Second-Order Nonlinear Optical Properties of the Four Tetranitrotetrapropoxycalix[4]arene Conformers

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Abstract: This paper reports a systematic experimental and theoretical study of the second-order nonlinear optical properties of multichromophoric molecules that range from *dipolar* symmetry to *three-dimensional octupolar* symmetry. The four possible conformers of tetranitrotetrapropoxycalix[4]arene (*cone*, *paco*, *1,2-alt*, *1,3-alt*) were studied by nanosecond hyper-Rayleigh scattering and a newly developed time-resolved femtosecond hyper-Rayleigh scattering technique. The latter enables to correct for long-lived fluorescence contributions to the second harmonic scattering intensity. The depolarization ratios $D_{x/z}$ prove the (partial) *octupolar* symmetry of the *1,2-alt* and *1,3-alt* conformers, and thus explain why their hyperpolarizabilities β_{FHRS} are of the same order of magnitude as those of the *dipolar cone* and *paco* conformers. The corresponding theoretical second-order nonlinear optical properties (both β_{FHRS} and $D_{x/z}$) were calculated using the conformations obtained from single-crystal X-ray diffraction, molecular mechanics (MM), and molecular dynamics (MD) calculations. In contrast with sum-over-state calculations presented in the literature, our theoretical method takes also into account octupolar contributions by linearly adding the NLO-properties of the separate chromophoric groups and using Bersohn's theory. The agreement between experimental and theoretical results is good both for the conformers having dipolar symmetry and for the conformers having (partly) three-dimensional octupolar symmetry. The *1,2-alt* and *1,3-alt* conformers of the tetranitrotetrapropoxycalix-[4]arene represent the first examples of multichromophoric molecules that have high hyperpolarizabilities β due to 3D octupolar symmetry.

Introduction

Organic molecules with second-order nonlinear optical (NLO) properties have various potential in the development of materials for applications, e.g., in frequency doubling and optical switching.[1] Molecules with high second-order NLO activities are related with high asymmetric polarizability, expressed in the hyperpolarizability β, which is a third-rank tensor consisting of 27 components. Typical examples of organic NLO-active molecules are *p*-nitroaniline, PNA (**1**), and dimethylaminonitrostilbene, DANS (**2**), as depicted in Scheme 1. In these molecules an electron-donating group (D) is connected to an electron-accepting group (A) *via* a π-conjugated system. These so-called D-π-A units meet thereby the requirement of asymmetric polarizability. The combination of several D-π-A units within one single molecule has the advantages that a high dipole moment is combined with a high hyperpolarizability β if the D-π-A units are organized in a *dipolar* configuration. Moreover, the possibility to enlarge β without the usually observed and undesired red shift of the charge transfer band[2] makes such

Scheme 1
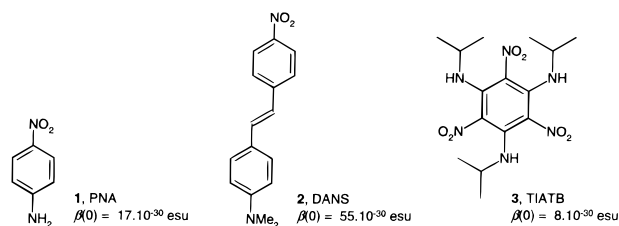
dipolar *multichromophoric systems* potentially suitable as materials for frequency doubling.[3,4] The triphenylcarbinol derivatives **4**,[5] the calix[4]arene derivatives **5**[6] (*cone* conformation, *vide infra*), and the bis-dipolar 6,6′-disubstituted binaphthol derivatives **6**,[7,8] as depicted in Scheme 2, are typical examples of such multichromophoric dipolar molecules.

The combination of several D-π-A units that are *not* perfectly aligned in a single molecule leads to more nonzero tensor

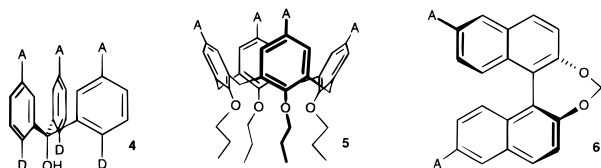[⊥] Laboratory of Supramolecular Chemistry and Technology.
[§] Applied Optics Group.
[‡] Laboratory of Chemical and Biological Dynamics.
[#] Laboratory of Chemical Physics.

(1) (a) Zyss, J.; Chemla, D. S. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: Orlando, 1987; Vol. 1. (b) Prasad, P.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*', John Wiley & Sons: New York, 1991.

(2) Zyss, J.; Ledoux, I.; Bertault, M.; Toupet, E. *Chem. Phys.* **1991**, *150*, 125.

(3) See, for example: (a) Wolf, J. J.; Längle, D.; Hillenbrand, D.; Wortman, R.; Matschiner, R.; Glania, C.; Krämer, P. *Adv. Mater.* **1997**, *9*, 138−143. (b) Verbiest, T.; Clays, K.; Samyn, C.; Wolff, J. J.; Reinhoudt, D. N.; Persoons, A. *J. Am. Chem. Soc.* **1994**, *116*, 9320. (c) Stadler, S.; Feiner, F.; Bräuchle, C.; Brandl, S.; Gompper, R. *Chem. Phys. Lett.* **1995**, *245*, 292.

(4) Kelderman, E.; Derhaeg, L.; Heesink, G. J. T.; Verboom, W.; Engbersen, J. F. J.; Van Hulst, N. F.; Clays, K.; Persoons, A.; Reinhoudt, D. N. *Adv. Mater.* **1993**, *5*, 925.

Scheme 2

components than only the β_{333} and β_{311} which dominate the β tensor in simple planar dipolar systems like PNA (Scheme 1). For most of the multichromophoric systems the contribution of the individual D-π-A units to the overall β tensor has not been analyzed in the literature. However, if such a multichromophoric system still has a considerable dipolar character, the different contributions to the overall β tensor can be obtained by analysis of the results of both electric-field-induced second-harmonic generation (EFISH) and hyper-Rayleigh scattering (HRS) because these techniques assess different combinations of the first hyperpolarizability tensor. This was shown previously by Deussen *et al.*[7] and Hendrickx *et al.*[8] in their investigation of the nonlinear optical properties of the bis-dipolar 6,6′-disubstituted binaphthol derivatives **6** (Scheme 2).

Upon reducing the dipolar arrangement of D-π-A units in such multichromophoric system, the *dipolar* component of the β tensor will decrease, eventually to zero. However, Zyss *et al.*[9,10] have shown that the third rank β tensor contains also an *octupolar* component, which starts to play an important role in *nondipolar* multichromophoric systems. Based on the mathematical properties of tensors they deduced that the hyperpolarizability β, which is a fully symmetric third-rank tensor under Kleinmann symmetry,[11] will have two irreducible components: a dipolar part of weight $J = 1$ and an octupolar part ($J = 3$, eq 1), each having $2J + 1$ independent coefficients.[10]

$$\beta = \beta_{J=1} + \beta_{J=3} \tag{1}$$

Due to the octupolar contribution, high hyperpolarizabilities β can also be obtained for nondipolar multichromophoric systems. Zyss[9b] has also shown that for molecules strictly belonging to a multipolar symmetry group of weight J, all irreducible tensorial components of weight lower than J cancel due to symmetry requirements. Thus, for molecules with octupolar symmetry ($J = 3$) all dipolar ($J = 1$) contributions vanish. The main difference between the equivalent dipolar system and these octupolar systems lies in the strongly different off-diagonal β_{311} values, while the diagonal β_{333} values are comparable. A typical example, triisopropylaminotrinitrobenzene (**3**, TIATB), is depicted in Scheme 1. A difficulty of studying nondipolar molecules is the lack of a dipole moment, thereby excluding the possibility of the use of the EFISH technique. Until now, mainly the nonlinear optical properties of molecules with highly dipolar or two-dimensional (planar) octupolar symmetry have been studied. Here we present a systematic investigation on

Scheme 3

certain conformers of calix[4]arenes, molecules containing three-dimensional octupolar symmetry.[11,12]

The calix[4]arene[13] cyclophanes consist of four phenol moieties connected by methylene bridges.[14] The calix[4]arene structure can adopt four extreme conformations: the *cone*, the *partial cone*, the *1,2-alternate*, and the *1,3-alternate* (Scheme 3).[15] Upon alkylation of the phenolic hydroxyl groups with four propyl groups, interconversion between these conformations is blocked resulting in four different *conformers*.[16] By subsequent introduction of four nitro groups at the para position of the phenoxy groups, four D-π-A units are combined within each calix[4]arene (Scheme 3).[4,6]

The relative orientation of the four D-π-A units in the four conformers is highly different, and the character of the conformers varies from strongly dipolar for the *cone* and partial cone (*paco*) conformers to an essentially nondipolar symmetry for the *1,2-alt*(ernate) and *1,3-alt*(ernate) conformers (Scheme 3). The *1,2-alt* and the *1,3-alt* conformers represent examples of *three-dimensional* nondipolar NLO molecules, in which the dipolar vectors of the four chromophoric units are oppositely oriented. Whereas the dipolar contribution will be significantly lower than those of the *cone* and *paco* conformers, the *1,2-alt* and *1,3-alt* conformers may exhibit interesting higher order (octupolar) contributions to the hyperpolarizability of these molecules.

In this paper we describe a systematic study of the nonlinear optical properties of molecules which range from a dipolar symmetry to a (partly) three-dimensional octupolar symmetry.

(5) Kelderman, E.; Starmans, W. A. J.; Van Duynhoven, J. P. M.; Verboom, W.; Engbersen, J. F. J.; Reinhoudt, D. N. *Chem. Mater.* **1994**, *6*, 412−417.

(6) Kelderman, E.; Heesink, G. J. T.; Derhaeg, L.; Verbiest, T.; Klaase, P. T. A.; Verboom, W.; Engbersen, J. F. J.; Van Hulst, N. F.; Persoons, A.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1074.
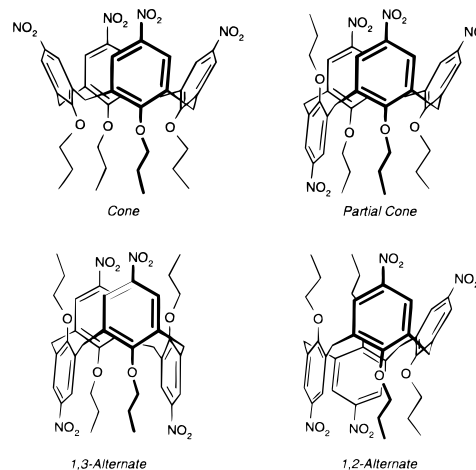
(7) Deussen, H.-J.; Hendrickx, E.; Boutton, C.; Krog, D.; Clays, K.; Bechgaard, K.; Persoons, A.; Bjornholm, T. *J. Am. Chem. Soc.* **1996**, *118*, 6841−6852.

(8) Hendrickx, E.; Boutton, C.; Clays, K.; Persoons, A.; Van Es, S.; Biemans, T.; Meijer, B. *Chem. Phys. Lett.* **1997**, *270*, 241−244.

(9) (a) Ledoux, I.; Zyss, J.; Siegel, J. S.; Brienne, J.; Lehn, J.-M. *Chem. Phys. Lett.* **1990**, *172*, 440−444. (b) Zyss, J. *J. Phys. Chem.* **1993**, *99*, 6583−6599.

(10) Zyss, J. *Nonlinear Opt.* **1991**, *1*, 1.

(11) Kleinman, D. A. *Phys. Rev.* **1962**, *126*, 1977.

(12) Recently, indications for three-dimensional octupolar symmetry in bacteriorhodopsin trimers have been reported: Hendrickx, E.; Vinckier, A.; Clays, K.; Persoons, A. *J. Phys. Chem.* **1996**, *100*, 19672−80.

(13) The official IUPAC name for the unsubstituted [1.1.1.1]metacyclophane without the hydroxyl groups: pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene.

(14) (a) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713−745. (b) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, 1989. (c) *Calixarenes. A Versatile Class of Macrocylcic Compounds*; Vicens, J., Böhmer, V., Eds.; Kluwer Academic Publishers: Dordrecht, 1991. (d) Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713−1734. (e) Pochini, A.; Ungaro, R In *Comprehensive Supramolecular Chemistry*; Vögtle, F.; Ed.; Pergamon Press: Oxford, 1996; Vol. 2, pp 103−144.

(15) (a) Van Loon, J.-D.; Arduini, A.; Coppi, L.; Verboom, W.; Pochini, A.; Ungaro, R.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem.* **1990**, *55*, 5639. (b) Groenen, L. C.; Van Loon, J.-D.; Verboom, W.; Harkema, S.; Casnati, A.; Ungaro, R.; Pochini, A.; Ugozzoli, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 2385. (c) Groenen, L. C.; Ruël, B. H. M.; Casnati, A.; Timmerman, P.; Verboom, W.; Harkema, S.; Pochini, A.; Ungaro, R.; Reinhoudt, D. N. *Tetrahedron Lett.* **1991**, *32*, 2675.

(16) Iwamoto, K.; Araki, K.; Shinkai, S. *J. Org. Chem.* **1991**, *56*, 4955−4962.

Scheme 4
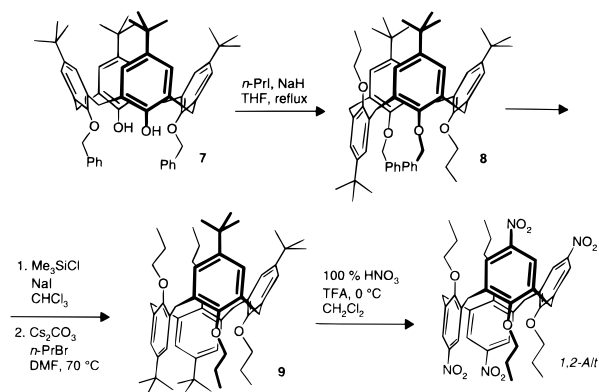
For that purpose the four possible conformers of tetranitrotetra-propoxycalix[4]arene were studied by nanosecond and time-resolved femtosecond hyper-Rayleigh scattering, NHRS and FHRS respectively, as described in the first part of this paper. In the second part of this paper the corresponding theoretical second-order nonlinear optical properties are calculated starting from conformations obtained from single-crystal X-ray diffraction, molecular mechanics (MM), and molecular dynamics (MD) calculations. In the third part the excellent agreement between experimental and theoretical results for molecules that range from dipolar to octupolar symmetries will be shown. This demonstrates the power of time-resolved femtosecond hyper-Rayleigh scattering measurements combined with calculations based on X-ray, MM, or MD structures in the full interpretation of the nonlinear optical properties of multichromophoric molecules of different symmetries in general.

Results and Discussion

Synthesis. The synthesis of the four different conformers of tetranitrotetrapropoxycalix[4]arene (Scheme 3) proceeds via alkylation of tetra-*tert*-butylcalix[4]arenes, using different reaction conditions for the respective conformers. Kelderman *et al.*[6,17] have already reported the selective preparation of three of the four different tetra-*tert*-butyltetrapropoxycalix[4]arene conformers, the *cone*, *paco*, and *1,3-alt*. They showed that consecutive *ipso*-nitration afforded the three corresponding tetranitrotetrapropoxycalix[4]arene conformers.[6,18]

The *1,2-alternate* conformer of tetra-*tert*-butyltetrapropoxycalix-[4]arene could be obtained via a stepwise route as described by Shinkai *et al.*[19,20] (Scheme 4). When the alkylation of tetra-*tert*-butyl-1,3-dibenzylcalix[4]arene **7** was performed in a mixture of DMF and THF, according to Shinkai *et al.*, less than 15% of the desired *paco* conformer **8** was obtained. However, the yield of **8** could be improved considerably (67%) when the reaction was performed in neat THF. Debenzylation of **8** and subsequent propylation yielded the *1,2-alt* conformer of tetra-*tert*-butyltetrapropoxycalix[4]arene (**9**), which was converted

(17) Kelderman, E.; Heesink, G. J. T.; Derhaeg, L.; Verbiest, T.; Klaase, P. T. A.; Verboom, W.; Engbersen, J. F. J.; Van Hulst, N. F.; Persoons, A.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1074.

(18) Verboom, W.; Durie, A.; Reinhoudt, D. N. *J. Org. Chem.* **1992**, *57*, 1313.

(19) The synthesis and analytical data of compounds **7**−**9** are described: Iwamoto, K.; Araki, K.; Shinkai, S. *Tetrahedron* **1991**, *47*, 4325-4342.

(20) The synthesis of **10** starting from **9** is described: Iwamoto, K.; Araki, K.; Shinkai, S. *J. Chem. Soc., Perkin Trans I.* **1991**, 1611−1613. The analytical data of **10** are described: Iwamoto, K.; Araki, K.; Shinkai, S. *J. Org. Chem.* **1991**, *56*, 4955−4962.
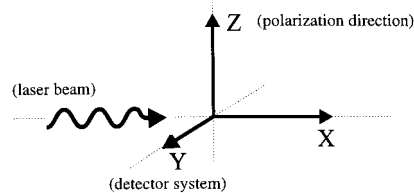
Figure 1. Configuration of the space-fixed coordinate system of the HRS experiments.

into the *1,2-alt* conformer of tetranitrotetrapropoxycalix[4]arene (**10**) in 83% yield by means of a modified *ipso*-nitration (Scheme 4).

I. Hyper-Rayleigh Scattering Experiments

Theory. From harmonic light scattering theory as developed by Bersohn *et al.*[21] in 1966, it is known that in the space-fixed coordinate system depicted in Figure 1, the intensities of the detected scattered light polarized in the x- and z-direction, I_x and I_z, respectively, are proportional to the macroscopic observables $\langle \beta_{zzz}{}^2 \rangle$ and $\langle \beta_{xzz}{}^2 \rangle$ (eq 1). In this configuration, the fundamental laser beam is propagating in the x-direction and is linearly polarized in the z-direction. The scattered second harmonic light is detected in the y-direction.

$$I_x \propto \langle \beta_{xzz}{}^2 \rangle$$

$$I_x \propto \langle \beta_{zzz}{}^2 \rangle \tag{1}$$

The total scattering intensity $I_{HRS} \propto \langle \beta_{HRS}{}^2 \rangle$ is proportional to the sum of the macroscopic observables (eq 2).

$$I_{HRS} \propto \langle \beta_{HRS}{}^2 \rangle = \langle \beta_{zzz}{}^2 \rangle + \langle \beta_{xzz}{}^2 \rangle \tag{2}$$

The hyperpolarizabilities β in eqs 1 and 2 are defined in a *macroscopic* space-fixed coordinate system. Bersohn *et al.*[21] have also derived these macroscopic expressions (eqs 1 and 2) in terms of *microscopic* β by averaging of the molecules-fixed axes relative to the space-fixed axes over all orientations. Obviously, these expressions depend on the symmetry of the molecule and become more simple upon increasing symmetry. For molecules with C_{2v} symmetry having *only* one nonzero β component β_{333}, the macroscopic observables are given by eq 3.

$$\langle \beta_{xzz}{}^2 \rangle \propto \frac{3}{105} \beta_{333}{}^2$$

$$\langle \beta_{zzz}{}^2 \rangle \propto \frac{15}{105} \beta_{333}{}^2 \tag{3}$$

For molecules with D_{3h} symmetry, with $\beta_{333} = -\beta_{311} = -\beta_{131} = -\beta_{113}$ and the other components being zero (2D octupole), the macroscopic observables are given by eq 4.

$$\langle \beta_{xzz}{}^2 \rangle \propto \frac{16}{105} \beta_{333}{}^2$$

$$\langle \beta_{zzz}{}^2 \rangle \propto \frac{24}{105} \beta_{333}{}^2 \tag{4}$$

The ratio of the macroscopic observables I_x and I_z is defined as the *depolarization ratio* $D_{x/z}$ (eq 5). Respectively, a horizontal and a vertical analyzer can be introduced in the detection path

(21) Bersohn, R.; Pao, Y-H.; Frisch, H. L. *J. Chem. Phys.* **1966**, *45*, 3184.
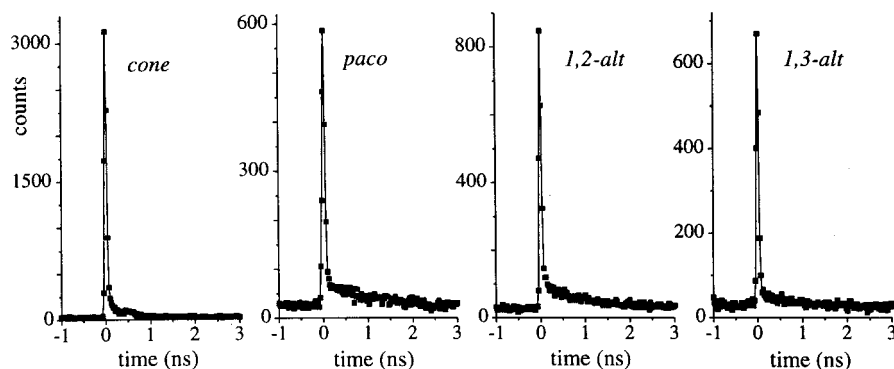
Figure 2. Typical time-dependent FHRS signals of the four conformers of tetranitrotetrapropoxycalix[4]arene. Note the different *y*-scales.

Table 1. Experimental Hyperpolarizabilities β (in $\cdot 10^{-30}$ esu; NHRS, FHRS) and Depolarization Ratios $D_{x/z}$ (FHRS) of All Four Conformers of Tetranitrotetrapropoxycalix[4]arene[a]

conformation	β_{NHRS}[b]	$\beta(0)_N$	β_{FHRS}[c]	$\beta(0)_F$	$D_{x/z}$[c]
cone	21	14	36	19	0.15 ± 0.02
paco	22[d]	14[d]	19	10	0.18 ± 0.04
1,2-alt	30[d]	19[d]	20	10	0.39 ± 0.06
1,3-alt	8	5	9	5	0.47 ± 0.18

[a] All measurements in CHCl₃ at room temperature, error: <20%. [b] Nanosecond hyper-Rayleigh scattering (NHRS) with Nd:YAG laser (1064 nm). [c] Femtosecond hyper-Rayleigh scattering (FHRS) with Ti-Sapphire laser (900 nm). [d] Values contain a fluorescence contribution.

in order to measure the I_x and I_z separately at a fixed intensity of the fundamental beam.

$$D_{x/z} + \frac{I_x}{I_z} = \frac{\langle \beta_{xzz}{}^2 \rangle}{\langle \beta_{zzz}{}^2 \rangle} \qquad (5)$$

The observables are dependent on the symmetry of the molecule as shown above. Consequently, the same holds for the depolarization ratio. For example, in case of C_{2v} symmetry (eq 3) the ratio of $\langle \beta_{zzz}{}^2 \rangle$ and $\langle \beta_{xzz}{}^2 \rangle$ is equal to 0.2, whereas in case of D_{3h} symmetry (eq 4, 2D octupole) this ratio is 0.67.

Measurements. The hyperpolarizabilities β of the four conformers were determined by two hyper-Rayleigh Scattering (HRS) methods operating in different time-windows. Firstly, the results with the nanosecond hyper-Rayleigh scattering (NHRS) technique[22] and then the results with the faster femtosecond hyper-Rayleigh scattering (FHRS) technique[23] are discussed.

Nanosecond Hyper-Rayleigh Scattering. The hyperpolarizabilities β of all four conformers of tetranitrotetrapropoxycalix[4]arene were determined by nanosecond hyper-Rayleigh Scattering (NHRS) at a fundamental wavelength of 1064 nm with chloroform as a reference. The β_{NHRS} data are listed in Table 1.[24] However, we should be careful in the interpretation of these hyperpolarizabilities obtained by NHRS. The HRS signal can possibly contain a fluorescence contribution from multiphoton processes as was described by Flipse *et al.*[25] and Hendrickx *et*

al.[26] Especially, excitation of the NLO chromophores by two or three photons can give rise to fluorescence emission in the range of the frequency-doubled light (multiphoton fluorescence). In the NHRS measurement both the contributions of hyper-Rayleigh scattering and multiphoton fluorescence are detected, as HRS and two-photon fluorescence are both incoherent processes that scale with the square of the fundamental intensity and occur on the same nanosecond time scale. Therefore, the NHRS technique will give rise to the higher apparent hyperpolarizability β if multiphoton fluorescence occurs.

Femtosecond Hyper-Rayleigh Scattering. The recently developed time-resolved femtosecond hyper-Rayleigh scattering (FHRS) technique[23] was used in order to correct for most of the long-lived fluorescence contributions to the hyperpolarizabilities of the four calixarene conformers. The time-dependent scattered signals of the conformers at four different concentrations were measured at a fundamental wavelength of 900 nm. In Figure 2 a typical time-dependent signal of each of the four calixarene conformers is given. The background signal that is present in all these measurements is due to dark counts from the microchannel plate photomultiplier tube as well as due to a constant electronic system response.[27]

For the *cone* and the *1,3-alt* conformer the time-dependent signal is very sharp and returns fast to the baseline. However, the time-dependent signals from the *paco* and the *1,2-alt* calixarene solutions show a clear contribution of fluorescence with a lifetime of approximately 2 ns. Although the signals of the *cone* and the *1,3-alt* are much more intense than the signal obtained of neat chloroform, they are all equal in shape and width. As the chloroform solution itself does not give rise to a substantial fluorescence signal, the signals from both the *cone* and the *1,3-alt* calix[4]arene solutions must also originate from instantaneously scattered second harmonic light and can be used as such to determine the hyperpolarizabilities β. However, for the *paco* and *1,2-alt* conformers the time-resolved measurements are essential to correct for the fluorescence contributions in order to obtain the hyperpolarizabilities β. By using a time-window of 0.3 ns centered at $t = 0$ most of the long-lived fluorescence contributions are eliminated. Unfortunately, (mathematical) correction for the fast fluorescent emission within the 0.3 ns time-window is difficult, as the starting point of this fast fluorescence is unknown and is overlapping with the actual second-harmonic signal.[23] The resulting hyperpolarizabilities

(22) (a) Clays, K.; Persoons, A. *Phys. Rev. Lett.* **1991**, *66*, 2980; (b) Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **1992**, *63*, 3285.

(23) Noordman, O. F. J.; Van Hulst, N. F. *Chem. Phys. Lett.* **1996**, *253*, 145−150.

(24) For the *cone* conformer β_{NHRS} values of $27\cdot10^{-30}$ esu have been reported earlier. See ref 4 and Heesink *et al.* (Heesink, G. J. T.; Van Hulst, N. F.; Bölger, B.; Kelderman, E.; Engbersen, J. F. J.; Verboom, W.; Reinhoudt, D. N. *Appl. Phys. Lett.* **1993**, *62*, 2015-2017). Since the other three conformers were not studied by HRS, also the *cone* conformer was synthesized and measured to allow for a good comparison.

(25) Flipse, M. C.; de Jonge, R.; Woudenberg, R. H.; Marsman, A. W.; Walree, C. A.; Jenneskens, L. W. *Chem. Phys. Lett.* **1995**, *245*, 297.

(26) Hendrickx, E.; Dehu, C.; Clays, K.; Bredas, J. L.; Persoons, A. Experimental and Theoretical Investigation of the Second Order Optical Properties of the Chromophore Retinal and its Derivatives. In *Polymers for Second-Order Nonlinear Optics*; Lindsay, G. A. and Singer, K. D., Eds.; ACS Symposium Series 601, American Chemical Society: Washington, DC, 1995; Chapter 6.

(27) Since these counts are not correlated with the laser pulses, they can easily be subtracted.
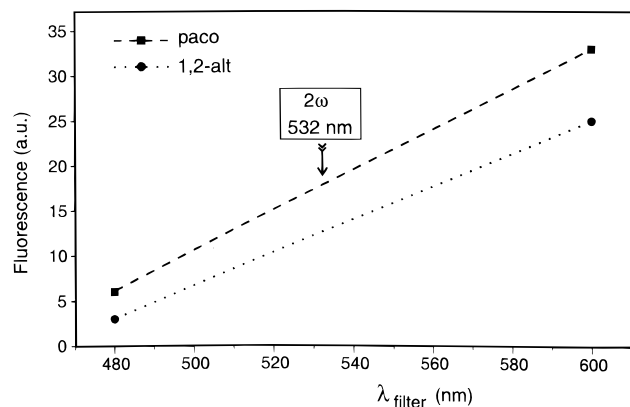
Figure 3. Schematic representation of fluorescence enhancement of the scattered signal.

β_{FHRS} of the four tetranitrotetrapropoxycalix[4]arene conformers are listed in Table 1. Comparison with the results of the NHRS measurements confirms that for a realistic comparison of the hyperpolarizabilities of the conformers, these time-resolved measurements are crucial. Nevertheless, still contributions from fast fluorescence to the β_{FHRS} values are possible.

In order to proof the occurrence of fluorescence during the NHRS measurements in the area of the second-harmonic wavelength, additional NHRS measurements were performed using different interference filters. Such filters allow only a certain range of wavelengths to pass through. This would explain the discrepancies between the hyperpolarizabilities from the nanosecond (β_{NHRS}) and femtosecond (β_{FHRS}) hyper-Rayleigh scattering measurements. Moreover, this should give also information about the relative contribution of fluorescence to the signal in the NHRS experiments for the different calixarene conformers at different wavelengths. Since no fluorescence could be detected in static fluorescence experiments using a common fluorospectrophotometer,[28] the measurements were performed with the same intense Nd:YAG laser as used in the NHRS experiments operating at a fundamental wavelength of 1064 nm. Chloroform solutions of *1,3-alt* and *cone* conformers showed only weak background fluorescence from the solvent if a 480 nm interference filter was positioned in the detection path. Solutions of the *paco* and the *1,2-alt* conformers exhibited a fluorescence intensity that was 6 and 3 times larger than the value for the solvent, respectively. The same experiment with a 600 nm interference filter showed a fluorescence enhancement of 33 and 25 times for the *paco* and *1,2-alt* conformer, respectively. For the *cone* conformer no and for the *1,3-alt* conformer only a slight fluorescence enhancement was observed at this wavelength. These results indicate that in the NHRS experiments of the *paco* and the *1,2-alt* conformers a substantial part of the signal intensity at 532 nm (the second harmonic wavelength is between the two wavelengths of the interference filters) is caused by fluorescence. This is schematically explained in Figure 3. Consequently, the real β_{NHRS} values for the *paco* and the *1,2-alt* conformers are lower as confirmed by FHRS. It is however impossible to correct the β_{NHRS} values quantitatively for the fluorescence contribution.

Most of the discrepancies between the observed FHRS and NHRS hyperpolarizabilities can be explained by taking the fluorescence contribution in the NHRS experiments into account. However, some other factors can play a role. The FHRS and NHRS experiments were performed at wavelengths of 900 and 1064 nm, respectively. According to the two-level model,[29] a 24% higher resonance enhancement is expected at 900 nm (1.93 vs 1.55 at 1064 nm with λ_{max} = 291 nm) for the four conformers.[30] Obviously, resonance corrections can only explain relative differences between the two sets of HRS data measured at different wavelengths. Furthermore, the experimental error in HRS data can be as high as 20%. Good agreement between NHRS and FHRS data is obtained by taking into account the fluorescence contributions and the two factors just mentioned (Table 1). As the FHRS data are corrected for long-lived fluorescence, these data will be used in the further discussion of this paper.

Depolarization Ratios. In order to obtain information about the symmetry of the four conformers, FHRS depolarization ratios $D_{x/z}$ were determined[23] (Table 1). These measurements were also performed with a 0.3 ns time-window to eliminate long-lived fluorescence.

Discussion. Based on the idealized symmetric structures of the four conformers, a very small or zero value of β is expected for the *1,2-alt* and *1,3-alt* conformers compared to the *cone* and *paco* conformers, which have a strongly dipolar character. Experimentally, however, the *1,2-alt* and *1,3-alt* conformers exhibit β_{HRS} values of the same order of magnitude as the *cone* conformer. One possible explanation is that the *1,2-alt* and *1,3-alt* conformers do not adopt solely the ideal symmetric structure in solution at the time-scale of the HRS measurement, but by thermal motions of the four chromophoric units in the molecule, considerable deviations occur. However, this cannot explain why the *cone* conformer in which the four dipoles of the D-π-A systems have a relatively high degree of alignment exhibits an even lower β than the *1,2-alt* conformer. Since all four conformers have the same absorption maximum of 291 nm (part of) the observed differences in hyperpolarizabilities cannot originate from differences in electronic structure or from differences in resonance enhancement either.

The depolarization ratios obtained for the four conformers (Table 1) explain the small difference between the β_{HRS} values of the dipolar *cone* and *paco* conformers ($D_{x/z}$ close to theoretical value of 0.2) compared to the nondipolar *1,3-alt* conformer ($D_{x/z}$ enhanced closer to the theoretical value of 0.67 for D_{3h} symmetry). In fact, the *1,3-alt* conformer is a 3D representative of a nondipolar, noncentrosymmetric molecule, in which the strong dipolar vectors of the individual NLO-phores in the molecule cancel. From such molecules considerable higher order (octupolar) contributions to the β tensor can be expected as explained above. The depolarization ratio of the *1,2-alt* conformer of 0.39 points to an intermediate, lower symmetry.

In view of these results, we have investigated the second-order nonlinear optical properties of the four conformers also at a theoretical level in order to obtain further evidence for the interpretation of the experimental results. This is the subject of the second part of this paper.

II. Theoretical Hyperpolarizabilities and Depolarization Ratios

In order to calculate the second-order nonlinear optical properties of a molecule, knowledge of the energetically favorable molecular conformations is required. Although in principle these conformations could be obtained by *ab initio* calculations, this would be a tremendous mathematical task for the multichromophoric calix[4]arene conformers studied in this

(28) These fluorescence spectra were recorded on a SPEX fluorolog 1691 spectrofluorometer (SPEX Industries, Edison, NJ) equipped with a 450 W SPEX 1907 Xenon light source.

(29) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.

(30) For the same reason, an enhancement of 16% for the β of chloroform was observed experimentally in accordance with the two-level model.

work. Alternatively, information about possible favorable conformations could be derived from single-crystal X-ray structures, if available. A second alternative is to calculate the conformations employing semiempirical force fields of molecular mechanics or dynamics packages. An advantage of molecular dynamics calculations is that also conformational dynamics in solution can be taken into account. The latter allows for a better comparison of the calculated, and the experimental results as the actual NLO properties are measured in solution.

Theory. Brouyere *et al.*[31] have calculated by using *sum-over-state calculations* hyperpolarizabilities of 24, 14, 1, and 1 ($\cdot 10^{-30}$ esu), respectively, for the *cone*, *paco*, *1,2-alt*, and *1,3-alt* conformers of tetranitrotetramethoxycalix[4]arene. In these calculations an averaged, symmetrical conformation for each conformer, obtained from single crystal X-ray structures of similar calix[4]arene conformers, is used. Although this method takes into account electronic transitions between the ground state and many excited states, as well as transitions between excited states it does not account for the conformational dynamics that can play an important role in a multichromophoric system in solution. Moreover, possible octupolar contributions to the second-order nonlinear optical properties have also not been taken into account.
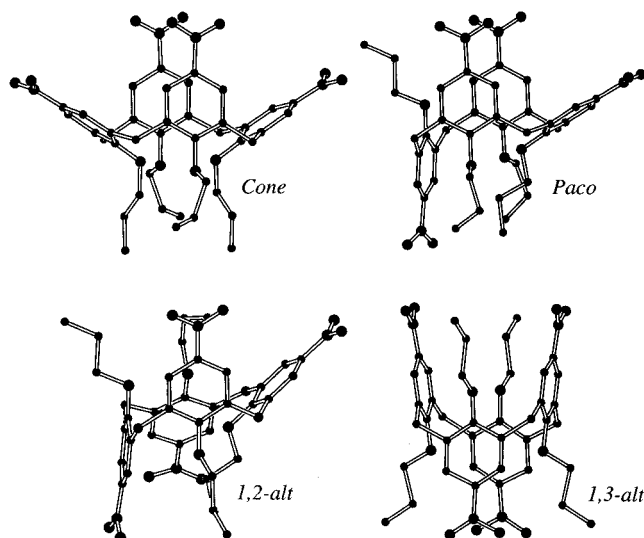
In this work the hyperpolarizabilities were calculated in a more qualitative way, but our method also takes possible octupolar contributions into account. The four D-π-A units in the molecule are considered to contribute *independently* to the molecular β. The latter implies that possible changes in the electronic structure due to interactions between the D-π-A systems are neglected. This seems a valid assumption as from the theoretical work by Di Bella *et al.*[32] it can be deduced that the four chromophoric units in the calix[4]arene structure have an effect of less than 10% on the mutual NLO properties. This effect is within the experimental error, being up to 20%. Furthermore, in the calculations it is assumed that the four separate D-π-A units in the calix[4]arene have two major components that contribute to the β tensor: the first in the direction of the dipole moment of the single D-π-A system (β_{333})[33] and the second perpendicular to the direction of the first, in the plane of the phenyl ring.[34] With this second vector also the β_{311}, β_{131}, and β_{113} tensor components are included. Next, all 27 components of the β tensor of each calix[4]arene conformation are calculated from all the β_{333}, β_{311}, β_{131}, and β_{113} tensor components of the individual D-π-A systems, taking into account their orientation with respect to the molecular plane through the four methylene groups that connect the four chromophoric units. The contribution of the separate D-π-A units to the β tensor of the calix[4]arene is calculated by performing a coordinate transformation of the β of each D-π-A unit to the coordinate system of the calix[4]arene. The four contributions are added linearly. Possible octupolar contributions are inherently taken into account in this way. From the resulting molecular β tensor, the macroscopic observables $\langle\beta_{zzz}^2\rangle$ and $\langle\beta_{xzz}^2\rangle$ are derived, and with those, the theoretical values for β_{HRS} and $D_{x/z}$ are calculated, all according to the Bersohn's theory.[21] In these calculations the ratio between the β_{311} and β_{333} tensor components of a single chromophoric unit was varied from -0.4 to 0.5 with steps of 0.1. A ratio of 0.0 denotes the

Figure 4. X-ray structures of all four tetranitrotetrapropoxycalix[4]-arene conformers.
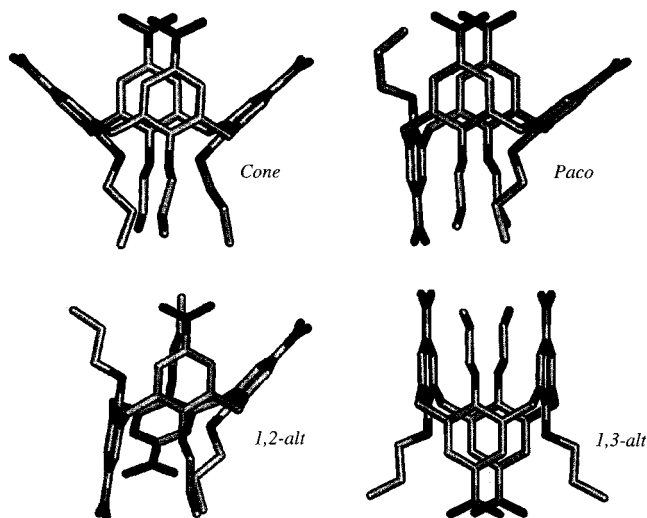
Figure 5. Energy minimized structures (MM) of all four tetranitro-tetrapropoxycalix[4]arene conformers.

situation that only the β_{333} of a single D-π-A system is nonzero. The resulting β_{HRS} value of the *cone* conformer was scaled to the experimental β_{FHRS} value of $36 \cdot 10^{-30}$ esu as these calculations result in relative rather than quantitative values.

Results. In this work the NLO properties of the four conformers were calculated by using conformations obtained from single crystal X-ray diffraction (Figure 4) as well as structures that were calculated by molecular mechanics (MM) in vacuum (Figure 5) and by molecular dynamics (MD) in chloroform using the CHARMm force field.[35,36]

X-ray Diffraction and Molecular Mechanics Calculations. From all four conformers crystals were grown that were suitable for single-crystal X-ray diffraction, and their structures have been elucidated (Figure 4). By using molecular mechanics calculations (MM) the energy minimized molecular structures

(31) Brouyere, E.; Persoons, A.; Bredas, J. L. *J. Phys. Chem.* **1997**, *101*, 4142−4148.

(32) Di Bella, S.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 5842.

(33) The vector connecting the oxygen of the propoxy group and the nitrogen of the nitro group.

(34) The vector connecting the C-atoms *ortho* to the nitro group.

(35) Quanta/CHARMm 4.1 was bought from Molecular Simulations, Burlington, MA, U.S.A.

(36) The CHARMM force field is described: (a) Brooks, B. R.; Bruccoleri, R. E.; Olafsen, B. D.; States, D. J.; Swaminathan, S.; Karplus, M. *J. Comput. Chem.* **1983**, *4*, 187. (b) Momany, F. A.; Klimkowski, V. J.; Schäfer, L. *J. Comput. Chem.* **1990**, *11*, 654. (c) Momany, F. A.; Rone, R.; Kunz, H.; Frey, R. F.; Newton, S. Q.; Schäfer, L. *J. Mol. Structure* **1993**, *286*, 1.

Table 2. Dihedral Angles of the X-ray Structures and of the Energy Minimized Structures (MM) of the Four Conformers of Tetranitrotetrapropoxycalix[4]arene

| conformer	ϕ_1 MM	ϕ_1 X-ray	ϕ_2 MM	ϕ_2 X-ray	ϕ_3 MM	ϕ_3 X-ray	ϕ_4 MM	ϕ_4 X-ray
cone	83.6	97.9	45.5	35.9	84.6	98.0	43.1	35.7
paco	88.3	96.7	39.2	31.5	88.0	98.5	−92.0	−87.4
1,2-alt	46.7	40.2	−46.7	−56.1	−81.8	−84.2	81.8	84.8
1,3-alt	90.2	83.8	−90.2	83.8	90.2	83.8	−90.2	83.8

Table 3. Calculated Hyperpolarizabilities β_{HRS} and Depolarization ratios $D_{x/z}$

$\beta_{311}{}^{a}/$ β_{333}		cone β_{HRS}	$D_{x/z}$	paco β_{HRS}	$D_{x/z}$	1,2-alt β_{HRS}	$D_{x/z}$	1,3-alt β_{HRS}	$D_{x/z}$
	X-ray	36	0.301	22.8	0.382	14.6	0.509	25.0	0.662
−0.4	MM	36	0.321	21.8	0.379	12.5	0.513	21.5	0.667
	MD	36	0.333	20.9	0.383	12.4	0.526	20.7	0.664
	X-ray	36	0.236	20.9	0.278	13.8	0.456	18.3	0.657
−0.3	MM	36	0.252	20.5	0.282	11.8	0.459	15.5	0.667
	MD	36	0.262	19.7	0.287	11.7	0.471	15.3	0.661
	X-ray	36	0.191	19.8	0.199	13.1	0.406	12.0	0.640
−0.2	MM	36	0.202	19.7	0.208	11.3	0.408	9.8	0.667
	MD	36	0.208	19.0	0.213	11.1	0.418	10.0	0.651
	X-ray	36	0.162	19.4	0.156	12.5	0.364	6.8	0.58
−0.1	MM	36	0.168	19.5	0.167	10.9	0.367	4.6	0.667
	MD	36	0.171	18.8	0.170	10.7	0.372	5.4	0.607
	X-ray	36	0.146	19.5	0.145	12.1	0.333	3.8	0.407
0.0	MM	36	0.146	19.7	0.153	10.6	0.337	0.0	0.667
	MD	36	0.147	19.1	0.154	10.3	0.337	2.5	0.408
	X-ray	36	0.137	20.0	0.154	11.7	0.313	5.2	0.511
0.1	MM	36	0.134	20.1	0.156	10.4	0.318	3.9	0.667
	MD	36	0.133	19.6	0.157	10.1	0.314	4.2	0.561
	X-ray	36	0.135	20.6	0.173	11.5	0.300	8.0	0.598
0.2	MM	36	0.129	20.6	0.170	10.3	0.308	7.2	0.667
	MD	36	0.125	20.1	0.169	10.0	0.299	7.1	0.627
	X-ray	36	0.135	21.3	0.195	11.4	0.294	10.8	0.628
0.3	MM	36	0.127	21.2	0.187	10.3	0.304	10.0	0.667
	MD	36	0.122	20.7	0.186	9.9	0.294	9.7	0.645
	X-ray	36	0.138	21.9	0.217	11.3	0.292	13.2	0.641
0.4	MM	36	0.128	21.8	0.206	10.3	0.304	12.4	0.667
	MD	36	0.123	21.3	0.204	9.9	0.293	11.9	0.652
	X-ray	36	0.142	22.5	0.238	11.3	0.293	15.2	0.648
0.57	MM	36	0.131	22.3	0.224	10.3	0.307	14.4	0.667
	MD	36	0.125	21.8	0.221	9.9	0.295	13.9	0.656

^{a} Ratio assumed for a single D-π-A system.

of the four conformers under vacuum conditions at a temperature of 0 K were obtained (Figure 5). The MM structures of the different conformers closely resemble their respective X-ray structures. The dihedral angles (ϕ_1, ϕ_2, ϕ_3, and ϕ_4) between the planes of the different *p*-nitropropoxyphenyl units and the molecular plane through the four methylene groups that connect the four chromophoric units of each conformation are listed in Table 2. The dihedral angles of the energy-minimized structures differ less than 15° from the angles found in the X-ray structures. Some differences between the structures obtained can be expected, as polarization within a π-conjugated system is not taken into account by the CHARMm force field module used in the MM calculations. Furthermore, the calculations are carried out in vacuum at 0 K, which means that no solvent interactions or thermal movements are taken into account.

The theoretical β_{HRS} values of each of these conformations (β_{MM} and β_{X-ray}) have been calculated as described above and are listed in Table 3. From both the MM and the X-ray structure of the *1,2-alt* conformer (Figures 4 and 5) it is evident that this molecule might not adopt a pure centrosymmetric conformation in solution, although this conformer is in principle centrosymmetric.[37] This noncentrosymmetry is indeed reflected in the
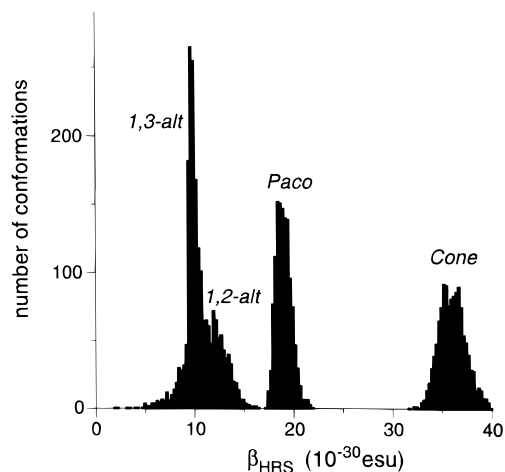
Figure 6. Distribution of the calculated β_{MD}s for the four calixarene conformers.

significant β values that were calculated for the *1,2-alt* conformer. The $D_{x/z}$ ratios calculated for the *1,3-alt* conformer clearly point to dominant octupolar contributions to the observed NLO-activity.

Molecular Dynamics Calculations. In the experiment, the conformers are dissolved in chloroform at a temperature of 300 K. Due to interaction with the solvent and the thermal motions of the molecule, the orientation of the D-π-A systems with respect to each other will vary continuously. In order to take these interactions into account MD calculations were carried out with the conformers placed in a chloroform box. After heating to 300 K and an equilibration period, a molecular dynamics run of 250 ps was performed. Every 0.2 ps a structure was recorded, resulting in 1250 structures for each conformer. The β_{HRS} tensors of all 1250 conformations of each conformer were calculated and averaged. The resulting β_{MD} values are listed in Table 3. In Figure 6 the distribution of the calculated β_{MD}'s is given at a β_{311}/β_{333} ratio of −0.2. The *1,3-alt* and *paco* conformers have a small distribution indicating that a small change in conformation does not influence the β_{MD} much. The *cone* and *1,2-alt* conformers have, in this order, an increasingly wider distribution of β_{MD}s. A conformational change in the latter two conformers has thus a more pronounced effect on the calculated β_{MD}.

Discussion. Our calculated hyperpolarizabilities (Table 3) differ significantly from those calculated by Brouyere *et al.*[31] (*vide supra*) especially for the *1,2-alt* and *1,3-alt* conformers. This can be explained by the fact that in their sum-over-state calculations possible octupolar contributions and conformational dynamics were not included. Closer examination of the data given in Table 3 shows that the fact that including also the off diagonal β_{311}, β_{131}, and β_{113} tensor components (varying the β_{311}/β_{333} ratio) in the calculations has a pronounced effect on the β_{HRS} values of especially the *1,3-alt* conformer and to a lesser extent on the results of the other conformers. Comparing the MM and MD results shows that inclusion of conformational dynamics in the calculations is not essential for the rather rigid calix[4]arene conformers as long as the off diagonal β_{311}, β_{131}, and β_{113} tensor components are taken into account ($\beta_{311}/\beta_{333} = 0$). However, for less rigid multichromophoric systems such

(37) A similar conformation was found in the single crystal structure of the *1,2-alt* conformer of tetra-*tert*-butyltetraethoxycalix[4]arene: Groenen, L. C.; Van Loon, J.-D.; Verboom, W.; Harkema, S.; Casnati, A.; Ungaro, R.; Pochini, A.; Ugozzoli, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 2385−2392.

Table 4.   Experimental Data for the X-ray Diffraction Studies on the Four Conformers

compound	*cone*	*paco*	*1,2-alt*	*1,3-alt*
morphology	colorless prism	colorless prism	colorless prism	colorless prism
formula	$C_{40}H_{44}N_4O_{12}$	$C_{40}H_{44}N_4O_{12}$	$C_{40}H_{44}N_4O_{12}$	$C_{40}H_{44}N_4O_{12}$
F_w (g·mol^{-1})	772.82	772.82	772.82	772.82
crystal system	orthorhombic	monoclinic	monoclinic	tetragonal
space group	Fddd	$P2_1/c$	$P2_1/n$	$P\text{-}42_1m$
a (Å)	23.936(2)	12.910(2)	12.300(5)	18.234(3)
b (Å)	33.007(2)	16.997(2)	12.699(5)	18.234(3)
c (Å)	20.590(2)	17.226(2)	25.236(7)	12.544(2)
β (deg)		91.73(3)	101.21(2)	
V (Å^3)	16267(1)	3773(4)	3866(4)	4141(3)
Z	16	4	4	4
D_{calc} (g/cm^3)	1.26	1.36	1.33	1.24
μ (cm^{-1})	0.879	0.095	0.090	0.086
R (%)	10.6	3.9	5.7	8.6
R_w (%)	13.4	4.3	8.2	9.9
S (GOF)	3.90	1.38	3.33	2.46

[a] With the intensity variations within statistical fluctuations. [b] Zachariasen, W. H. Acta Crystallogr. **1963**, *16*, 1139.

as the triphenylcarbinoles[5] (*vide supra*) these thermal movements will probably play an important role in the overall NLO activity.

Morley *et al.*[38] have shown by sum-over-state calculations that for our tetranitrotetrapropoxycalix[4]arene in the *cone* conformer the propoxy donor groups are forced into unfavorable orientations, which substantially reduce the conjugation between the lone pair electrons and the π-electron system of the respective aromatic rings.[39] (This aspect is not included in our or in Brouyere's calculations.) This gives rise to a lower hyperpolarizability per D-π-A system in the calix[4]arene *cone* conformer than expected on the basis of a similar D-π-A reference compound. Especially in the *1,2-alt* conformer, however, the rotations of the propoxy groups are not significantly hindered. This leads to the expectation that relative to the *cone* conformer higher β values are expected for the individual chromophoric groups and thus also for the *1,2-alt* conformer. Recently, a critical dependence of β_{HRS} on the conformation of the alkoxy donor group was also shown for 6,6′-disubstituted binaphtol derivatives (*vide supra*).[8]

In the final section the calculated hyperpolarizabilities and depolarization values of part II are compared with the experimental results as reported in the first part of this paper.

III. General Discussion

Comparison of Experimental and Calculated Data. Since the calculated hyperpolarizabilities β_{MM}, β_{X-ray}, and β_{MD} are scaled to the β_{FHRS} value of the *cone* conformer, they can only be compared with the experimental β_{FHRS} values of the other three conformers. The calculated hyperpolarizabilities for the *paco* conformer (Table 3) correspond well with the experimental β_{FHRS} value (Table 1), irrespective of the β_{311}/β_{333} ratio. For the *1,3-alt* conformer the theoretical and experimental data only agree well at a β_{311}/β_{333} ratio of 0.3 and -0.2. Generally, for a monochromophoric molecule this ratio also has a value around $+/-0.3$.[1] If both hyperpolarizabilities and depolarization ratios of the four conformers are taken into account, best agreement between the experimental and theoretical results is found for a β_{311}/β_{333} ratio of -0.2. Of the eight β and D values only one dissonant remains. The calculated hyperpolarizabilities of the 1,2-alt conformer vary roughly from 10 to $14\cdot10^{-30}$ esu, while a value of $20\cdot10^{-30}$ esu was observed experimentally. This discrepancy between experiment and calculation can have a number of reasons: Variation of the orientations of the D-π-A systems have a large relative influence on the observed β_{HRS} value, especially for the *1,2-alt* conformer, due to the antiparallel

orientation of the D-π-A systems (Figure 6). Thus small differences of the conformations used in the calculations from those actually present in solution can result in considerable deviations in the calculated hyperpolarizabilities. A second reason for the discrepancy between experimental and theoretical results for the *1,2-alt* conformer can be the enhancement of the β_{FHRS} value by fast fluorescent emission within the 0.3 ns time-window used in the FHRS measurements. The third and probably most important factor is the orientation and mobility of the electron donating propoxy groups in the different conformers as shown by Morley *et al.*[38] The high mobility of the propoxy groups in the 1,2-alt conformer can lead to higher β_{HRS} values.

Conclusion

The second-order nonlinear optical hyperpolarizabilities β_{HRS} of the four possible conformers of tetranitrotetrapropoxycalix-[4]arene have been measured by nanosecond as well as by time-resolved femtosecond hyper-Rayleigh scattering at different wavelengths. In this way the β_{HRS} values could be corrected for fluorescence contributions.

A good correspondence between the experimental data (β_{FHRS} and $D_{x/z}$) and the theoretical data as calculated from single crystal X-ray diffraction, molecular mechanics (MM), and dynamics (MD) structures is observed for the *cone*, *paco*, and *1,3-alt* conformers if a β_{311}/β_{333} ratio of -0.2 is assumed. The relatively high experimental β_{FHRS} value for the 1,2-alt conformation is explained by a still substantial contribution of fast fluorescent emission to the scattered signal and the higher freedom of rotation of the electron-donating propoxy donor groups compared with the other conformers.

In contrast to the MM and MD calculations that are presented here, both polarization of the D-π-A systems as well as mutual interactions between the D-π-A systems have been taken into account in the sum-over-state calculations performed by Morley *et al.*[38] and Brouyere *et al.*[31] Furthermore, the sum-over-state method gives *absolute* values for the hyperpolarizabilities, whereas in our calculations only *relative* hyperpolarizabilities are calculated. However, our calculations show that it is of eminent importance that in calculations of the hyperpolarizability in multichromophoric systems such as these calix[4]arenes, *octupolar contributions* are also taken into account. The latter

(38) Morley, J. O.; Naji, M. *J. Phys. Chem.* **1997**, *101*, 2681−2685.

(39) This was also theoretically studied for *p*-cyanodimethylaniline: Leung, P. C.; Stevens, J. In *Nonlinear optical properties of Organic Molecules II. SPIE.* **1989**, *1147*, 48−60.

is especially apparent for nondipolar multichromophoric systems such as the *1,2-alt* and *1,3-alt* calix[4]arene conformers. This also explains the poor agreement of the sum-over-state calculations reported earlier in the literature[31] with the experimental data presented in this paper.

For the first time the second-order nonlinear optical properties of a series of closely related multichromophoric molecules ranging from dipolar to octupolar symmetry are described. Moreover, a good agreement of the experimentally determined hyperpolarizabilities and depolarization ratios with the calculated values was found. In general, these results show that time-resolved HRS measurements combined with calculations give a clear insight of the symmetry and second-order nonlinear optical properties of multichromophoric systems such as tetranitrotetrapropoxycalix[4]arenes.

Experimental Section

Hyper-Rayleigh Scattering Experiments. The hyperpolarizabilities of the four conformers have been determined with the nanosecond hyper-Rayleigh Scattering technique (NHRS)[22] and with the recently developed time-resolved femtosecond hyper-Rayleigh Scattering technique (FHRS) which enables elimination of fluorescence contributions.[23] Since it is hardly possible to determine absolute β values by measuring the intensity of the fundamental laser beam and scattered second harmonic intensities, the internal reference method as introduced by Clays *et al.* was used.[22] The organic molecule with unknown β is dissolved in a solvent with known microscopic β. When plotting the quadratic coefficient against the concentration, the unknown β_{FHRS} can be obtained graphically by substituting the intersect and the slope of the straight line obtained for each compound in eq 6. In this formula N_{solv} is the solvent concentration, and β_{solv} the value for pure chloroform ($-0.49 \cdot 10^{-30}$ esu), which was used as the internal reference in both NHRS and FHRS.

$$\langle \beta_{FHRS}^2 \rangle = \left(\frac{slope}{intersect} N_{solv} \right) \langle \beta_{solv}^2 \rangle \qquad (6)$$

The *NHRS experiments* were performed with a Nd:YAG laser operating at a fundamental wavelength of 1064 nm with 10 ns pulses, as described in ref 22.

The time-resolved *FHRS experiments* were performed with a Ti-Sapphire laser operating at a wavelength of 900 nm with 80 fs pulses in combination with an interference filter ($\lambda = 450$ nm) in the detection path. Time traces were recorded using time correlated single photon counting as described in ref 23. The fundamental laser beam (900 nm) is propagating in the *x*-direction through a sample solution and is linearly polarized in the *z*-direction. The scattered second harmonic light is detected in the *y*-direction.

The *depolarization ratios* $D_{x/z}$ were obtained with the FHRS setup by measuring at a fixed fundamental intensity the horizontal (I_x) and vertical (I_z) polarized scattered second harmonic signal with a horizontal and a vertical analyzer, respectively. In order to obtain the correct depolarization values a low numerical aperture (NA) of 0.14 was used. Earlier research showed that this value is sufficiently low to obtain correct ratios.[40] This low NA results in low levels of the scattered signal. Consequently, high concentrations of typically 40 mmol·L^{-1} of the calixarene conformers were necessary. The dependence of the quadratic coefficient on the concentration at these high concentrations is linear, and consequently reliable data for the polarized scattered second harmonic signal could be obtained.[41]

Supporting Information Available: Experimental Section with MM and MD calculations, synthesis, and X-ray analyses, including X-ray data for the *cone*, *paco*, *1,2-alt*, and *1,3-alt* conformers of tetranitrotetrapropoxycalix[4]arene (6 pages, PDF/print). See any current masthead page for ordering and Web access instructions.

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(40) Tukker, T.; Van Hulst, N. F. *Optics. Commun.* Submitted for publication.

(41) The dependency of the quadratic coefficient on the concentration might become nonlinear at high concentrations due to intermolecular effects, leading to erroneous depolarization values.