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Investigations of the Hyperpolarizability in Organic Molecules from Dipolar to Octopolar Systems

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Abstract: In this paper we report the first systematic nonlinear optical study of molecules with octopolar charge distribution. First hyperpolarizabilities were determined by the Hyper-Rayleigh Scattering technique and depolarization of the harmonic scattered light was measured and linked to the symmetry of the scatterers. It is shown experimentally that octopolar molecules have nonlinear optical properties that compare favorably to those of their dipolar counterparts. The hyperpolarizability of octopolar molecules is shown to be solvent independent, in contrast to the hyperpolarizability of dipolar systems.

Introduction

The classical molecular requirements for second-order nonlinear optical (NLO) effects have led to the development of strongly elongated and conjugated molecules, asymmetrized by interacting donor and acceptor groups. Such compounds are (highly) anisotropic dipolar structures like *p*-nitroaniline derivatives, substituted stilbenes, and push-pull polyenes. Although they often exhibit extremely large hyperpolarizabilities, some major drawbacks are associated with their dipolar character, e.g. a high tendency toward unfavorable aggregation, difficult non-centrosymmetric crystallization, and small off-diagonal tensor components.

Recently, it was recognized that octopolar molecules can circumvent the aforementioned disadvantages, since these nonpolar molecules combine excellent (second-order) NLO characteristics with a strict cancellation of all vectorial properties.¹ Hence, it seems worthwhile to start the search for new octopolar molecules and materials where the drawbacks of dipolar materials are absent. Since they cannot be oriented in an electric field, the hyperpolarizability cannot be measured by the traditional electric field induced second-harmonic generation (EFISHG) method.² As a consequence, octopolar molecules have not yet been thoroughly investigated experimentally. However, with the recently developed Hyper-Rayleigh Scattering (HRS) technique, the hyperpolarizability of nonpolar compounds is accessible.^{3,4}

In this paper we report the first systematic study of the second-order NLO properties of a series of octopolar molecules with the HRS technique. Hyperpolarizabilities and absorption characteristics of octopoles are compared with those of their dipolar counterparts and the influence of solvent on the octopolar hyperpolarizability is discussed.

Theoretical Treatment

In order to discuss the properties of octopolar molecules, some knowledge about the irreducible components of tensors and the concept of multipolar groups is required. These issues were

already extensively discussed by Jerphagnon and Zyss and we will only give a brief overview of these concepts.⁵⁻⁷

Any tensor $T(n)$ of rank n can be decomposed in a sum of irreducible tensorial components that subtend a weight- J irreducible representation of the three-dimensional rotation group SO_3 and can be written as:

$$T(n) = \sum_{\gamma, J} T_{(n)}^{(\gamma, J)} \quad (1)$$

where the superscript γ distinguishes between linearly dependent components of rank J . This equation is called the reduction spectrum of the tensor $T(n)$. In the special case of a fully symmetric tensor the reduction spectrum involves only one irreducible tensor of weight J if $n + J$ is even, and none otherwise. This means that the hyperpolarizability β , which is a fully symmetric third-rank tensor under Kleinmann symmetry,⁸ will only have two irreducible components of weight $J = 1$ (vector or dipolar part) and weight $J = 3$ (septor or octopolar part). Each irreducible component has $2J + 1$ independent coefficients.

Recently, Zyss has shown that for molecules belonging to a multipolar symmetry group of order J , all irreducible tensorial components of order strictly lower than J cancel due to symmetry requirements.⁷ The multipolar order of a group can be readily obtained from a simple manipulation of the character table of the symmetry group. Since octopolar molecules belong to an octopolar space group ($J = 3$), all dipolar quantities ($J = 1$) vanish, and only octopolar β -contributions remain. Purely octopolar groups are for example the orthorhombic D_2 , the hexagonal D_{3h} , and the cubic T symmetry groups.

Since molecules belonging to octopolar groups have a zero dipole moment, their first hyperpolarizability cannot be determined with the EFISHG technique, since this technique relies upon the orientation of the molecules in an electric field. However, the recently developed Hyper-Rayleigh Scattering (HRS) technique provides a sensitive tool for the determination of β of nonpolar molecules in solution.

When an isotropic sample is illuminated by intense laser pulses of intensity $I(\omega)$, the incoherent second-harmonic scattered light $I(2\omega)$ is called HRS. On a molecular scale HRS depends on the

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hyperpolarizability tensor β in the expansion of the dipole moment induced in a molecule by an electric field:

$$\mu_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k \quad (2)$$

E_j is the electric field in direction j and α_{ij} and β_{ijk} are the first and the second polarizability (or first hyperpolarizability), respectively (the usual summation convention applies). The strict requirement of non-centrosymmetry for second-order nonlinear optical processes is obvious from this equation since for molecules with inversion symmetry all components of β do vanish identically. On a macroscopic scale, the induced dipole moment per unit volume at frequency 2ω is given by:

$$P_i(2\omega) = B_{ijk}E_j(\omega)E_k(\omega) \quad (3)$$

B_{ijk} being the nonlinear susceptibility tensor. In HRS the necessary non-centrosymmetry on the macroscopic scale arises from fluctuations in molecular orientation.^{9,10}

If the incident light travels in the x -direction with polarization in the z -direction and the scattered light is observed in the y -direction, the intensity of the HRS signal is given by (assuming that the values of B_{ijk} at two different points are correlated only over distances small compared to a wavelength):¹¹

$$I_j(2\omega) = g\langle B_{jzz}^2 \rangle I^2(\omega) \quad (4)$$

$I_j(2\omega)$ is the intensity of the light at 2ω polarized in the j direction and $\langle \rangle$ indicates orientational averaging. The factor g takes into account scattering geometry and instrumental factors. In the case of absorption of the light scattered at 2ω by the nonlinear optical molecules, a correction term has to be included:

$$I_j(2\omega) = g\langle B_{jzz}^2 \rangle I^2(\omega) \times 10^{-\epsilon(2\omega)Nl} \quad (5)$$

$\epsilon(2\omega)$ is the absorption cross section (in cm^2) at the harmonic frequency, N is the number density (in cm^{-3}) of the absorbing molecules, and l (in cm) is an effective optical path length.

For two-component systems, e.g. solute molecules in a solvent, and in the case of randomly oriented individual molecules, the averaged nonlinear susceptibility $\langle B_{jzz}^2 \rangle$ is given as:

$$\langle B_{jzz}^2 \rangle = F_\omega^4 F_{2\omega}^2 [N_S \langle \beta_{jzz}^2 \rangle_S + N_s \langle \beta_{jzz}^2 \rangle_s] \quad (6)$$

F are local field factors at optical frequencies, and S and s represent solvent and solute, respectively. At low solute concentration N_S can be taken as constant and $I_{2\omega}$ will depend linearly upon N_s . From the intercept and the slope of a plot of $I(2\omega)/I^2(\omega)$ vs N_s , $\langle \beta_{jzz}^2 \rangle_s$ can be calculated provided $\langle \beta_{jzz}^2 \rangle_S$ is known, or vice versa. This approach (the Internal Reference Method, IRM) effectively eliminates the need for the knowledge (or estimation) of local field factors since these factors are divided out by measuring in nearly the same local field (as far as the number density of the solute molecule does not significantly change the refractive index of the solution). Alternatively—and in the case of a centrosymmetric solvent—we can use an external reference, i.e. comparing two slopes of different plots with each other and taking one of them as a reference.

The relation between β_{jzz} in laboratory coordinates and β_{uvw} (u, v , and w are numbers) in molecular coordinates has been

thoroughly described elsewhere.¹¹ For a scatterer with D_{3h} symmetry, with nonzero β -components $\beta_{333} = -\beta_{311} = -\beta_{131} = -\beta_{113}$, this relation is given by:

$$\begin{aligned} \langle \beta_{zzz}^2 \rangle &= \frac{24}{105} \beta_{333}^2 \\ \langle \beta_{xxx}^2 \rangle &= \frac{16}{105} \beta_{333}^2 \end{aligned} \quad (7)$$

and the depolarization ratio $\langle I_z(2\omega) \rangle / \langle I_x(2\omega) \rangle$ is 1.5.

For scatterers with C_{2v} symmetry and assuming only one dominant β -component, these relations are given by:

$$\begin{aligned} \langle \beta_{zzz}^2 \rangle &= \frac{15}{105} \beta_{333}^2 \\ \langle \beta_{xxx}^2 \rangle &= \frac{3}{105} \beta_{333}^2 \end{aligned} \quad (8)$$

with a depolarization ratio of 5.

Experimental Section

HRS signals, i.e. the intensity of light scattered at the double frequency, were measured with an injection-seeded Nd:YAG laser (Q-switched Nd:YAG Quanta Ray GCR3, 1064 nm, 8 ns pulses, 10 pps) focused into a small cell (3.5 mL) containing the sample. The intensity of the incident beam is varied by using a system of a rotating half-wave plate and polarizers. Part of the laser pulse is sampled by a photodiode to measure the incident light intensity that is vertically or circularly polarized. The HRS light is collected with an efficient condenser system under 90° and detected with a photomultiplier. The scattering at twice the fundamental frequency was discriminated from linear scattering by appropriate filters. Gated integrators were used to retrieve actual values for the intensities of the incident and second-order scattered light pulses. Details of the experimental setup have been given elsewhere.¹² Depolarization measurements were performed without the condenser, using a numerical aperture of 0.1 and a rotating polarizer before the photomultiplier. The incident light was always vertically polarized. For the measurements at a wavelength of 872 nm we used the first Stokes of a Raman shifter (filled with H_2 gas) which was pumped with a dye laser.

Results

An octopolar molecule recently studied by the powder method is triaminotrinitrobenzene (TATB).¹³ Since this molecule is insoluble in organic solvents, we used a slightly modified version of this molecule (triisopropylaminotrinitrobenzene, TIATB) to investigate octopolar β -contributions (Figure 1). In all our measurements, the theoretically expected quadratic dependence of the HRS signal on the incident intensity was always observed. First of all we carried out depolarization measurements to determine the molecular symmetry. The intensity of the HRS signal was recorded as a function of its polarization state for vertically polarized incident light. If TIATB has D_{3h} symmetry, we would expect a depolarization ratio of 1.5. The experimental value of 1.5 ± 0.1 is in full agreement with the value expected from theory, indicating the molecule having at least near D_{3h} symmetry. In this case, the molecule has four nonzero β -components, i.e. $\beta_{333} = -\beta_{311} = -\beta_{131} = -\beta_{113}$. The concentration dependence of the HRS signal is shown in Figure 2, and using the solvent as an internal reference,³ we calculated β_{333} in chloroform and nitromethane. The experimentally measured

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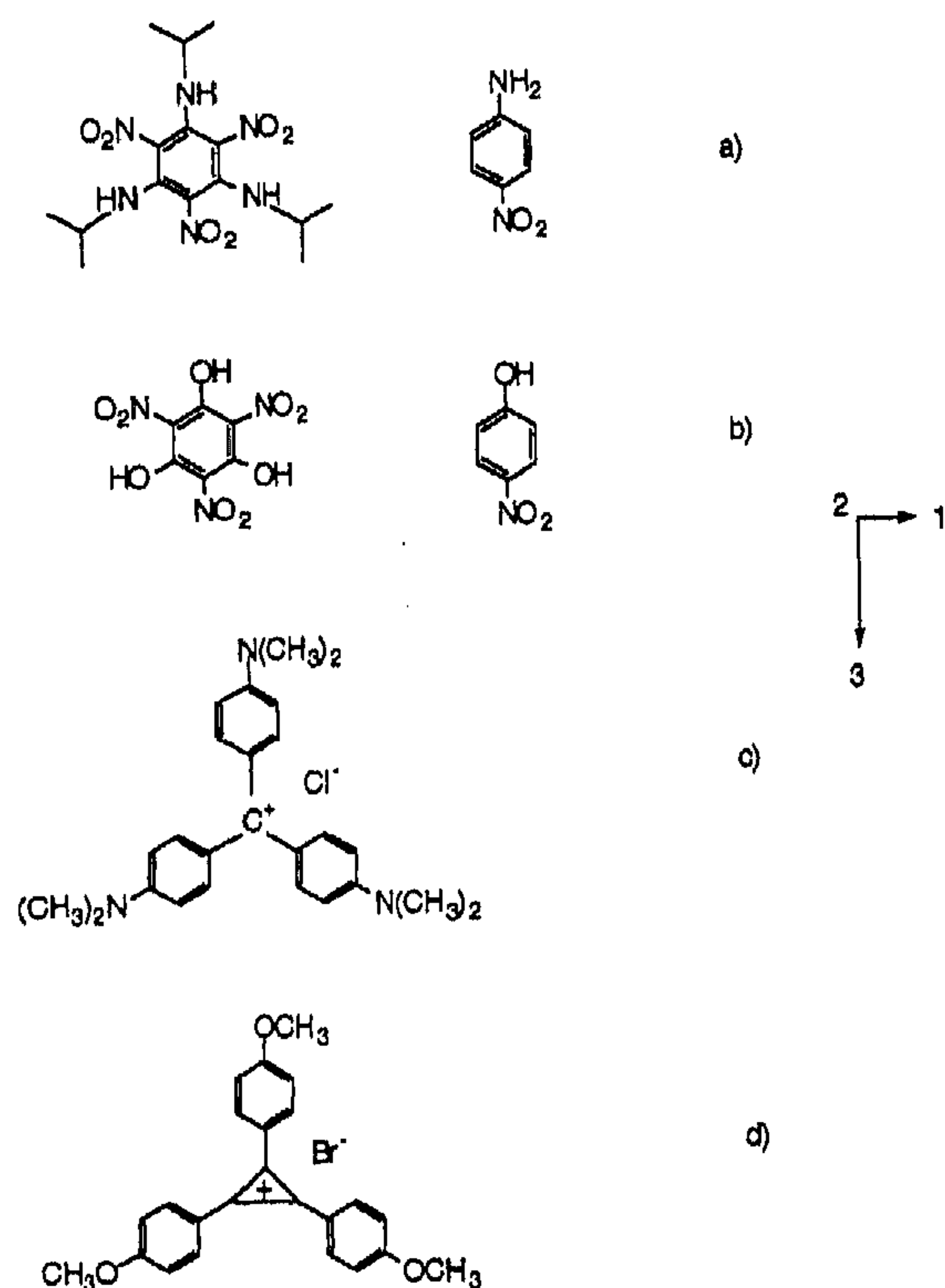


Figure 1. Triisopropylaminotrinitrobenzene with its dipolar counterpart *p*-nitroaniline (a), trihydroxytrinitrobenzene with its corresponding dipole *p*-nitrophenol (b), crystal violet (c), and tris(4-methoxyphenyl)cyclopropenyl bromide (d).

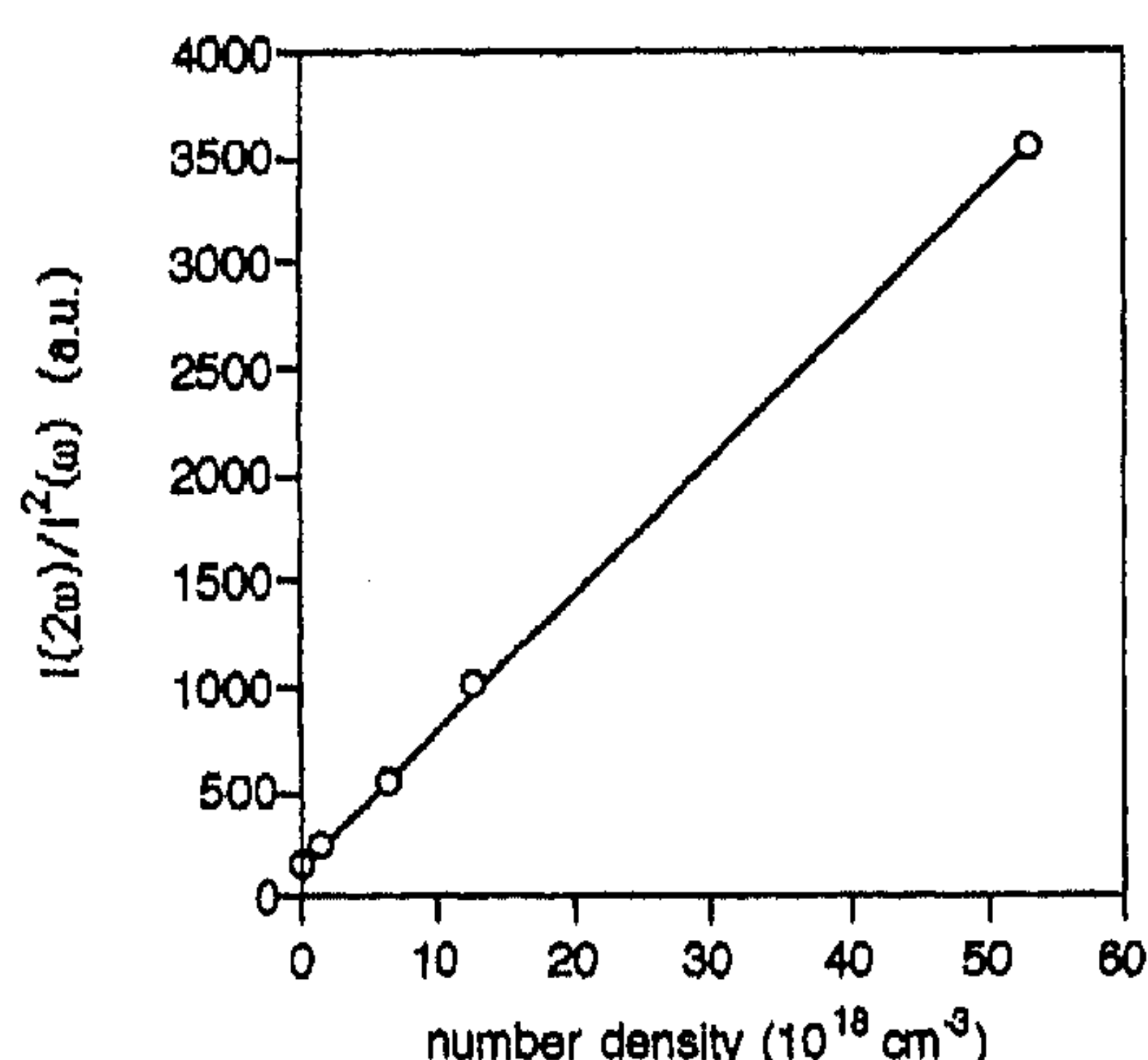


Figure 2. Quadratic coefficient $I(2\omega)/I^2(\omega)$ vs N , the number density of TIATB in chloroform at 293 K.

linear concentration dependence, as expected from a system of independent scatterers, indicates that no orientation correlations exist between neighboring molecules. The experimental values are listed in Table 1 together with the wavelength of maximum absorption (λ_{\max}) and the dielectric constant (ϵ) of the solvents. The corresponding parameters for the dipolar counterpart are listed in the second part of the table.

We also studied the related trihydroxytrinitrobenzene (THTB, Figure 1) in acetone and methanol. Trihydroxytrinitrobenzene is a planar molecule with D_{3h} symmetry, as confirmed by the experimentally determined depolarization ratio of 1.5 ± 0.1 . All experimental values (hyperpolarizability and wavelength of maximum absorption) are listed in Table 1, together with the results for the dipolar counterpart nitrophenol.

Another important group of octopolar molecules is the so-called "central-atom analogues", with crystal violet (CV) as an

Table 1. Hyperpolarizabilities (in 10^{-30} esu), Dielectric Constants of Solvents, and Wavelength of Maximum Absorption (in nm) for TIATB, THTN, pNA, and NP

	β_{333}	λ_{\max}		β_{333}	λ_{\max}
TIATB			PNA		
chloroform ($\epsilon = 4.8$)	16 ± 4	375	<i>p</i> -dioxane ($\epsilon = 2.2$)	16.9^a	354
nitromethane ($\epsilon = 37.45$)	19 ± 5	383	chloroform ($\epsilon = 4.8$)	23.0^a	349
			nitromethane ($\epsilon = 37.45$)	34.6 ± 7	370
THTN			NP		
acetone ($\epsilon = 30.7$)	27 ± 6	395	nitromethanol ($\epsilon = 35.7$)	25 ± 4	313
methanol ($\epsilon = 32.6$)	25 ± 6	385			

^a EFISHG values, see for example, ref 3.

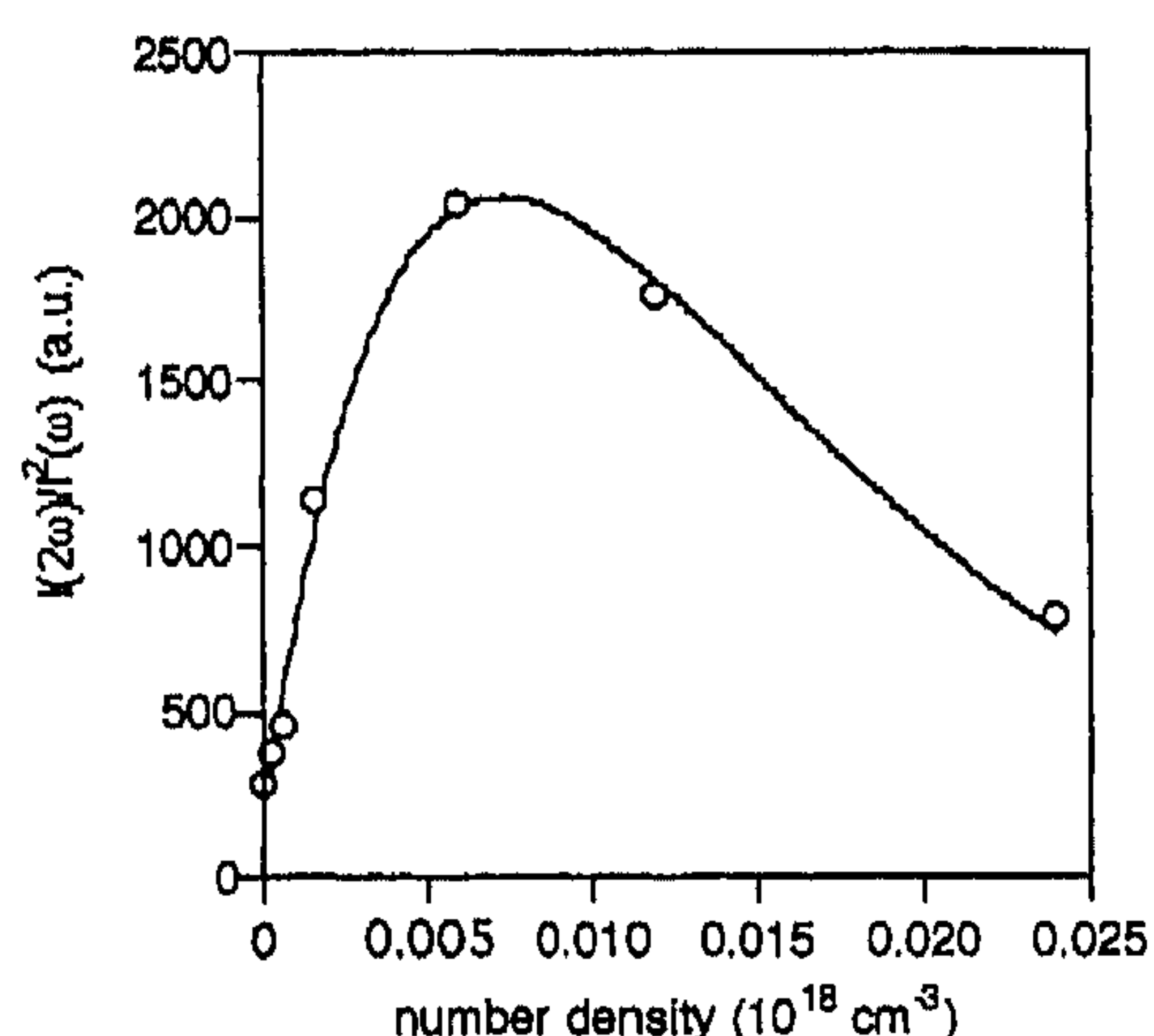


Figure 3. Quadratic coefficient $I(2\omega)/I^2(\omega)$ vs N , the number density of crystal violet in methanol at 293 K.

Table 2. Hyperpolarizabilities (in 10^{-30} esu) for Excitation at 872 and 1064 nm, Dielectric Constants of Solvents, and Wavelength of Maximum Absorption (in nm) of Crystal Violet

	β_{333}	$\ \beta\ $	λ_{\max}	solvent (ϵ)
872 nm	433 ± 130	866 ± 260	588	methanol (32.6)
1064 nm	3060 ± 750	6120 ± 1500	588	methanol (32.6)

example (Figure 1). Depolarization measurements on CV indicate C_3 symmetry, and this is confirmed by other studies.¹⁶ Analogous to D_{3h} scatterers, CV has only four nonzero β -components, i.e. $\beta_{333} = -\beta_{311} = -\beta_{131} = -\beta_{113}$. No linear concentration dependence was observed for crystal violet in methanol since absorption of the HRS light occurs and eq 5 has to be used to calculate the hyperpolarizability. From the appearance of this equation, it is clear the HRS signal as a function of number density of the solute will display a maximum. This was experimentally confirmed as shown in Figure 3, and the data analysis results in the experimental value of the first hyperpolarizability. We also determined β_{333} at a wavelength of 872 nm. In this case the 436 nm HRS signal is right in the absorption window of the spectrum and much less absorption of the HRS light occurred. The hyperpolarizabilities and maximum absorption wavelength are listed in Table 2.

Another cation we studied is a cyclopropenyl cation derivative (Figure 1). Depolarization ratios also indicate C_3 symmetry. It differs from crystal violet in the sense that the positive charge is localized in the aromatic ring. The hyperpolarizability component β_{333} in methanol was found to be $(90 \pm 20) \times 10^{-30}$ esu, and the maximum absorption wavelength is 359 nm.

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Discussion

For TIATB we can conclude from Table 1 that there exists no significant solvent dependence of the hyperpolarizability in the case of TIATB, in contrast to its dipolar counterpart pNA (*p*-nitroaniline). pNA has C_{2v} symmetry and only one dominant β -component, i.e. β_{333} .¹⁵ When going from a nonpolar solvent (low ϵ) to a polar one (high ϵ) the hyperpolarizability of TIATB does not significantly change, while the β of pNA changes drastically. This solvent independence of the octopolar β is attributed to the absence of a dipole moment in the ground state as well as in the excited states for octopolar molecules, reducing the dielectric interactions with the molecular environment. It is very difficult to compare β_{333} of TIATB with β_{333} of pNA because of the large solvent dependence of this last parameter. Nevertheless, it seems reasonable to choose β_{333} of pNA in *p*-dioxane for comparison, since in this case no strong dipolar interactions occur between solvent and solute. In this case $\beta_{333}(\text{TIATB}) \approx \beta_{333}(\text{PNA})$ and since pNA has only one significant β -component, this means that the modulus of the β -tensor (the square root of the sum of the squares of all tensor components) of TIATB is approximately twice that of PNA, i.e. $\|\beta\|(\text{TIATB}) \approx 2\|\beta\|(\text{PNA})$. Note that the wavelengths of maximum absorption of both materials are comparable. The increased value of the β -modulus as compared to that of the corresponding dipolar molecules was already discussed by Zyss,⁷ and the ratio between both moduli is given by:

$$\frac{\|\beta_{\text{octopole}}\|}{\|\beta_{\text{dipole}}\|} = \frac{2\beta_{333}^{\text{octopole}}}{[(\beta_{333}^{\text{dipole}})^2 + 3(\beta_{311}^{\text{dipole}})^2]^{1/2}} \quad (9)$$

If we assume that the dipolar molecules in our investigation have only one β -component (β_{333}) and if the charge transfer pathways are the same in both dipole and octopole, the ratio of the moduli is 2. This is what we find experimentally, and the same result was also obtained from quantum mechanical calculations on TATB.¹⁶

The same conclusions can be drawn for THTB. From Table 1 we observe no significant solvent dependence of the hyperpo-

larizability of THTB, and this confirms our findings for the TIATB molecule. Note that also in this case, β_{333} of THTB is equal to the β_{333} component of the corresponding dipolar molecule nitrophenol (NP). Of course, due to the large solvent dependence of the hyperpolarizability of dipolar molecules, one has to be careful when comparing hyperpolarizabilities of octopolar and dipolar materials.

The unusually high β -value of CV is probably due to strong resonance enhancement. That is why we also determined β_{333} at a wavelength of 872 nm. In this case the 436 nm HRS signal is right in the absorption window of the spectrum. The much smaller β -value obtained at this wavelength, which is still comparable with β -values of absorbing dipolar molecules, is consistent with the large resonance enhancement expected at 1064 nm since 532 nm is almost the absorption maximum.

The experimentally determined hyperpolarizability of the cyclopropenylum derivative in methanol of $(90 \pm 20) \times 10^{-30}$ esu is also extremely high, especially when taking into account the transparency of the molecule in the visible part of the spectrum. This unique combination of transparency and high NLO properties can be of great importance for future NLO applications.

Conclusion

We have shown that octopolar molecules have NLO properties that are comparable with those of dipolar molecules. An important advantage is the improved efficiency/transparency trade-off, due to the higher off-diagonal β -components without a shift in absorption wavelength. We have also shown that the hyperpolarizability of octopolar molecules is solvent independent. An additional advantage of octopolar molecules is the absence of a dipole moment, since (centrosymmetric) dipolar aggregation is avoided. However, since these molecules cannot be oriented in an electric field, new ordering methods have to be sought to align these molecules in a proper medium. Because of all these important advantages, we believe that octopolar systems can play an important role in the development of new (macroscopic) NLO materials.