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Third-Order Nonlinear Optical Properties of π-Conjugated Systems Involving Sulfur Atoms: A Proposal of Multi-Property Materials Combining Conductivity and Unique Third-Order Nonlinearity

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Third-Order Nonlinear Optical Properties of π-Conjugated Systems Involving Sulfur Atoms: a Proposal of Multi-Property Materials Combining Conductivity and Unique Third-Order Nonlinearity

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We investigate the third-order nonlinear optical property for 1,6,6a-trithiapentalene (TTP) by using density functional method. A unique spatial contribution of π-electrons to the second hyperpolarizability (γ) is elucidated. Based on our classification rule of γ, the features of γ for other π-conjugated systems involving sulfur (S) atoms are also discussed from the viewpoint of the possibility of combining conductivity and third-order nonlinear optics.

Keywords: third-order nonlinear optics; second hyperpolarizability; sulfur atom; conductivity; multi-property

INTRODUCTION

Recently, a large number of π–conjugated compounds have been investigated experimentally and theoretically toward the molecular designing of nonlinear optical materials. We proposed a classification rule of second hyperpolarizability (γ), which is the origin of third-order nonlinear optical properties, based on the time-dependent perturbation theory[1]. From this rule, the molecule which has large contribution of symmetric resonance structure with inversible polarization (SRIP) tends to exhibit a static negative γ which is rare in organic compounds and is important for application in quantum optics. In this study, we first investigate the static γ for a symmetric π-conjugated systems with sulfur (S) atoms, i.e., 1,6,6a-

trithiapentalene (TTP), by using a density functional (B3LYP) method[2]. Although this system is not considered to have large SRIP contribution, a unique linear arrangement of three-center S atoms exists. Therefore, this compound is expected to provide interesting features of its longitudinal γ. The spatial contribution of γ is elucidated by using γ density analysis[3]. Secondly, other π-conjugated compounds involving S atoms with large SRIP are proposed and the possibility of multi-property materials combining negative γ and conductivity is discussed.

CALCULATION METHODS AND MOLECULAR GEOMETRIES

Recent experimental and theoretical studies elucidated that the TTP can be a C_{2v} symmetrical equilibrium structure with a unique linear arrangement of three-center S atom[4]. Namely, the resonance structure shown in Fig. 1(a) contributes to the ground state of TTP. The geometry of TTP optimized by B3LYP using 6-311G** is shown in Fig. 1(b). In this study, B3LYP calculations are performed by using GAUSSIAN 94[5].

The static γ density can be expressed by a third-derivative of the electron density with respect to the applied electric fields. In this study, we confine our attention to the γ density ($\rho^{(3)}_{zzz}(r)$) corresponding to γ_{zzzz}. We consider a pair of localized $\rho^{(3)}_{zzz}(r)$. The arrow from a positive (white region) to a negative (black region) $\rho^{(3)}_{zzz}(r)$ shows the sign of the contribution determined by the relative spatial configuration between two $\rho^{(3)}_{zzz}(r)$. The sign of the contribution becomes positive when the direction of the arrow coincides with the positive direction of the coordinate system, while the sign of the contribution becomes negative in the inverse case.

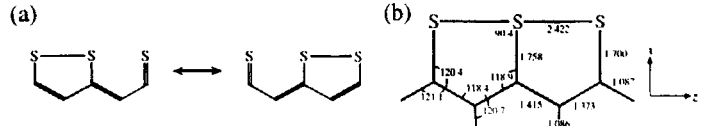

FIGURE 1 (a) Resonance structures of TTP. (b) Bond lengths [Å] and bond angles [°] of TTP optimized by B3LYP using 6-311G**.

γ DENSITY ANALYSIS OF TTP

Figure 2 shows the γ value and γ density plot for TTP calculated by B3LYP using an extended basis set (6-31G*+pd)[6]. The γ value is found to be positive. It is found that the π-electron contributions in S-S-S region are positive, while those in H-C-CH-C-CH-C-H region are small negative. This feature of π-electron contributions to γ is considered to be caused by the difference in the magnitude of SRIP contributions in the two regions. Namely, the SRIP contribution in H-C-CH-C-CH-C-H region is predicted to be larger than that in S-S-S region.

A PROPOSAL OF OTHER UNIQUE SYSTEMS INVOLVING S ATOMS

Although the total γ of TTP is not negative, the π-electron contribution of H-C-CH-C-CH-C-H becomes negative. This is considered to be the

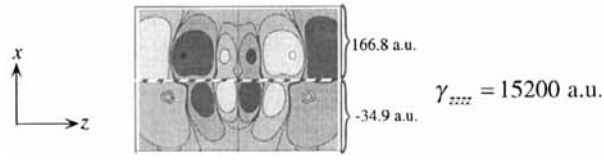

FIGURE 2 γ and γ density plots of TTP located at 2 a.u. above the molecular plane. B3LYP/6-31G*+pd method is used.

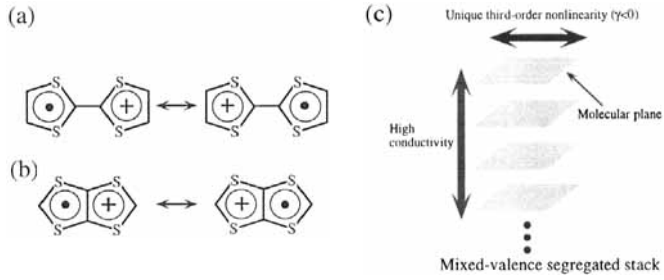

FIGURE 3 SRIP for cation radical states of (a) tetrathiafulvalene and (b) tetrathiapentalene. (c) a molecular mixed-valence stack model exhibiting high-conducting and unique third-order nonlinearity ($\gamma < 0$)

same case as the charged-soliton like oligomers[3], which have large SRIP contribution. In this study, we newly propose other π-conjugated systems involving S atoms with large SRIP contributions (See Figs. 3(a) and 3(b)). The longitudinal γ of the cation radical systems, (a) tetrathiafulvalene (TTF) and (b) tetrathiapentalene, are presumed to be negative in sign. These are considered to be the same cases as the anion radical pentalene and *s*-indacene[6]. These systems ((a) and (b)) and related systems are also well-known to be good donor molecules constructing high-conductivity molecular aggregates[7]. Therefore, in the case of high-conductivity aggregates, e.g., mixed-valence stacks composed of partially cation radical states of donor molecules, the conduction electrons are considered to transfer in the stacking direction and the unique negative γ is also predicted to be generated in the direction perpendicular to the stacking direction (See Fig. 3(c)). This suggests a possibility of multi-property materials combining high-conductivity and unique third-order nonlinearity ($\gamma < 0$). Theoretical calculations of these compounds are now in progress in our laboratory.

Acknowledgments

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