Optical Materials 56 (2016) 8–17

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Ab-initio and DFT methodologies for computing hyperpolarizabilities and susceptibilities of highly conjugated organic compounds for nonlinear optical applications

A. Karakas [a,*], M. Karakaya [b], Y. Ceylan [a], Y. El Kouari [c], S. Taboukhat [c,e], Y. Boughaleb [c], Z. Sofiani [d]

[a] Selcuk University, Faculty of Sciences, Department of Physics, Campus, Konya, Turkey
[b] Sinop University, Department of Energy Systems, Faculty of Engineering & Architecture, Sinop 57000, Turkey
[c] University Hassan II of Casablanca, Morocco
[d] UIT – University Ibn Tofail, Kenitra, Morocco
[e] LUNAM Université, Université d'Angers, CNRS UMR 6200, Laboratoire MOLTECH-Anjou, 2 bd Lavoisier, 49045 ANGERS cedex, France

ARTICLE INFO

Article history:
Received 24 November 2015
Received in revised form 13 January 2016
Accepted 18 January 2016
Available online 25 January 2016

Keywords:
Nonlinear optical properties
Density functional theory
Time-dependent Hartree–Fock
Two-photon absorption

ABSTRACT

In this talk, after a short introduction on the methodologies used for computing dipole polarizability (α), second and third-order hyperpolarizability and susceptibility; the results of theoretical studies performed on density functional theory (DFT) and ab-initio quantum mechanical calculations of nonlinear optical (NLO) properties for a few selected organic compounds and polymers will be explained. The electric dipole moments (μ) and dispersion-free first hyperpolarizabilities (β) for a family of azo-azulenes and a styrylquinolinium dye have been determined by DFT at B3LYP level. To reveal the frequency-dependent NLO behavior, the dynamic α, second hyperpolarizabilities (γ), second ($\chi^{(2)}$) and third-order ($\chi^{(3)}$) susceptibilites have been evaluated using time-dependent HartreeFock (TDHF) procedure. To provide an insight into the third-order NLO phenomena of a series of pyrrolo-tetrathiafulvalene-based molecules and pushpull azobenzene polymers, two-photon absorption (TPA) characterizations have been also investigated by means of TDHF. All computed results of the examined compounds are compared with their previous experimental findings and the measured data for similar structures in the literature. The one-photon absorption (OPA) characterizations of the title molecules have been theoretically obtained by configuration interaction (CI) method. The highest occupied molecular orbitals (HOMO), the lowest unoccupied molecular orbitals (LUMO) and the HOMO–LUMO band gaps have been revealed by DFT at B3LYP level for azo-azulenes, styrylquinolinium dye, push–pull azobenzene polymers and by parametrization method 6 (PM6) for pyrrolo-tetrathiafulvalene-based molecules.

1. Introduction

The search of new materials with NLO properties is an important research field. Significant interest still exists in the design and development of materials exhibiting large second-order NLO response because of the potential application in telecommunications, optical computing and optical signal processing [1]. Actually, the third-order response governed by the second hyperpolarizability offers more varied and richer behavior than the second-order NLO process due to the higher dimensionality of the frequency space. The azo-azulene derivatives are interesting materials for the study of second and third-order NLO properties [2]. Recently one can observe a huge increase for NLO properties of conjugated and functionalized organic compounds due to their potential applications in optoelectronics devices [3–8]. Due to the extended π system and strong electron donating character of the tetrathiafulvalene (TTF)-moiety, TTF-based systems exhibit very interesting NLO properties [9]. Dyes with related structures have now gained increasing interest not only because of the effect of solvent polarity on their optical properties but also because of their potential applicability in NLO, as optical sensors, and in physiology/biochemistry areas [10]. The azobenzene moieties covalently attached to the polymer usually result in more stable systems with increased density of chromophores and enhanced NLO response [11].

In this work, we have preferred to separate all studied compounds as two groups, one is **TTF1–TTF3** and **S1–S3** performed *Z*-scan experiments, and the other one is a family of azo-azulenes and a styrylquinolinium dye obtained SHG and THG measurements. The aim of this paper is to determine the second and

---

* Corresponding author.
E-mail address: akarakas@selcuk.edu.tr (A. Karakas).

http://dx.doi.org/10.1016/j.optmat.2016.01.036
0925-3467/

third-order optical nonlinearities of the examined compounds (Figs. 1–4) utilizing the theoretical approaches and also to compare all calculated results with their experimental data already published. In addition to NLO properties, the HOMO–LUMO energies and gaps of outer most molecular orbitals and also the electronic transition wavelengths of the lowest lying transitions have been calculated by DFT/B3LYP, PM6 and CI methods, respectively.

2. Theoretical calculations

The geometries of the investigated compounds have been firstly optimized. The geometry optimizations for the molecules in Figs. 1 and 2 have been followed by the calculations of μ and static β values. The electric dipole moments and dispersion-free first hyperpolarizabilities have been calculated using the finite field (FF) scheme [12]. All geometry optimization, μ and static β calculations have been performed by GAUSSIAN03W [13] at DFT/B3LYP level with 6-311+G(d, p) basis set. We rely on the widely used B3LYP which denotes the hybrid functional [14], a linear combination of the gradient functionals proposed by Becke [15] and by Lee et al. [16] together with the Hartree–Fock local exchange function. The magnitude of β_{tot} (total first static hyperpolarizability) has been calculated using the following expression [17]:

$$\beta_{tot} = \left[(\beta_{xxx}+\beta_{xyy}+\beta_{xzz})^2 + (\beta_{yyy}+\beta_{yzz}+\beta_{yxx})^2 + (\beta_{zzz}+\beta_{zxx}+\beta_{zyy})^2\right]^{1/2} \tag{1}$$

Frequency-dependent hyperpolarizabilities have been frequently implemented at the self-consistent field level of theory (known as TDHF) [18]. $\alpha(-\omega;\omega)$ and $\gamma(-3\omega;\omega,\omega,\omega)$ calculations at $\omega = 0.08562$ atomic units (a.u.) (*i.e.* at $\lambda = 532$ nm wavelength) for **AAP**, **ABT**, **AHP**, **AT** (Fig. 1) and at $\omega = 0.04282$ a.u. for styrylquinolinium dye (Fig. 2) according to laser frequency used in third-harmonic generation (THG) measurements have been carried out using the TDHF method with 6-311+G(d, p) basis set implemented in the GAMESS [19] program. The frequency-dependent $\gamma(-3\omega;\omega,\omega,\omega)$ computations at ω frequencies given above were carried out by THG group of the TDHF procedure.

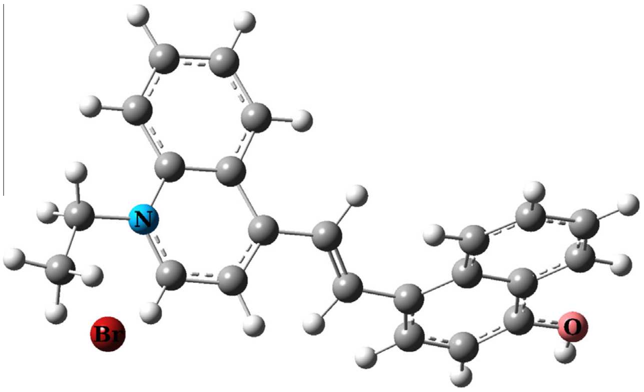


Fig. 2. Chemical structure of the studied styrylquinolinium dye.

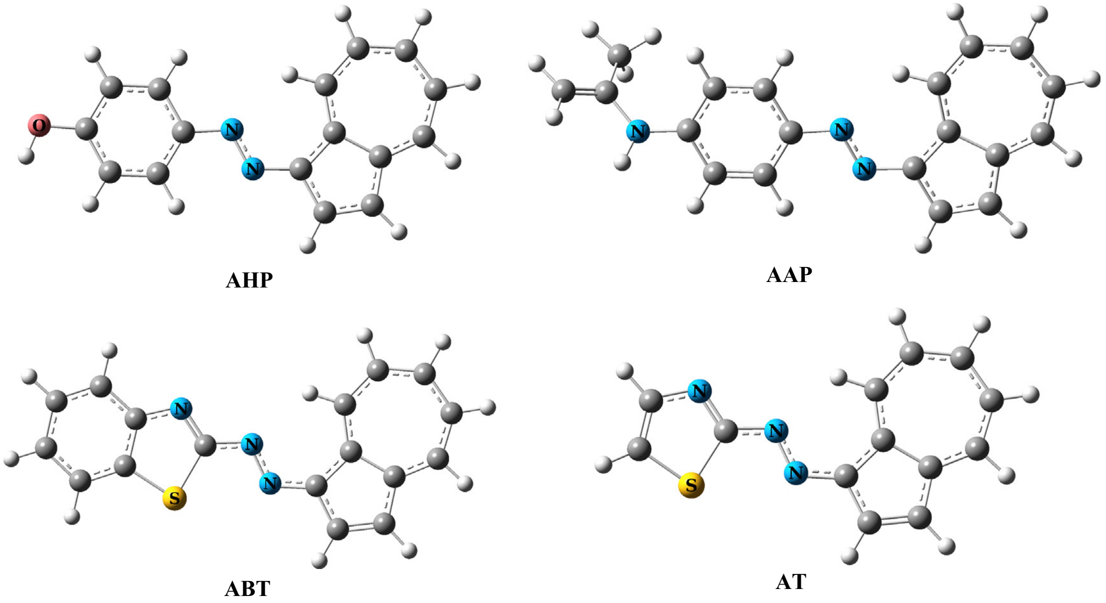
The averaged (isotropic) dipole polarizability $\langle\alpha\rangle$ and third-order hyperpolarizability $\langle\gamma\rangle$ values have been calculated using the following expressions, respectively [20]:

$$\langle\alpha\rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \tag{2}$$

$$\langle\gamma\rangle = (1/5)\left[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\left(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz}\right)\right] \tag{3}$$

We have also computed the orientationally averaged (isotropic) values of second-order susceptibility $\langle\chi^{(2)}(-\omega;\omega,0)\rangle$ and third-order susceptibility $\langle\chi^{(3)}(-\omega;\omega,-\omega,\omega)\rangle$ which represent the nonlinear interaction of second and third orders. $\langle\chi^{(2)}(-\omega;\omega,0)\rangle$ and $\langle\chi^{(3)}(-\omega;\omega,-\omega,\omega)\rangle$ calculations at $\omega = 0.08562$ a.u. for **AAP**, **ABT**, **AHP**, **AT** (Fig. 1) and $\omega = 0.04282$ a.u. for styrylquinolinium dye (Fig. 2) were carried out by electro-optics Pockels effect (EOPE) and optical Kerr effect (OKE) groups, respectively, of the TDHF method with 6-311+G(d, p) basis set implemented in the GAMESS [19] program.

The TPA efficiency of a molecule at optical frequency $\omega/2\pi$ can be characterized by the TPA cross-section $\delta(\omega)$. It can be directly related to the imaginary part of the second hyperpolarizability $\gamma(-\omega;\omega,-\omega,\omega)$ by [21]:



AHP

AAP

ABT

AT

Fig. 1. Chemical structures of the studied compounds **AHP** – azulene-1-azo-(4-hydroxyphenyl), **AAP** – azulene-1-azo-(4-acetamidophenyl), **ABT** – azulene-1-azo-(2-benzothiazole), and **AT** – azulene-1-azo-(2-thiazole).