	$\pi \rightarrow \pi^*$

Table 3. Calculated thermodynamic parameters of APPTS employing HF and B3LYP using 6-31G(d).

Thermodynamic parameters	B3LYP/6-31G(d,p)	HF/6-31G(d,p)
Zero-point vibrational energy (kcal mol $^{-1}$)	157.63417	169.85385
Rotational constants (GHz)	1.02805 0.15796 0.15247	1.03369 0.15287 0.15031
Rotational temperature (K)	0.04934 0.00758 0.00732	0.04961 0.00734 0.00721
Total energy (kcal mol $^{-1}$)	168.657	180.056
Translational energy (kcal mol $^{-1}$)	0.889	0.889
Rotational energy (kcal mol $^{-1}$)	0.889	0.889
Vibrational energy (kcal mol $^{-1}$)	166.880	178.278
Heat capacity at const. volume (cal mol $^{-1}$ K $^{-1}$)	64.562	59.294
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	58.600	53.333
Entropy (cal mol $^{-1}$ K $^{-1}$)	147.261	139.807
Translational	42.635	42.635
Rotational	33.828	33.870
Vibrational	70.798	63.302

Table 4. The charge distribution calculated by the Mulliken and natural bond orbital (NBO) methods using DFT/B3LYP/6-31G(d) of APPTS molecule.

Sl. no.	Atoms	Mulliken charges	Natural charges
1	C	-0.52863	-0.68765
2	C	0.178116	-0.02726
3	C	-0.17675	-0.23193
4	C	-0.1453	-0.21122
5	C	-0.12202	-0.32451
6	C	-0.14562	-0.20835
7	C	-0.17653	-0.23074
8	S	1.154115	2.44146
9	O	-0.54498	-0.9776
10	O	-0.62802	-1.03006
11	O	-0.68419	-1.06765
12	H	0.460148	0.48072
13	N	-0.65142	-0.51923
14	C	0.611043	0.45145
15	C	-0.18367	-0.30618
16	C	-0.08349	-0.15603
17	C	-0.18325	-0.31221
18	C	0.118557	0.08086
19	N	-0.80414	-0.79785
20	H	0.419356	0.46686
21	H	0.352143	0.42229
22	H	0.159518	0.25308
23	H	0.168625	0.25528
24	H	0.16817	0.26036
25	H	0.23011	0.2783
26	H	0.155094	0.25474
27	H	0.119494	0.23165
28	H	0.154532	0.23723
29	H	0.166407	0.24453
30	H	0.155979	0.23823
31	H	0.121705	0.23275
32	H	0.164901	0.2587

vibrational energy, total energy at room temperature and pressure have been calculated at B3LYP/6-31G(d) and HF/6-31G(d) levels of theory. The changes in the total entropy of the investigated molecule using different methods are only marginal. Scale factors have been recommended for the accurate prediction of zero-point vibrational energy, entropy and heat capacities with the values of this table. All the theoretically obtained information about the thermodynamic properties is very fruitful for the further study on APPTS molecule. Thermodynamical parameters are summarized in table 3.

3.5 Mulliken atomic charge distribution

The Mulliken atomic charge distribution has been calculated for the APPTS molecule by DFT/B3LYP method with 6-31G(d) basis set. The computed Mulliken atomic charge values are listed in table 4.

The Mulliken atomic charge distribution of a molecule plays an important role in influencing the dipole moment, polarizability, electronic structure and vibrational modes. The process of electronegativity equalization and model of electrostatic potential outside the molecular surface has been described on the basis of Mulliken atomic charge distribution [18]. In the titled molecule, all the N and O atoms are negatively charged. All the H and S atoms are positively charged but carbon atoms have both positive and negative charges. This explains the influence of a substituent on carbon atoms of APPTS molecule. If electronegative atoms are bonded with carbon, the charge of the carbon atom changes from negative to positive. This shows that the delocalization of charges mainly arises via the carbon atoms [19]. The highest positive charge is distributed over the C14 and S8 atoms, while the highest negative charge is located over N19 atoms of the pyridine ring. The atoms having the highest positive and negative charges suggest the reactive sites of the molecule [20].

4. Conclusion

A theoretical investigations on nonlinear optical behaviour, electronic and optical properties of an organic nonlinear optical crystal APPTS are reported. Optimized geometry shows satisfactory matching with the experimental structure. Calculated values of static hyperpolarizability confirm good nonlinear behaviour of the molecule. Electronic behaviour and global reactivity descriptor parameters are calculated and analysed through HOMO–LUMO analysis. Energy band gap and simulated UV–visible spectrum show good agreement with experimental results.

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