Experimental Determination of the First Hyperpolarizability of New Chiral and Achiral Octupolar Tertiary Amines by Hyper-Rayleigh Scattering

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Tertiary amines with a fully sp^2-hybridized nitrogen as central atom and acceptor-substituted phenyl or diazabiphenyl units as peripheral groups (hereafter shortly referred to as "sidewing-octupoles") exhibit relatively high β values at short absorption wavelengths. Donor substitution of those sidewings results in a drop in the first hyperpolarizability β at comparable absorption wavelengths. One of the octupoles investigated has three chiral carbon atoms so that it should crystallize in a noncentrosymmetric structure. This is interesting since there is no other way to obtain macroscopic $\chi^{(2)}$ structures from octupolar molecules due to the lack of a permanent dipole moment. The first hyperpolarizability β of these octupolar molecules has been measured via the recently developed hyper-Rayleigh-scattering technique (HRS) at 1064 nm.

Introduction

The recent interest in new organic materials for second-order nonlinear optical processes has led to numerous efforts in the synthesis of molecules with high nonlinearities.[1,2] Since classical dipolar NLO chromophores with large first hyperpolarizabilities, such as donor−acceptor-substituted benzenes, stilbenes, styrenes, etc., normally absorb at long wavelengths,[3,4] new concepts for organic frequency-doubling materials are required to avoid absorption of the second harmonic. One way to circumvert this problem is anomalous dispersion phase-matching, where the absorption band falls between ω and 2ω. However, residual 2ω absorption may still cause problems. A second way to circumvert this transparency-nonlinearity tradeoff[5] is the concept of the so-called octupolar systems, recently introduced by Zyss et al.[6−8] First β measurements on an octupolar system were carried out on the tricyanomethanide ion.[9] Further results were presented on ruthenium complexes with bifunctional ligands,[10] crystal violet,[11] and 1,3,5-donor−2,4,6-acceptor-substituted benzenes.[12] Recently we reported tertiary amines with a fully sp^2-hybridized nitrogen as central atom and acceptor-substituted phenyl or diazabiphenyl units as peripheral groups.[13] Measurements of the first hyperpolarizabilities of these sidewing octupoles and their corresponding dipolar subunits clearly highlighted the high potential of these octupolar systems. While the absorption maxima of the octupoles were only moderately red shifted compared to those of the dipoles, the observed β values were up to 4 times larger.

In this work we investigated the influence of a donor group in the sidewings of these octupoles (Figure 1). The replacement of the acceptor groups in the sidewings by donor groups results in a drop in β while the absorption maxima are only slightly blue shifted. One of the octupoles, ***4***, has chiral carbon atoms and should therefore crystallize in a noncentrosymmetric lattice, which may be beneficial for solid-state frequency conversion.

Experimental Section

Since octupolar molecules have no ground-state dipole moment, their molecular hyperpolarizabilities cannot be measured with the EFISH technique.[14] With the recently developed hyper-Rayleigh-scattering method (HRS), however, it is not necessary to orient the molecules[15] so that nonpolar species can be investigated. Figure 2 shows the experimental setup of the HRS experiment. Our laser source is a Continuum

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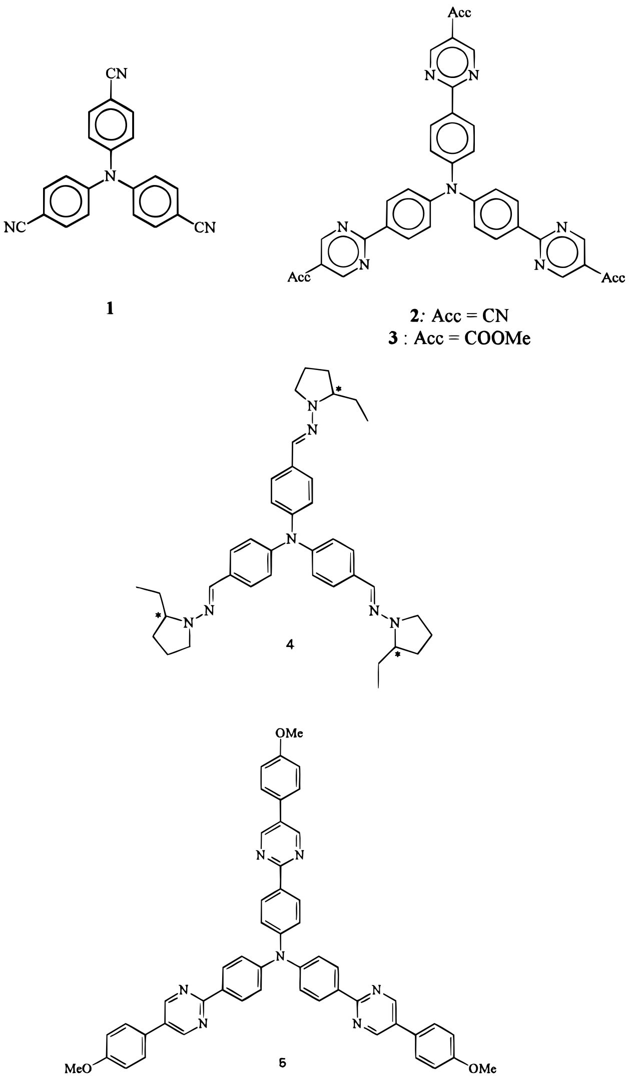

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2*:* Acc = CN
3 : Acc = COOMe

4

5

Figure 1. Structures of the investigated octupoles.

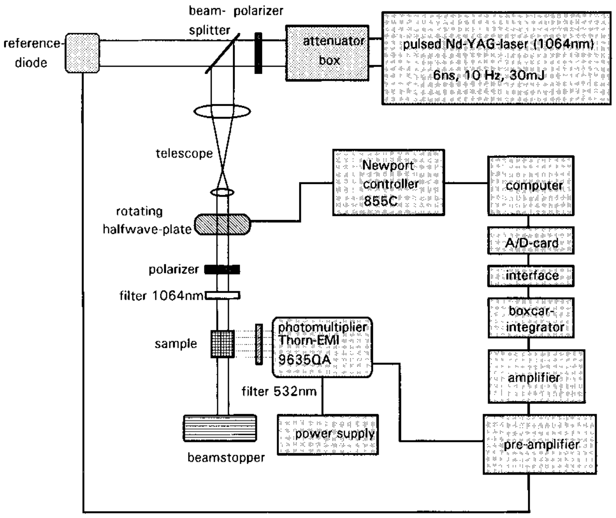

Figure 2. Experimental setup of the HRS experiment.

Surelite Nd:YAG laser (10 Hz repetition rate, 5 ns pulse width, 300 mJ pulse energy) whose power is lowered to 5 mJ by a set of partial reflectors. For variation of fundamental intensity we use a motor-driven half-wave plate between two crossed polarizers. The motor is controlled by a Newport 855C controller unit, which is connected to a computer via an IEEE card. The current of the Thorn-EMI 9635QA multiplier is changed into voltage by a HMS 564 preamplifier which is connected to our self-built boxcar integrator. The signals are sent to the computer via a D/A card. For data acquisition we use programs developed under Lab Windows (National Instruments). In contrast to the setup of Clays and Persoons[16] the beam is not focused into the sample cell but reduced before to a diameter of 1.5 mm with the help of a telescope, so that there are no problems with dielectric breakdowns within the sample. Because of the large effective cathode diameter of the Thorn-EMI 9635QA, there is no need for focusing the second harmonic scattered light into the photomultiplier, which makes the adjustment much less complicated. To avoid signal contributions from small amounts of dye adsorbed at the glass walls and the glass walls themselves, both ends of the cuvette are shielded.

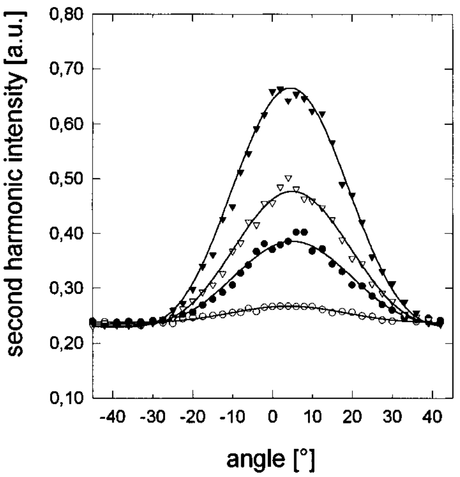

Figure 3. Intensity of the frequency-doubled light as a function of the rotating angle φ for four different concentrations (number densities) of **3** in chloroform. The rotation of the angle φ corresponds to an increase and a decrease of the light intensity $I(\omega)$ of the fundamental laser beam. The experimental data are fitted with eq 1.

The intensity $I(2\omega)$ of the second harmonic scattered light depends quadratically on the intensity of the fundamental $I(\omega)$. Variation of $I(\omega)$ obtained by rotating the half-wave plate (rotating angle φ, starting angle α) between the two crossed polarizers is given by

$$I(2\omega) = \alpha[\sin(2\varphi + \alpha)]^4 + b$$
$$\text{with} \quad a = G(N_g\beta_g^2 + N_l\beta_l^2)I(\omega)^2 \qquad (1)$$

where G is a geometrical factor and b an intensity offset. N_g (N_l) and β_g (β_l) represent the number density and the β value of the solute (solvent). Figure 3 shows typical HRS curves for different number densities of compound **3**. Measurements at different number densities of the solute show a linear dependence of the fit parameter a in eq 1 on N_g. This is pictured in Figure 4 for compound **3**. From the intercept c and the slope m, the hyperpolarizability of the chromophore can be calculated when that of the solvent is known or vice versa (*internal reference method*):

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

To obtain β_g, it is also possible 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*):

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

However, if the molecules investigated and the reference

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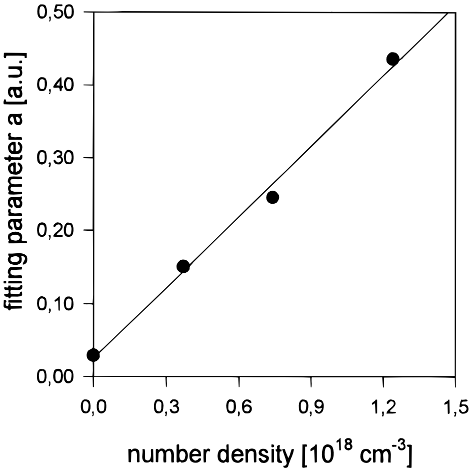

Figure 4. Plot of the parameter *a* as a function of the number density of **3** in chloroform. From the slope *m* the β value of **3** can be obtained with eq 3 and the corresponding β value of the external reference (PNA).

Table 1. β_{333} Values and Absorption Maxima of Compounds 1−5

compound	λ_{max} [nm]	β_{333} [10^{-50} C m^3 V^{-2}]^a
1	340	12
2	425	24
3	415	31
4	378	5
5	396	8

[a] Error limits approximately ±15%.

molecule belong to different symmetry groups, orientational factors are necessary which reflect how the different components of the hyperpolarizability tensor contribute to the detected HRS intensity.[12] Since the reference molecules normally are dipoles like *p*-nitroaniline with one dominating tensor component β_{333} whose values are taken from EFISH measurements, it is useful to present this component for the octupolar molecules too. For dipolar molecules $\langle\beta_{HRS}\rangle = \sqrt{6/35}\beta_{333}$, while for octupolar molecules $\langle\beta_{HRS}\rangle = \sqrt{8/21}\beta_{333}$.[12] Therefore the obtained β values of the octupoles (with a dipolar external reference) have to be divided by a factor of 1.49 to get the β_{333} values. All the compounds presented in this paper were measured in chloroform as solvent using the β_{333} value of 6.3×10^{-50} C m^3 V^{-2} for PNA in chloroform (which was determined via the internal reference method and is in good agreement with the literature[17]) as an external reference.

Results and Discussion

Figure 1 shows the investigated octupolar molecules, and Table 1 gives the absorption maxima along with the experimentally determined first hyperpolarizabilities β. The HRS measurements as well as the absorption measurements were carried out in chloroform as solvent. In a previous paper[13] we demonstrated by X-ray diffraction analysis and semiempirical calculations that sidewing octupoles of this kind are propeller-like molecules with C_3 symmetry (the twisting angles for the three sidewings are almost the same, between 31° and 35° for **1**) and sp^2 hybridization of the central nitrogen. The calculated dipole moment of **1** for instance is 0.13 D, that of **2** is 0.27 D (AM1 Hamiltonian of the program MNDO93 implemented on a Cary Y-MP 8/864 with the user interface UNICHEM running on a Silicon Graphics Iris W-4D25G).

Table 1 demonstrates that **2** and **3** exhibit much larger β values (which are relatively high for their short absorption wavelength) than **5**, whose sidewings are donor substituted. This is remarkable since the absorption maxima of **2**−**5** are quite similar and **5** enlarged by one phenylene unit in every sidewing compared to **2** and **3**. On the other hand, one can see from a comparison between **1** and **4** that the replacement of the electron-withdrawing cyano group by the electron releasing 2-aza-(1′-aza-2′-ethylcyclopentyl)vinyl group leads to a reduction of the first hyperpolarizability by a factor of >2 despite the increased conjugation. The latter red shifts the absorption maximum 40 nm compared to **1**. Since the central nitrogen serves as an electron donor, the implementation of an additional donor group in the sidewing leads to a charge compensation in every branch of the molecule and therefore a drop in the hyperpolarizability.

This seems to be an indication that the transparency-nonlinearity tradeoff (whose theoretical justification is based on the two-level model[18] for dipoles and the three-level model[11] for octupoles) is somewhat different if octupolar instead of dipolar molecules are investigated. For the latter one would expect a simultaneous drop in the hyperpolarizability and the absorption maximum when changing from a Do−π-Acc system to a Do−π-Do system.

As can be seen from Figure 1 compound **4** is a chiral molecule with one chiral carbon atom in every sidewing (marked by a star). Therefore it should crystallize in a noncentrosymmetric lattice. Since octupolar molecules cannot be implemented in guest−host systems due to their lack of a permanent dipole moment, preparation of noncentrosymmetric crystals is the only way to achieve macroscopic systems that may be suitable for $\chi^{(2)}$ devices. Other novel techniques for octupolar orientation based on laser interference have been proposed[19] but may not be easily implemented. Because of the small β value, we abstained from preparing crystals so that we are not able to present results of X-ray diffraction analysis. We plan, however, to synthesize other chiral octupoles with acceptor-substituted sidewings which should exhibit high β values.[20]

Summary and Conclusion

We have presented some new octupolar molecules consisting of a nitrogen as the center atom and “sidewings” made up of phenyl, diazabiphenyl, and diazaterphenyl units which are either acceptor or donor substituted. The first molecular hyperpolarizabilities β of the octupolar molecules have been measured via hyper-Rayleigh scattering at 1064 nm. The β values of the octupoles with acceptor-substituted sidewings are considerably large in respect to their relatively short absorption wavelengths. Donor substitution of the sidewings results in a drop in the first hyperpolarizability β even for molecules with a larger π-electron system and therefore red-shifted absorption maxima. Since octupolar molecules cannot be oriented in the electric field, macroscopic devices on the basis of guest−

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host systems are not available. The only way to get macroscopic noncentrosymmetric structures from octupoles is the growing of crystals without a center of symmetry. Since chiral molecules crystallize in a noncentrosymmetric lattice, we also synthesized and investigated a chiral sidewing octupole. Due to the relatively small hyperpolarizability, we did not prepare crystals for X-ray diffraction analysis. It is planned, however, to synthesize more chiral octupolar molecules with higher β values in the near future.

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