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Research Article

DFT study of Molecular structure, and optical properties of charge transfer complexes derived from Tetrathiafulualene and Tetracyanoquinodimethane derivatives

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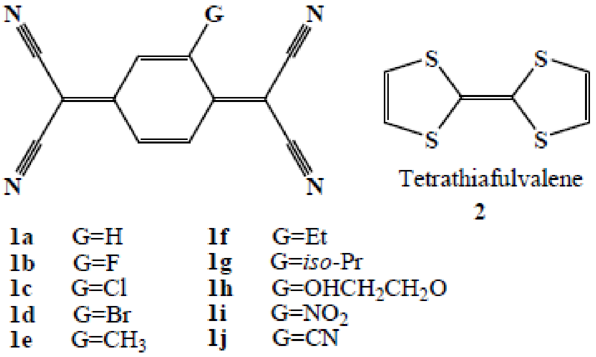
ABSTRACT

During the past decades organic nonlinear optical (NLO) materials have been attracted much attention because NLO materials have potential applications in the field of optoelectroni**.** Experimental measurements and theoretical calculations on molecular hyper polarizability become one of the key factors in the NLO materials design. Theoretical determination of hyper ploarizability is quite useful both in understanding the relationship between the molecular structure and nonlinear optical properties. Several organic derivatives are designed with large first hyper polarizability (β). Among the interesting type of organic materials, charge transfer complexs (CTC) have recently been identified as promising NLO materials. The present study is dedicated to perform a theoretical investigation using B3LYP/6- 311G++ (d, p) level of theory, about the linear and nonlinear optical properties, represented as dipole moment (μ), α, and β of CTCs of, tetracyano quinodimethane derivatives (TCNQ, **1**) and tetrathiafulualene (TTF, **2**). Our aim is designing new NLO materials that can be synthesized in future.

Keywords: Tetrathiafulualene (TTF); Tetracyanoquinodimethane (TCNQ); Polarizability; Hyperpolarizability, Charge transfer complex; DFT.

1. Introduction

In recent years, great efforts had been made to develop new organic, inorganic, and semi organic nonlinear optical materials due to their widespread applications in technologies like lasers, optoelectronics, frequency conversion, high-speed information processing, optical advantage of both inorganic (high thermal and mechanical stability) and organic (broad optical frequency range and second harmonic conversion efficiency) materials. The development of materials with non-linear optical properties is an active topic of research with industrial applications for optical devices [1 –4]. So far several kinds of organic compounds have designed with large first hyper polarizability. Among these compounds, charge transfer complexes have recently been identified as promising NLO materials due to long range conjugation and mesomeric effect in the molecules. The term of charge transfer complex was introduced firstly by Mulliken [5-6], and discussed widely by Foster [7]. In this work our designed CTCs were obtained from imaginary following reaction (Scheme 1). Then molecular geometry and optical property of these CTCs theoretically were studied.



Scheme 1. The structure of CTCs

Quantum chemical calculations were performed on ten molecules at *DFT*/ B3LYP level of theory, employing the split valence basis set 6-311G (d, p). Calculated optimized molecular structure, dipole moment, polarizability, and first hyperpolarizability for all of molecules were dedicated.

2. Experimental

At first all the molecules were obtained by Gussview05 program. Then the dipole moment (μ value), polarizability (α value), and the first static hyperpolarizability (β value) of all aimed molecules, were calculated by Gaussian09 program based on the finite field approach. All the ground state geometries of the molecules are optimized without imposing any symmetry constraint. The stationary points of all structures were found and potential energy hyper surfaces were characterized using freq keyword and standard analytical harmonic vibrational analysis. The absence of the imaginary (negative) frequencies, as well as of negative eigenvalues of the second-derivative matrix, confirms that all molecules correspond to local true minima of the potential energy. Density functional theory has been employed using Becker's three parameter hybrid exchange functional with Lee-Yang-Parr correlation functional and 6-311G++ (d, p) basis sets to optimization and calculating the optical properties of all molecules by polar keyword after optimization, in alternative step as separately.

3. Results and discussion

The polarizability and hyperpolarizability are the tendency for a molecule to form an induced dipole in an applied electric field. This parameter evaluates the linear optical property of a system. They determine not only the strength molecular interactions (long-range intermolecular induction, dispersion forces, etc.) as well as the cross sections of different scattering and collision processes, but also the nonlinear optical properties of the system. Polarizability was calculated at B3LYP/ 6-311++G (d, p) level of theory using the standard Gaussian09w keyword 'Polar'. This keyword means that the polarizabilities were obtained analytically rather than by numerical differentiation. The polarizability is presented in the output from Gaussian 09w in the standard orientation in lower triangular order: αxx, αxy, αyy, αxz, αyz, αzz . The average polarizability (αave), using xx, yy, and zz components are defined as the equation given below:

$$\alpha ave = (\alpha xx + \alpha yy + \alpha zz\ ) /3 \ (\mathbf{1})$$

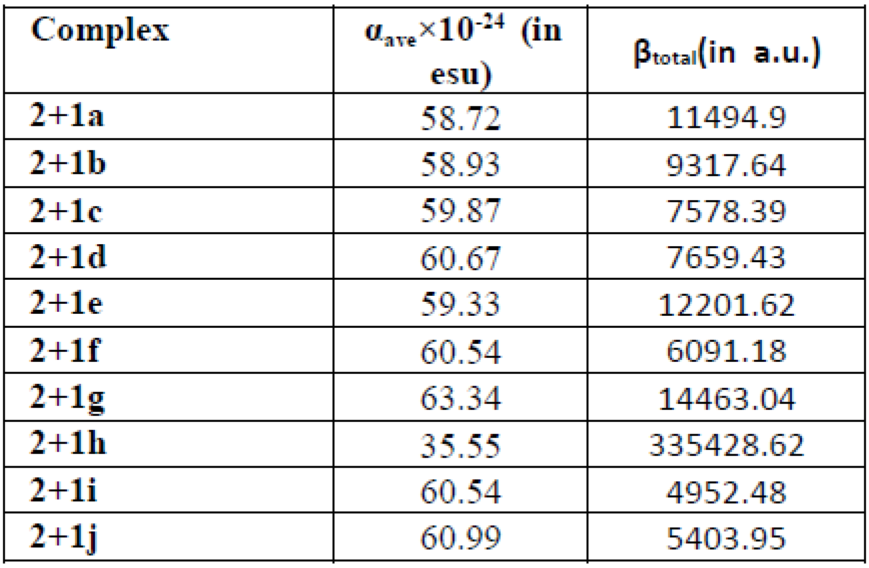
Since the values of polarizability tensors on the output file of Gaussian09w are reported in atomic units (a.u.), the calculated values (αave) were converted into electrostatic units. (1 a.u. equals with 0.1482×10-24 esu). The results for studied molecules are mentioned in the Table 1. Polarizability values show linear optical property for these CTSs are more because of long conjugated system in these compounds.

To investigate the nonlinear optical properties of the molecules is very important because of the key functions of frequency shifting, optical modulation, optical switching, optical logic and optical memory for the emerging technologies in areas such as in telecommunications, signal processing and optical interconnections. The first hyperpolarizability is a third-rank tensor that can be described by a 3 × 3 × 3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry. It can be given in the lower tetrahedral format. The complete equation for calculating the magnitude of the total first static hyperpolarizability is given by the following equation:

$$\beta total=[(\beta xxx +(\beta zzz + \beta zyy + \beta zxx)^{2} \ (\beta yyy + \beta yzz + \beta xzz)^{2}]^{1/2} \ (\beta xyy \ \beta yxx)^{2}$$

As hyperpolarizability is difficult to measure directly, computational calculation is an alternate choice. The first order hyper polarizability of these novel molecular systems were calculated using B3LYP level of theory with the standard 6-311++G (d, p) basis set, based on the finite field approach. Since calculated values of *ß* are in atomic units (a.u), these values have been converted into electrostatic units (esu) (1 a.u = 8.6393 × 10 -33 esu). The results of hyperpolarizability for molecules are mentioned in the below Table. βtot values of all these molecules are at least 7 times more than that of urea (0.77 × 10-30) at the same level of theory B3LYP/6-311++G(d, p) (Urea is one of the prototypical molecules used for the NLO properties of the molecular systems for comparative purposes).

Table 1. Calculated polarizability, first hyperpolarizability (β) and using B3LYP level of theory and 6-311G++(d,p) basis sets for some



Complex	$\alpha_{ave}\times10^{-24}$ (in esu)	β_{total}(in a.u.)
2+1a	58.72	11494.9
2+1b	58.93	9317.64
2+1c	59.87	7578.39
2+1d	60.67	7659.43
2+1e	59.33	12201.62
2+1f	60.54	6091.18
2+1g	63.34	14463.04
2+1h	35.55	335428.62
2+1i	60.54	4952.48
2+1j	60.99	5403.95

4. Conclusions

The molecular structures of 10 CTCs were studied using DFT/ B3LYP level of theory and 6-311++ G (d, p) basis sets. Linear and Non-linear optical properties were studied by calculating the dipole moment, the mean polarizability and the first hyperpolarizability using the same method. This research showed that the investigated compounds are good candidates as a nonlinear optical material. Especially have larger the first hyperpolarizability β values, which makes these compounds attractive objects for future studies of nonlinear optics.

References:

[1] J. Stamatoff, R. DeMartino, D. Haas, G. Khanarian, H.T. Man, R. Norwood, H.N. Yoon, *Angew. Makromol. Chem*. 183 (1990) 151.

[2] T. Kaino, S. Tomaru, *Adv. Mater*. 5 (1993) 172.

[3] T.J. Marks, M.A. Ratner, *Angew. Chem*, 107 (1995) 167.

[4] C. Bosshard, *Adv. Mater*, 8 (1996) 385.

[5] R. S. Mulliken, *J. Am. Chem. Soc*, 72 (1950) 4493.

[6] R.S. Mulliken, W.B. Pearson, Molecular Complexes, Wiley Publishers, New York, 1969.