

Determination of the First Hyperpolarizabilities of Octupolar Molecular Ions Made from Symmetric Cyanine Dyes

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Symmetric cyanine dyes of the kind $\text{Me}_2\text{N}^+=\text{CH}-(\text{CH}=\text{CH})_n-\text{NMe}_2$ normally exhibit no first hyperpolarizabilities β but have relatively long absorption wavelengths. Therefore they are not suitable NLO chromophores for second-order applications. However, if these chromophores are converted into octupolar molecules either by coupling an extra aldiminium group onto the dye molecule or by grafting three vinamidinium units onto a benzene ring, NLO chromophores with considerable first hyperpolarizabilities are obtained. To prove this, the β values of both kinds of octupoles have been determined via hyper-Rayleigh scattering in solution at 1064 nm.

Introduction

Recently the search for organic and organometallic molecules with large optical nonlinearities has become an important task of organic synthesis.^{1,2} Classical charge-transfer molecules like donor-acceptor-substituted benzenes, stilbenes, styrenes, etc., exhibit large first hyperpolarizabilities only when they absorb at long wavelengths.^{3,4} For electrooptical devices, this so-called transparency-nonlinearity tradeoff⁵ is—except for molecules which are absorbing at very long wavelengths—not a problem since no frequency conversion occurs in this process. Organic frequency-doubling materials, on the other hand, are required to have an optical window at both the frequency of the second harmonic and fundamental. The transparency-nonlinearity tradeoff, valid for certain dipolar chromophores⁶ can be explained theoretically by the two-level model.⁷ For octupolar molecules, recently introduced by Zyss et al.,^{8–10} the two-level model no longer holds. The first measurement of an octupolar molecule ion with hyper-Rayleigh scattering, the only technique capable of measuring the hyperpolarizability of nonpolar and/or ionic molecules was carried out by Verbiest et al.¹¹ A systematic

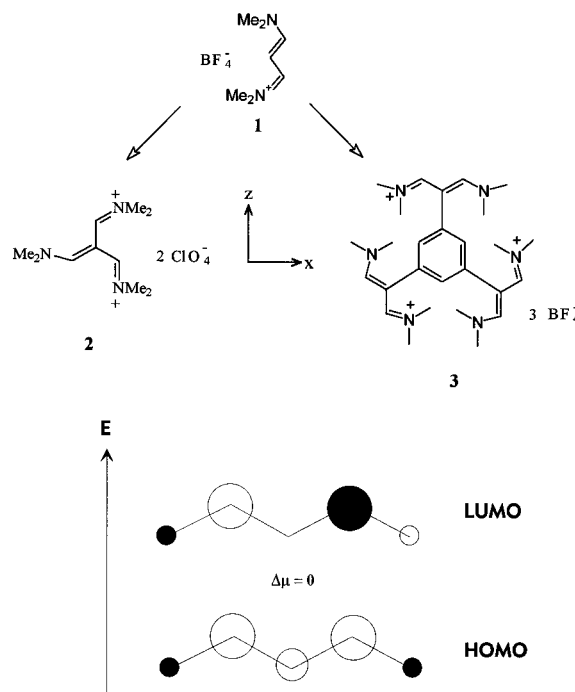


Figure 1. Top: Structures of the investigated cyanine **1** and the octupolar vinamidinium salts **2** and **3**. Bottom: Frontier orbitals for **1**, indicating that there is no difference in ground-state and excited-state dipole moments along the charge-transfer axis.

nonlinear optical study of molecules with octupolar charge distribution can be found in ref 12.

In this paper we present octupolar structures that are derived from symmetric cyanine dyes (Figure 1). The

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latter show no solvatochromism and no first hyperpolarizabilities due to the lack of a difference in the “dipole moments” of the ground and the first excited state along the charge-transfer axis (Figure 1) whereas the derived octupoles exhibit considerably large β values.

Experimental Section

The 1,5-diazapentadienium salt **1** was synthesized according to literature procedures.¹³ **2** can be obtained by reaction of **1** with dimethylformamide (DMF) and POCl_3 .¹⁴ Compound **3** is available from 1,3,5-triacetylbenzene, which is converted to 1,3,5-benzenetriacetic acid via the Wilgerodt–Kindler reaction. With $(\text{COCl})_2$ and DMF the latter yields the octupolar molecule **3**.¹⁵

1–3 are charged; the two octupoles additionally lack a ground-state “dipole moment” preventing the use of the well-established EFISHG technique⁷ to determine β . The recently developed hyper-Rayleigh scattering experiment (HRS) is capable of measuring ionic and/or octupolar molecules. The experiment is described adequately in the literature,^{16,17} but the principle of measurement and evaluation of data is shortly discussed.

Solutions of a NLO chromophore in a suitable solvent are irradiated with strong laser light (in our case a pulsed Continuum Surelite Nd:YAG laser with 300 mJ pulse energy, 6 ns pulse width, and 10 Hz repetition rate, whose energy is reduced to about 5 mJ). For different number densities of the chromophore, the intensity of the generated frequency doubled scattered light $I(2\omega)$, which depends quadratically on the fundamental intensity, $I(\omega)$, is monitored with a THORN EMI 9635QA photomultiplier as a function of $I(\omega)$. The latter is varied by rotating a half-wave plate between two crossed polarizers which leads to the following fit formula:

$$I(2\omega) = A[\sin(2\varphi + \alpha)]^4 + b$$

with $A = G(N_g\beta_g^2 + N_l\beta_l^2)I(\omega)^2$ (1)

where G is a geometrical factor, A the maximum HRS intensity, φ and α the rotating and deviation angles, respectively, of the half-wave plate, and b an intensity offset. N_g , N_l , and $\beta_g\beta_l$ represent the number density and the β value of the solute or solvent, respectively. Measurements at different number densities of the solute show a linear dependence of the fit parameter A in eq 1 on N_g .

From the intercept c and the slope m from a plot of A against N_g , the hyperpolarizability of the chromophore can be calculated when that of the solvent is known or vice versa (**internal reference method**):

$$|\beta_g| = \sqrt{\frac{mN_l}{c}}|\beta_l| \quad |\beta_l| = \sqrt{\frac{c}{mN_l}}|\beta_g| \quad (2a,b)$$

Due to the uncertainty in the intercept, especially for high- β molecules, it is normally better to compare the slope m of the substance to be measured with the slope of a known substance, e.g., *p*-nitroaniline (PNA) in the same solvent (**external reference method**):

$$|\beta| = \sqrt{\frac{m}{m_{\text{PNA}}}}|\beta_{\text{PNA}}| \quad (3)$$

Figure 2 shows the linear dependence of the parameter A on the number density for compound **3** and PNA as an external reference in acetonitrile. The β value of 29×10^{-30} esu for PNA in CH_3CN was taken from the literature.¹⁸ The hyperpolarizability of **2** was determined via the internal reference

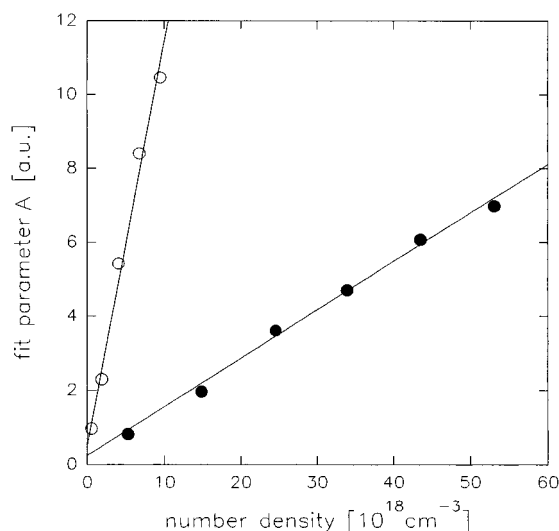


Figure 2. Plot of the parameter A as a function of the number density of PNA (filled circles) and **3** (hollow circles) in acetonitrile. From the ratio of the slopes the β_{zzz} value of **3** can be obtained with eqs 3 and 6.

method because PNA is not soluble in water. The β value of 0.19×10^{-30} for water was taken from the literature.¹⁹ Since this is a gas-phase value, there might be an uncertainty in transferring it to a liquid system such as a chromophore solution.

$I(2\omega)$ is proportional to the orientational average over the square of the β tensor, $\langle\beta^2\rangle$. For a dipolar molecule of symmetry C_{2v} and the charge-transfer axis lying in the z direction, we can write, assuming other tensor components than β_{zzz} are negligible small,

$$\langle\beta_{C_{2v}}^2\rangle = \frac{6}{35}\langle\beta_{zzz}^{C_{2v}}\rangle^2 \quad (4)$$

whereas for an octupolar molecule with D_{3h} symmetry we obtain²⁰

$$\langle\beta_{D_{3h}}^2\rangle = \frac{8}{21}\langle\beta_{zzz}^{D_{3h}}\rangle^2 \quad (5)$$

Using a dipolar molecule as a reference for an octupolar sample (with unpolarized detection), we have to write

$$|\beta_{zzz}^{D_{3h}}| = \sqrt{\frac{6/35\langle\beta_{D_{3h}}^2\rangle}{8/21\langle\beta_{C_{2v}}^2\rangle}}|\beta_{zzz}^{C_{2v}}| \quad (6)$$

where the ratio $\langle\beta_{D_{3h}}^2\rangle/\langle\beta_{C_{2v}}^2\rangle$ corresponds to the ratio of the slopes from eq 3.

Results and Discussion

Table 1 shows the results of the HRS measurements and the UV/vis data. Compound **1** displays no solvatochromism as expected. This can be easily understood looking at the electron density in the ground state and the first excited state (Figure 1 pictures the frontier orbitals for **1** calculated with the AM1 parametrization of the MNDO Hamiltonian), which both are symmetrically distributed so that the “dipole moments” along the charge-transfer axis of both states are zero. According to the two-level model the first hyperpolarizability β is proportional to the difference in the dipole

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Table 1. Experimentally Determined β Values and Absorption Maxima of 1–3

compound	solvent	λ_{\max} [nm]	β_{zzz} [10^{-30} esu]
1	chloroform	309	
	water	309	
2	water	321	18
3	acetonitrile	365	56
PNA	acetonitrile	366	29 ^a

^a From ref 18. The typical errors in the HRS experiment are $\pm 15\%$.

moments in the ground and excited state, $\Delta\mu$. Since $\Delta\mu$ is zero for **1** (at least along the charge-transfer axis), β also is expected to be 0. Indeed we could not detect second harmonic intensities from concentrated solutions of **1** in water and chloroform beyond those of the pure solvents in our HRS setup.

However, it is possible to obtain a nonzero β chromophore by coupling an extra aldiminium group onto the cyanine molecule. The absorption maximum of the resulting octupole **2** is only slightly redshifted compared to **1**, while the β value is considerably large for a molecule of that size. Semiempirical calculations (AM1 parametrization of the Hamiltonian with the program MNDO94) show that **2** possesses D_3 symmetry.

Another possibility to obtain β -active molecules from **1** is to graft three vinamidinium units onto a benzene ring. The resulting propeller-shaped (the W-shaped vinamidinium groups are twisted by an angle of 70.7° against the benzene ring) octupole **3** also has D_3 symmetry (which is proven by X-ray diffraction analysis and semiempirical calculations) and an almost vanishing dipole moment of 0.020 D (for practical reasons the dimethylamino group was replaced by an amino group for the calculation). While the absorption maxima of **3**

and PNA are almost identical the β_{zzz} value of **3** is significantly larger. The absorption data along with the experimentally determined hyperpolarizabilities are shown in Table 1.

Since **2** and **3** are ionic and lack a ground-state dipole moment, they cannot be implemented into guest–host systems for macroscopic devices. Compound **3** belongs to the space group $R\bar{3}c$ and therefore to the centrosymmetric trigonal crystal class $\bar{3}m$. Whether **2** crystallizes in a noncentrosymmetric lattice is not yet clear since we do not have X-ray diffraction data so far.

Summary and Conclusion

In this paper we have shown that it is possible to obtain nonzero- β chromophores from zero- β symmetric cyanine dyes by converting them into octupolar structures by two different methods. First, it is possible to couple an extra aldiminium group onto the merocyanine molecule. The resulting totally blue-transparent small octupole absorbs at only slightly longer wavelengths than the cyanine but exhibits a considerably large first hyperpolarizability. Second, the vinamidinium units can be grafted onto a benzene backbone. The resulting octupole absorbs at the same wavelength as PNA while the hyperpolarizability is significantly larger. Since the two new octupoles we presented lack a ground-state dipole moment and also are ionic, the hyper-Rayleigh scattering technique was the only method to experimentally investigate their nonlinear optical properties.

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