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Quadratic nonlinear optical properties of correlated chromophores: cyclic 6,6'-dinitro-1,1'-binaphthyl-2,2'-ethers

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Abstract

The first hyperpolarizability, β, of a series of cyclic 6,6'-dinitro-1,1'-binaphthyl-2,2'-ethers has been analyzed with hyper-Rayleigh scattering and electric-field-induced second-harmonic-generation and compared with the absorption data and semi-empirical calculations. The results show the critical dependence of β on the conformation of the alkoxy donor and the dihedral angle of the binaphthyl unit.

The search for new organic molecules with large first hyperpolarizabilities, β, is of considerable interest [1]. In contrast to their (mono-)dipolar and octopolar counterparts, the multi-dipolar molecules combine several charge-transfer units within a single molecule and hence can provide larger hyperpolarizabilities, without the classic bathochromic shift of the charge transfer band. Apart from the calixarenes [2], the 6,6'-disubstituted derivatives of binaphthol are emerging as useful multi-dipolar molecules [3,4]. In this Letter we present new experimental results on hyper-Rayleigh scattering (HRS) and electric-field-induced second-harmonic-generation (EFISHG) measurements on chiral 6,6'-disubstituted binaphthyl ethers in which the dihedral angle is varied by bridging the two oxygen atoms with alkyl chains of different lengths (Fig. 1).

The synthesis of these molecules will be published elsewhere [5]. An important advantage of the binaphthyl derivatives is their chirality, which may provide a non-centrosymmetric structure of the active dipolar subunits in the crystalline phase.

As these molecules are composed of two dipolar subunits, the EFISHG and HRS measurements have to be analyzed using a vector model for the hyperpolarizability tensor of the bis-dipolar molecule. We have shown the validity of this approach for bis-dipolar binaphthyl derivatives [6] poly(isocyanide)s [7], and bacteriorhodopsin [8]. Quantum-chemical calculations and depolarized HRS measurements have shown that for dipolar molecules the hyperpolarizability tensor is dominated by the tensor component along the direction of the charge-transfer [9,10]. Thus we start from the assumption that the hyperpolarizability tensor of the dipolar subunits can be approximated by a single tensor component ($\beta_{mono} = \beta_{zzz}$, with z along the (mono)molecular charge-transfer axis). If we assume that the two dipolar
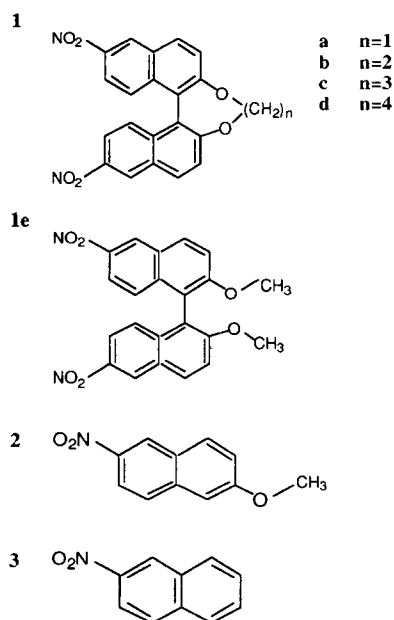
Fig. 1. Molecular geometries of the compounds examined. Molecules **2** and **3** were used as model compounds.

subunits are lying in a plane parallel to the ZX plane and Z is directed along the direction of the two-fold axis and dipole moment of the bis-dipolar molecule (Fig. 2), the hyperpolarizability tensor components of the bis-dipolar molecule can be expressed as a function of the dihedral angle between the two con-
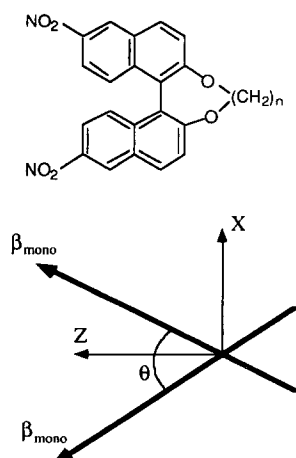

Fig. 2. Constituent units and dihedral angle of the molecules examined.

stituent units (θ) and the hyperpolarizability of the dipolar subunits (β_{mono}):

$$\beta_{ZZZ} = 2\left(\cos\frac{\theta}{2}\right)^3 \beta_{mono},$$

$$\beta_{ZXX} = \beta_{XZX} = \beta_{XXZ} = 2\left(\cos\frac{\theta}{2}\right)\left(\sin\frac{\theta}{2}\right)^2 \beta_{mono}.$$

$$(1)$$

It is important to note that this model geometry is only an approximation, since it does not represent the chirality of the bis-dipolar molecule. Nevertheless, these assumptions have proven their accuracy for the analysis of HRS and EFISHG measurements performed on similar molecules [6].

For a molecule with the four non-zero tensor components, as given in Eq. (1), the experimentally observed quantity in an HRS experiment [11–14], $\langle \beta_{HRS}^2 \rangle$, can be written as:

$$\langle \beta_{HRS}^2 \rangle = \frac{6}{35}\beta_{ZZZ}^2 + \frac{16}{105}\beta_{ZZZ}\beta_{ZXX}$$
$$+ \frac{38}{105}\beta_{ZXX}^2,$$

$$(2)$$

and the result of an EFISHG measurement [15–17] reduces to:

$$\beta_{Z,\text{EFISHG}} = \beta_{ZZZ} + \beta_{ZXX}.$$

$$(3)$$

Thus, EFISHG and HRS are sensitive to the same hyperpolarizability tensor components of the bis-dipolar molecule, β_{ZZZ} and β_{ZXX}. $\langle \beta_{HRS}^2 \rangle$ and $\beta_{Z,\text{EFISHG}}$ were measured in chloroform at 1064 nm as described by the procedure outlined in Ref. [6]. The β of para-nitroaniline in chloroform (23×10^{-30} esu)[13] was used as an external reference for the HRS measurements in the same solvent. Hence, no local field corrections at optical frequencies are needed. The HRS measurement of **1d** was not possible due to multi-photon absorption induced fluorescence. No multi-photon induced fluorescence could be observed for the other compounds. The permanent dipole moment was calculated using the Onsager theory for polar molecules dissolved in a polar solvent [18]. The angle θ was determined by AM1 semi-empirical calculations. With this angle, the ratio of the two independent tensor components of the bis-dipolar molecule can be calculated by taking the ratio of the two tensor components as defined in Eq. (1). Using this ratio, both β_{ZZZ} and β_{ZXX} can be calculated using either $\langle \beta_{HRS}^2 \rangle$ or $\beta_{Z,\text{EFISHG}}$ (Eqs. 2

Table 1
Absorption maxima ($CHCl_3$) and AM1 calculated dihedral angle of the molecules studied

Compound	λ_{CT} (nm)	θ (deg)
1a	306	44
1b	308	72
1c	326	56
1d	332	90
1e	336	92
2	336	–
3	305	–

Table 3
Hyperpolarizability tensor components calculated from HRS experiments ($CHCl_3$, 10^{-30} esu, 1064 nm) of 1a–1c, 2 and 3. (Note that HRS experiments on 1d were not possible due to multiphoton absorption induced fluorescence)

Compound	β_{ZZZ} (esu)	β_{ZXX} (esu)	β_{mono} (esu)
1a	19	3	12
1b	20	10	18
1c	34	9	24
2	–	–	27
3	–	–	10

and 3). β_{mono} can be calculated from either β_{ZZZ} or β_{ZXX} and θ (Eq. 1). Table 1 shows the evolution of the angle θ and the absorption maximum. The EFISHG results are summarized in Table 2 and the HRS results in Table 3.

Several tendencies can be observed on passing from 1a to 1d. As the length of the alkyl chain between the two ether oxygen atoms increases from 1a to 1d, the angle θ increases from 44° to 90°. The fact that even for 1a the molecule is not planar can be attributed to the strong steric repulsion between the hydrogen atoms in 8,8' positions [19]. In the absorption spectra, several transitions can be observed. The transitions between 200 and 300 nm can be attributed to the naphthalene system. As indicated by the two-level model [20], the important parameter for the discussion of the hyperpolarizability is the λ_{max} of the low-lying charge-transfer transition. This absorption maximum shifts from 306 to 336 nm, indicating an increasing extent of charge-transfer. For 1a, the λ_{max} is equal to that of 2-nitronaphtha-

Table 2
Dipole moments ($CHCl_3$) and hyperpolarizability tensor components calculated from EFISHG experiments ($CHCl_3$, 10^{-30} esu, 1064 nm) of 1a–1e, 2 and 3

Compound	μ (debye)	β_{ZZZ} (esu)	β_{ZXX} (esu)	β_{mono} (esu)
1a	5.6	16	2.5	10
1b	6.7	19	10	18
1c	7.5	22	6.5	16
1d	8.3	18	20	27
1e	6.2	17	19	26
2	4.5	–	–	26
3	4.0	–	–	8

lene (3), showing that the electron donating effect of the oxygen atom is virtually annihilated due to the conformational strain that precludes overlap between the naphthalene conjugated system and the lone electron pair of the oxygen atom. As the λ_{max} of the low-lying charge-transfer transition of 1d and 1e coincides with that of 6-nitro-2-methoxynaphthalene (2), the electron donating capabilities of the oxygen atom are completely expressed. In 1b and 1c, the conformational strain is not yet fully relieved and electron-donating capabilities are not fully employed.

The effect of the conformational strain is even stronger for the magnitude of the first hyperpolarizability. First, as the angle θ increases, β_{ZXX} increases in magnitude relative to β_{ZZZ}. For 1d and 1e, β_{ZXX} is even larger than β_{ZZZ}. This is in strong contrast with the more traditional dipolar chromophores, where β_{zzz}, with z along the charge-transfer axis, is considered the only significant hyperpolarizability tensor component. As the conformational strain is relieved, the electron donating capabilities of the oxygen atom and the charge-transfer character of the first excited state increase. This strongly affects the absolute magnitude of the hyperpolarizability tensor components of the bis-dipolar molecule and the value calculated for the hyperpolarizability of the dipolar subunits (β_{mono}). As was the case for the position of the absorption maxima, the hyperpolarizability of the dipolar subunits of 1a is almost equal to the hyperpolarizability of 3, again indicating that the electron donating capabilities of the oxygen atom are absent. For 1d and 1e, the oxygen atom is fully conjugated and the first hyperpolarizability of the constituent monomer is equal to that of 2. For 1b and 1c, β_{mono} is intermediate

between the hyperpolarizability of the two reference molecules. This observation is in agreement with the hyperpolarizability measurements using Raman spectroscopy [21].

Also note the good agreement that is obtained between the tensor components calculated from EFISHG (Table 2) and HRS (Table 3). While for the dipolar reference molecules the analysis of the EFISHG and HRS measurements is straightforward, the analysis of the results for the bis-dipolar binaphtol molecules, has to take into account the relative magnitude of the different tensor components. This good agreement suggests that good accuracy can be obtained by modelling the hyperpolarizability tensor of these bis-dipolar molecules by a vector model and that, at the level of the electronic hyperpolarizability, the interactions between the two naphthalene units can be neglected. Using INDO/S quantum-chemical calculations, it has been shown by Di Bella et al. that for a dimer of para-nitroaniline these interactions gain importance when the dihedral angle between the two units decreases [22].

In summary, these measurements show that conformational strain can be used to modify both the magnitude and the ratio of the tensor components of 6,6'-substituted binaphthyl ethers. The magnitude of the tensor components is influenced mainly by the effect of the conformational strain on the electron donating capabilities of the oxygen atom. The ratio of the tensor components is determined by the dihedral angle between the two dipolar subunits. It remains to be seen how the chiral bis-dipolar structure of these molecules can be used for the preparation of noncentrosymmetric crystals or poled polymer films.

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