Theoretical study of static second-order nonlinear optical properties of push–pull heteroquinonoid dimers

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Abstract

The static first-hyperpolarizabilities (β) of a number of donor–acceptor substituted heteroquinonoid dimers has been calculated analytically by using the time-dependent Hartree Fock (TDHF) method and split-valence basis sets. The evolution pattern of β of mono-substituted quinoid rings has been found to mirror the pattern of variation of β of the corresponding polyenes. The charge transfer (CT) characteristics of the chosen quinonoid chromophores have been studied in terms of effective CT parameters (η_f^{XR}) which have been found to fairly correlate with the calculated β of mono-substituted quinonoids. The relative trend in β of quinonoid dimers has been rationalized on the basis of calculated hardness parameter η and $\eta_f (=\eta_f^{DR1} + \eta_f^{AR2})$ which exhibit linear relationships with the ZINDO-S/CI calculated vertical transition energy corresponding to HOMO→LUMO excitation. The analytically evaluated response property, β correlates fairly with the corresponding two-state calculated β_0 and relevant spectroscopic quantities. The general qualitative trend in β obtained for 3-21G and 6-31G** basis sets has been found to be same. The aromatic factor does not play any significant role in the evolution of second-order NLO responses in heteroquinonoid compounds.
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Keywords: Heteroquinonoid rings (R); Hardness parameter (η); Effective charge transfer parameter (η_f^{XR}); Static second-order polarizability; Two-state model

1. Introduction

Nonlinear optics is currently an active area of research. The development of NLO compounds aims at to optimize higher-order polarizabilities at the molecular as well as material levels [1–3]. The second-order polarizability of organic dipolar molecules depends primarily on the strength of electron push–pull substituents and on the nature of intervening π-conjugation. Many attempts focused on the NLO properties of benzene- and polyene-based chromophores while comparatively much less attention was given on the NLO responses of quinoid-based molecular systems [4–14]. The importance of quinoid structure to enhance optical nonlinearity was exploited by Marder et al. [15] in their two-state four-orbital independent electron analysis of first-hyperpolarizability. They showed that chromophores having aromatic and quinoid rings in equal proportion possess rather higher β value. These kinds of charge

transfer molecules, which do not lose or gain resonance energy on electronic excitation are called π-electron degenerate system. The EFISH result of β obtained for dimethylaminoindoaniline (DIA) [15] strongly supports their theoretical prediction. However, quinoid rings attached to stronger donor–acceptors possess much smaller β due to pronounced aromatic character of the ground state which leads to rather higher dipole moment. The dipolar component of β of some quinoid species [1,16] was found to be negative. The NLO responses of quinoids are highly sensitive to their structural modifications. Thus, there remains a scope to improve the optical nonlinearity of quinoid systems by properly modifying its electron transfer character. This can be achieved either by using the donor–acceptor of moderate strength or for a given donor–acceptor pair by changing the quinoidal character of ring with heteroatom substitutions. It is well known [17–20] that with incorporation of heteroatom in the benzene ring (aromatic-form) and also by using non-benzenoid heterocycles the extent of charge transfer can be considerably enhanced due to lowering in resonance energy which in turn leads to larger NLO responses. Recently, McMahon et al. [19] showed that chromophores having thiazole ring could exhibit rather large variation in β due to asymmetric charge

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distribution of thiazole, which can act as both an auxiliary donor and acceptor when attached to a donor group at C5 and an acceptor group at C2, respectively.

Jiang and Zhu [10] on the basis of their theoretical investigation on linear and nonlinear polarizabilities of quinoid-type polyfurans, polythiophenes and polypyrroles showed that these molecules possess appreciably larger NLO responses compared to analogous polyenes. They rationalized the evolution of NLO properties on increasing chain length in terms of BACS parameter (calculated as the sum of the charge on each atom on the molecular bridge). The variation of NLO responses follows the delocalization energy of the corresponding aromatic heterocycles, thiophene > pyrrole > furan. However, it will be interesting to find the influence of heteroquinoids on the NLO properties of chromophores having different kinds of heterocycle rings in between the donor and acceptor substituents. The NLO responses of such quinonoid species were not studied previously.

In the present investigation, we have considered a number of push–pull heteroquinoid molecules (Schemes 3a and 3b) to study the second-order polarizability on the basis of calculated charge transfer related quantities and the two-state model. The mono-substituted quinonoids (Scheme 1) have also been considered in order to understand the precise role of quinonoid ring on the variation of CT interaction and NLO responses, which will subsequently be used to explore the evolution pattern of β in the dimers (Schemes 3a and 3b). Based on the structure property relationship the quinoid-based molecules having higher β value can be designed. Since, the selected intramolecular charge transfer (ICT) quinoids in Schemes 3a and 3b possess identical length of conjugative path for a given substituent-pair, the donor–acceptor CT interaction is expected to be strongly modified by the heteroquinoidal rings. The second-order polarizability (β) of the chosen heteroquinonoid dimers have been calculated at the ab initio HF level using the split-valence basis sets including polarization functions. Since, the lowest lying excited state contributes dominantly to the second-order polarizability in most of the organic charge transfer molecules, we have, therefore considered two-state model to calculate static first-hyperpolarizability (β_0) to rationalize the variation in β in quinonoid dimers (Schemes 3a and 3b).
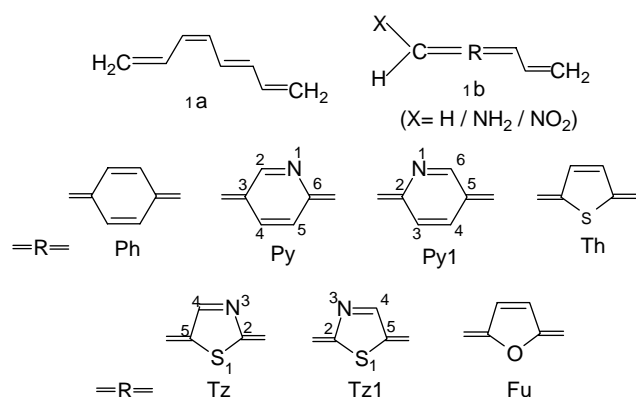
2. Method of calculation

The ground state geometry of the chosen molecules (Schemes 1–3) has been fully optimized at the RHF/3-21G level. The molecules are found to be planar. The first-hyperpolarizability of these molecules (Schemes 1–3) have been calculated analytically at the equilibrium geometry by employing the TDHF method [21] for a static electric field and using 3-21G and 6-31G** basis sets. At the HF level 3-21G basis set properly accounts for the evolution of both electronic structure and second-order response property of quinoidal 2H-pyrrole derivatives [22]. Therefore, the present theoretical study is expected to predict correct trend of β for a series of structurally similar quinoids (Schemes 3a and 3b). The geometry optimization and single point TDHF calculations have been carried out using the GAMESS programs [23].

The average static linear polarizability (α) has been calculated as one-third of the trace of linear polarizability tensor

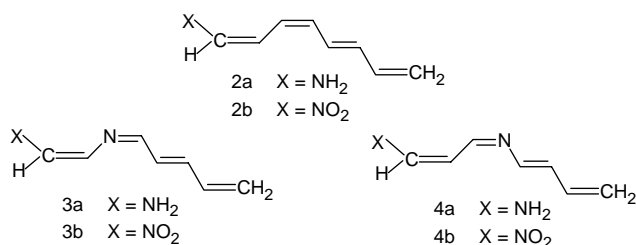$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \qquad (1)$$

In the present study, we report the calculated second-order polarizability as,

$$\beta_{\text{vec}} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \qquad (2)$$

where β_i ($i = x, y, z$) is given by, $\beta_i = (1/3) \sum_{j=x,y,z} (\beta_{ijj} + \beta_{jij} + \beta_{jji})$.

Here, β_{vec} is equivalent to β_{tot} as used by others. The EFISH measurement generally gives β_{vec} projected along the direction of dipole moment, which is also sometimes represented as $\beta_\mu = \beta\mu/|\mu|$ [24]. β_{vec} is generally extracted as β_z when the predominant charge transfer takes place along the molecular dipole moment (z-axis). In our subsequent discussions, β_{vec} will be referred to as β. The quadratic polarizability calculated by using Eq. (2) should be always positive, even though the individual vector component, β_i ($i = x, y, z$) may be negative. In the present investigation, we do not consider the effects due to frequency dispersion and solvent on the second-order NLO property since our main objective is to elucidate the structure property relationship for a series of structurally similar chromophores (Schemes 3a and 3b).

The static quadratic polarizability (β_0) in the two-state model of Oudar and Chemla [25] has been calculated using Eq. (3) that differs from other conventions [26] by appropriate numerical factors. In this model, β_0 emerges from the mixing between the lowest lying ICT and the ground states through the action of the electric field.

Scheme 1.

Scheme 2.