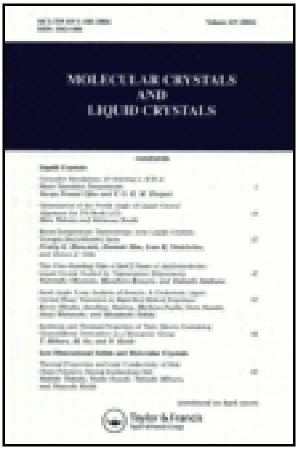

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Theoretical Study on the Second Hyperpolarizabilities for Small Radical Systems

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Theoretical Study on the Second Hyperpolarizabilities for Small Radical Systems

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It is shown that magnitude and signs of second hyperpolarizabilities (γ) for iso-electronic three-center radicals are sensitively influenced by the charged states. These features are found to be closely related to the contribution of symmetric resonance structures with inversible polarization (SRIP).

Keywords: third-order nonlinear optics; second hyperpolarizability; open-shell system; one- and three-center radicals

INTRODUCTION

Although it is well-known that organic systems usually possess positive static second hyperpolarizabilities (γ), we have proposed a structure-property correlation rule of realizing unique systems with negative γ[1]. Namely, the system with large contribution of symmetric resonance structure with inversible polarization (SRIP) tends to exhibit a negative γ. Based on this rule, we predicted nitronyl nitroxide (NN) radical has a negative γ, and actually found that the main component of γ is negative at high-order electron correlation levels[2]. To explore the general nature of γ for radical systems, we firstly investigated γ for iso-electronic small radicals, *i.e.*, $BH_3^{\cdot -}$, CH_3 and

NH_3^{+}[3], which are referred to as one-center radicals. It was found that magnitude, signs and electron-correlation dependencies of γ for such systems sensitively reflect the difference in the charge distributions and the degree of SRIP contribution. BH_3^- is found to have a positive γ at high-order electron-correlation level, though it is considered to have SRIP contribution. This suggests that SRIP contribution in BH_3^- is significantly reduced due to strong Coulomb repulsion in the resonance structures and that an excess electron in BH_3^- enhances the positive contribution originating in the virtual excitation processes involving high-lying excited states[1]. In this study, we further investigate γ for iso-electronic three-center radicals, *i.e.*, $BH(CH_2)_2^-$, $CH(CH_2)_2$ and $NH(CH_2)_2^+$ using ab initio molecular orbital calculations. Fig.1 shows SRIP for three-center radicals.

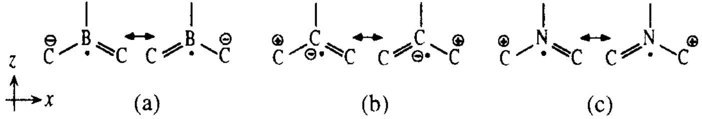


FIGURE 1 Resonance structures of three-center radicals; (a) $BH(CH_2)_2^-$, (b) $CH(CH_2)_2$ and (c) $NH(CH_2)_2^+$.

CALCULATION METHODS AND MOLECULAR GEOMETRIES

The three-center radicals shown in Fig. 2 are assumed to be planar structures. We use an extended basis set (6-311G+*f*/*d*[3]) in the calculation of γ. The electron correlation effects on γ are examined by the *n*th-order Møller-Plesset (MP*n*), coupled-cluster (CC) and quadratic configuration-interaction (QCI) methods. We confine our attention to the main components of γ, *i.e.*, γ_{xxxx}, which are calculated by finite field method.

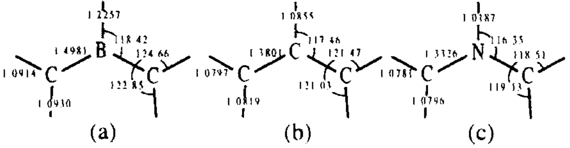


FIGURE 2 Geometries of three-center radicals ((a) $BH(CH_2)_2^-$, (b) $CH(CH_2)_2$ and (c) $NH(CH_2)_2^+$) optimized using B3LYP method with 6-311G(2d,2p) basis set.

We also perform hyperpolarizability density analysis[4] in order to elucidate the spatial contribution to the γ. The second hyperpolarizability

(γ) density is a quantity defined as the third derivative of charge density with respect to the applied fields. In order to explain the analysis procedure, let us consider an arrow drawn from a positive (white region) to a negative (black region) γ density. The sign of the contribution becomes positive when the direction of the arrow coincides with the positive direction of the coordinate system. The contribution becomes more significant when the distance between them is larger.

RESULTS AND DISCUSSION

As shown in Fig.1, $CH(CH_2)_2$ is not expected to have large SRIP contribution by the destabilization of the resonance structures due to the charge separation, while $BH(CH_2)_2^-$ and $NH(CH_2)_2^+$ are expected to have large SRIP contributions. However, judging from the case of one-center anion radical, the SRIP contribution in $BH(CH_2)_2^-$ is predicted to be considerably reduced and an excess electron in $BH(CH_2)_2^-$ tends to enhance the positive contribution. Thus, the γ for $BH(CH_2)_2^-$ is predicted to be positive. As a result, only $NH(CH_2)_2^+$ is expected to have negative γ.

Fig.3 shows electron-correlation dependencies of γ for the three-center radicals. As shown in Fig.3(a), all MP*n* methods provide large negative γ for $BH(CH_2)_2^-$, while CC methods provide positive γ. On the other hand, the γ of $CH(CH_2)_2$ at MP2 level is positive and is shown to be close to that at CCSD(T) level (See Fig.3(b)). As shown in Fig.3(c), the electron correlation effects at MP*n* levels provide negative contribution to γ similarly to the case of $BH(CH_2)_2^-$. In this case, however, the γ for $NH(CH_2)_2^+$ remains negative at CCSD(T) level.

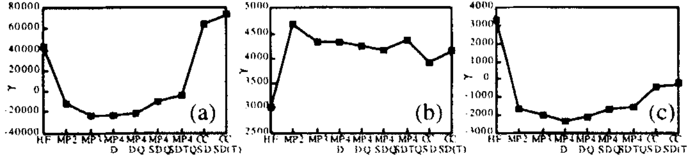
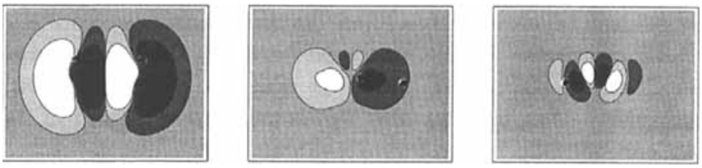


FIGURE 3 Electron correlation dependence of γ for (a) $BH(CH_2)_2^-$, (b) $CH(CH_2)_2$ and (c) $NH(CH_2)_2^+$.

Fig. 4 shows the γ values and γ density plots for three-center radicals calculated by QCISD method, which can well reproduce γ at CCSD level.. A plane at which the γ density is drawn is located at 1.0 a.u. above the molecular plane. The extent of γ density distributions are considered to reflect the difference in each charge distribution. Namely, it is shown that the γ density distribution region of $BH(CH_2)_2^-$ is the largest, while that of $NH(CH_2)_2^+$ is the smallest. Only $NH(CH_2)_2^+$ is shown to have dominant negative contribution region (See Fig. 4(c)). This is in good agreement with our prediction based on SRIP rule.

It is concluded from the present study that the difference in γ sensitively reflects the difference in the charge distributions and the degree of SRIP contributions, similarly to the case of one-center radicals. The present results also provide a useful guideline of designing unique third-order nonlinear optical materials with negative γ. For example, it is expected that one-dimensional molecular aggregates arranged along the longitudinal axis of n-center radical systems exhibit large negative γ in the direction.



(a) $BH(CH_2)_2^-$ γ= 60000 au (b) $CH(CH_2)_2$ γ= 4100 au (c) $NH(CH_2)_2^+$ γ= -420 au

FIGURE 4 γ density distribution of (a) $BH(CH_2)_2^-$, (b) $CH(CH_2)_2$ and (c) $NH(CH_2)_2^+$. The contours are drawn in the region from -10.0 to 10.0 au.

Acknowledgments

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