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Intramolecular dipolar coupling enhancement of the first-order molecular hyperpolarizability in a polar solvent

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Abstract

The effect of intramolecular coupling on the first-order molecular hyperpolarizability in a bis-chromophoric system was theoretically and experimentally investigated. According to finite-field calculations using AM 1 parameters, the effective hyperpolarizability of a bis-chromophore is essentially a vectorial addition of that of the corresponding monomers. However, the EFISH-derived effective hyperpolarizabilities of the bis-chromophores do not follow the additive model. Interestingly, the effective hyperpolarizabilities of the bis-chromophores are significantly enhanced as the solvent polarity increases, which is not observed in those of the corresponding monomeric counterparts.

Recently, there has been an increase in research activity in the development of new and highly efficient organic non-linear optical materials for photonic applications which present potential advances in optical telecommunication technology, optical information processing and storage [1,2]. Materials exhibiting large quadratic optical non-linearities are an essential prerequisite for device applications [3]. Most research efforts have focused on the enhancement of molecular hyperpolarizability, β , which is responsible for the bulk second-order response, by means of modifying the structural and electronic properties of a chromophore. In general, the β value can be enhanced by an increase in donor and acceptor strengths, a decrease in aromatic character in the ground-state, an extension of the π -conjugated length of a chromophore and an improvement in the planarity of the conjugated system. Unfortunately, this

usually causes a red shift in the transparency cut-off which limits its potential applications such as second harmonic generation (SHG) [4,5].

In the theory of organic non-linear optics, molecules are weakly coupled by a Van der Waals interaction so that each molecule is considered to act as an independent NLO source. As approximated by the oriented gas model [6], the second-order bulk susceptibility, $\chi^{(2)}$, is related to the microscopic hyperpolarizability, β , as well as the local field correction factor, F , which is due to the screening electric field generated from neighboring molecules and expressed as:

$$\chi^{(2)} = N\beta F, \quad (1)$$

where N is the number of chromophores in the bulk. Analogously, the effective hyperpolarizability, β_{eff} ,

of a molecular cluster or assembly can be described by the same model which becomes:

$$\beta_{\text{eff}} = n\beta F, \quad (2)$$

where n is the number of chromophores in a cluster. However, when the chromophoric distance is shorter than the Van der Waals limit, molecule–molecule interactions may not be ignored. Recently, Robello et al. [7] have observed the intrachromophoric interaction in their double chromophore assemblies based on dibenzobicyclo[2.2.2]octadiene in which the effective β is less than the theoretical maximum. In addition, a related theoretical study of the chromophoric interaction of non-covalently bonded molecular assemblies showed that there was a sharp increase in effective hyperpolarizability of the molecular assemblies at a distance of less than 3.3 Å [8]. As a result, this further arouses our interest in investigating the influence of intramolecular dipolar interactions on effective β in a multi-chromophoric system in which the chromophores are in closer contact.

The bis-dipolar molecules **1a** and **b** as well as their corresponding monomers **2a** and **b** (Fig. 1) were designed and the syntheses described in our previous work [9]. This class of bis-dipolar molecules is basically formed from two identical chromophores which are directly bonded in a V-shaped assembly.

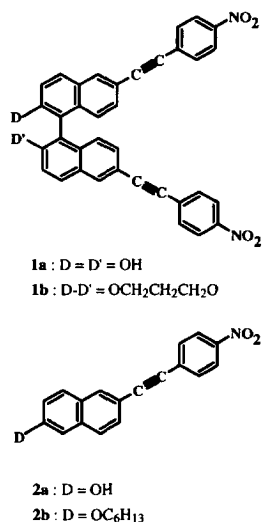


Fig. 1. Racemic 6,6'-bis(phenylethynyl)-1,1'-binaphthyls **1a,b** and 6,4'-disubstituted 2-naphthylacetylenes **2a,b**.

In such a preorganized fashion, the two charge-transfer chromophores are close enough to interact and/or influence each other within a molecular unit. In order to control the relative position of the two chromophores within a molecule and understand its influence on β , a bis-ether linkage was introduced into the binaphthol framework.

The results of quadratic microscopic non-linearities measured from EFISH using a 1.91 μm fundamental frequency, dipole moment measurements, electronic absorption spectroscopic measurements, and quantum mechanical calculations are summarized in Table 1. Semi-empirical AM 1 calculations [10] were employed to probe not only ground-state molecular properties such as dipole moment and molecular geometry but also β . The finite-field method [11] was used to calculate the β based on the optimized geometry of the molecule. According to the calculations, both μ and β of **1a** show approximately a vectorial addition of two independent monomers of **2a** [12]. On the other hand, both μ and β of **1b** are smaller than the additive model. It is probably due to the destruction of coplanarity of the oxygen donor and the naphthyl ring imposed by the strain of the nine-membered ring resulting in the poor overlapping of the p-orbital and thus decreasing its charge-transfer character [9,12].

In view of the electronic absorption spectra, both monomers and bis-chromophores show positive solvatochromism with the exception of **1a** measured in CHCl₃. Such an anomalous behavior is also observed in the μ and $\mu\beta_{\mu}(2\omega)$ performed in CHCl₃. There is no essential change in λ_{ICT} , μ and $\mu\beta_{\mu}(2\omega)$ of bis-chromophore **1a** as compared to those of monomer **2a** in this solvent. The nature of this phenomenon is not known yet. However, this is not the case when measurements were performed in the non-polar solvent dioxane and the highly polar solvent dimethylsulfoxide, DMSO. The intramolecular charge-transfer band, λ_{ICT} , of **1a** shifts to a longer wavelength relative to that of **2a** in both of the solvents. Interestingly, the $\mu\beta_{\mu}(2\omega)$ of **1a** measured in DMSO is twice as large as that obtained in dioxane. On the contrary, the $\mu\beta_{\mu}(2\omega)$ of monomer **2a** is not significantly affected by the solvent polarity. The increase in $\mu\beta_{\mu}(2\omega)$ in response to the solvent polarity which would result from a change in molecular conformation of **1a** is excluded by consid-

Table 1
Results of physical measurements of **1a**, **b** and **2a**, **b**

| Compound | Measured in dioxane | | | | Measured in chloroform | | | | Measured in dimethylsulfoxide | | | | Calculations | | | |
|-----------|---------------------|---|--|--------------------------------|------------------------|---|--|--------------------------------|---|--------------------------------|---|--------------------------------|-------------------|---|---|---|
| | μ (D) | $\mu\beta_\mu(2\omega)$ $\times 10^{-48}$ (esu) | $\beta_\mu(0)$ $\times 10^{-30}$ (esu) | λ_{ICT} (nm) | μ (D) | $\mu\beta_\mu(2\omega)$ $\times 10^{-48}$ (esu) | $\beta_\mu(0)$ $\times 10^{-30}$ (esu) | λ_{ICT} (nm) | $\mu\beta_\mu(2\omega)$ $\times 10^{-48}$ (esu) | λ_{ICT} (nm) | $\mu\beta_\mu(2\omega)$ $\times 10^{-48}$ (esu) | λ_{ICT} (nm) | Calc μ (D) | Calc $\beta_\mu(0)$ $\times 10^{-30}$ (esu) | Calc $\beta_\mu(0)$ $\times 10^{-30}$ (esu) | Calc $\beta_\mu(0)$ $\times 10^{-30}$ (esu) |
| 1a | 6.8 | 230 | 28 | 364 (4.9) | 6.0 | 150 | 21 | 361 (4.8) | 480 | 386 (3.1) | 480 | 386 (3.1) | 9.2 | 49 | 38 | 38 |
| 1b | 8.4 | 250 | 25 | 359 (4.2) | 9.3 | 340 | 31 | 365 (4.0) | 420 | 371 (3.1) | 420 | 371 (3.1) | 10.7 | 42 | 41 | 41 |
| 2a | 6.1 | 170 | 23 | 359 (2.4) | 5.9 | 160 | 22 | 361 (2.0) | 215 | 379 (2.3) | 215 | 379 (2.3) | 6.4 | 37 | 37 | 37 |
| 2b | 5.8 | 175 | 25 | 359 (3.3) | 6.7 | 200 | 25 | 368 (2.3) | 175 | 372 (3.1) | 175 | 372 (3.1) | 7.1 | 42 | 42 | 42 |

μ , dipole moment derived from the Debye equation.

$\mu\beta_\mu(2\omega)$, determined by EFISH experiment using a fundamental frequency at 1.91 μm with precision $\pm 15\%$.

$\beta_\mu(0)$, static hyperpolarizability derived from a two-level model.

λ_{ICT} , intramolecular charge-transfer transition band. The values in parentheses are ϵ_{ICT} , molar absorptivity at λ_{ICT} measured in the corresponding solvents.

Calc μ , dipole moment based on the optimized geometry calculated by semi-empirical AM 1 method.

Calc $\beta_\mu(0)$, static hyperpolarizability calculated by the finite-field method using AM 1 parameters based on the optimized geometry. In order to have the same convention as the measurement, a factor of 1.5 was introduced to the $\beta_\mu(0)$ value obtained from MOPAC.

Calc_{Add} $\beta_\mu(0)$, static hyperpolarizability calculated based on the vectorial addition of $\beta_\mu(0)$ of two corresponding monomers conformed with 70°.

ering the dihedral angle between two naphthyl planes. The latter, obtained by an NMR study using the relaxation time technique [13], is about 70° for **1a** in both CDCl_3 and $\text{DMSO}-d_8$ (vs. 86.7° in the AM 1 optimized geometry). The vectorial sum of $\beta_\mu(0)$ of two monomers **2a** conformed with 70° is 38×10^{-30} esu; on the other hand, the $\beta_\mu(0)$ measured in dioxane of **1a** is 28×10^{-30} esu. Contrarily to the theoretical results, the additive model is not fulfilled in this solvent. Unfortunately, the more interesting $\beta_\mu(0)$ value in DMSO could not be derived due to the indeterminable μ in this solvent.

Concerning bis-chromophore **1b**, the non-coplanarity of the oxygen donor and naphthyl moiety also leads to a slightly blue-shift of λ_{ICT} with respect to that of **2b**. Again, the $\mu\beta_\mu(2\omega)$ of **1b** is substantially enhanced as the solvent polarity increases but it is not observed in the corresponding monomer. It is unlikely that the enhancement of $\mu\beta_\mu(2\omega)$ of **1b** is due to a conformational change in various solvents because of the rigid ring structure. This is further confirmed by NMR study [13]. The increase in μ in the polar solvent is significant; however, it does not account for all the contributions. It seems that the enhancement of β also plays an important role [$\beta_\mu(0) = 25 \times 10^{-30}$ esu in dioxane and $\beta_\mu(0) = 31 \times 10^{-30}$ esu in CHCl_3].

The origin of this β enhancement in **1a** is believed not to be caused by the chelation or hydrogen-bonding interaction of the hydroxyl donors with DMSO since this solvent enhancement effect is consistently found in bis-chromophore **1b**, which bears no hydroxyl donors. It presumably arises from an intramolecular coupling of the two nearby chromophores within a molecular unit. Such an effect could be negligible in a non-polar solvent as the coupling is rather weak between the relatively neutral neighboring chromophoric units. But the chromophoric units become more polarized in the ground state in a polar solvent owing to the dipole–dipole solute–solvent interaction leading to the observed coupling. Solvent effects on hyperpolarizabilities of chromophores have been recognized recently [14].

In conclusion, the first example of β enhancement in two bis-chromophoric systems is evidenced in a polar solvent. Since this solvent enhancement effect is not found in the corresponding monomeric counterparts, it is attributed to the intrachromophoric

interaction of the proximate chromophores within a molecular unit.

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