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Nonlinear Optical Properties of Benzylic Amide [2] Catenanes: a Novel Versatile Photonic Material

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Benzylic amide catenanes are a class of synthetically-accessible interlocked molecular rings which can rotate one through the other depending on the nature of the local environment. The rings contain four phenyl units each and interlocking also affords their packing in novel, highly interacting ways that may lead to unexpected properties thus opening up the possibility of developing new materials. Third harmonic generation in benzylic amide catenane solutions was measured at a wavelength of $\lambda = 1064$ nm, with the fundamental and the harmonic wavelengths in the region of transparency of the material. The thoroughly non resonant value of the hyperpolarisability $\gamma(-3\omega; \omega, \omega, \omega)$ was found to be $(6.5 \pm 0.7) \times 10^{-35}$ esu with a negligible imaginary part, in agreement with the value of $(6.8 \pm 0.9) \times 10^{-35}$ esu calculated from a bond-additivity model of hyperpolarisability. The static second order hyperpolarisability predicted by a Molecular Orbital model was about a factor four less than the experimental value. Second hyperpolarizability values of several solvents were also measured at the fundamental wavelength of $\lambda = 1064$ nm.

Keywords: catenanes; optical properties; third harmonic generation; hyperpolarizability; molecular switching

INTRODUCTION

Catenanes[1] — molecular interlocked rings — have recently attracted attention as promising candidates for the development of 'smart' materials, information storage system components, and nanoscale devices (molecular switches and shuttles).[2-4] In parti cular, the dynamics of the mechanical bond which holds together the interlocked macrocycles or rings of catenanes can be used to switch the molecule properties through chemical or electronic stimuli, local

environment, and external optical and electric fields. Benzylic amide [2]catenanes (BACs) form a family of newly synthesised catenanes derived in one step from 1,3-dicarbonyl compounds and benzylic diamines.[3, 5-7] In view of their ease of preparation and tolerance to structural variations, BACs appear to be an ideal backbone onto which functional groups and subunits can be attached and the special dynamic properties of catenanes exploited to get artificial materials with useful electronic or optical properties (e.g. switchable dipole moment and susceptibility). The isophthaloyl [2]catenane[3] (BAC1) is the smallest interlocked ring system yet isolated. It consists of two identical, interlocked, 26-membered macrocyclic rings with an internal cavity of 46 Å. X-ray spectroscopy of single crystals of BAC1 showed that the solid state structure is dominated by an array of inter- and intramolecular hydrogen bonds and π-stacks of four aromatic rings. Unlike in the solid state, in polar solvents the intermacrocyclic hydrogen bonds are weakened and fast circumrotation of one macrocyclic ring through the other occurs.[5,6] Exploitation of the interlocked architecture can also take advantage of the presence of a large number of chromophores (up to eight) in relative orientations and with interactions that are unique to benzylic amide catenanes.

Here, we report on the linear and non linear optical properties of BAC1 in solutions. BAC1 does not contain any additional functional groups and can be considered as a prototypical model for the whole BAC family.[7] First, we measured the absorption spectrum and the refractive index of BAC1 solutions in DMSO. Then, we performed third harmonic generation (THG) experiments to determine the real and imaginary parts of the second order hyperpolarisability $\gamma(-3\omega; \omega, \omega, \omega)$, which will be indicated as γ throughout the manuscript for the sake of simplicity. Finally, we evaluated the second order hyperpolarisability of BAC1 by a simple bond-additivity model[8] and by an *ab initio* calculation based on the Sum Over Molecular Orbitals description of non linear optical properties.[9] The knowledge of γ is useful not only to improve the presently scarce understanding of the properties of this novel class of interlocked ring molecules, but also as a starting point towards the design of switchable optical devices based on catenanes.

EXPERIMENTAL DETAILS

Benzylic amide [2]catenane 1 (Figure 1) was derived in one step from isophthaloyl dichloride and xylylenediamine. The details of the synthetic procedure of BAC1 are given in Reference 5. The catenane was further purified by dissolving the material in dimethylformamide and subsequently precipitating it with ethanol. Solutions of BAC1 were prepared in dimethylsulfoxide (DMSO) with a concentration up to 200 g/l. A concentration larger than 11 g/l could only be obtained by slowly evaporating the solvent in a vacuum apparatus (0.1-1 mm Hg) at a temperature of about 50 °C. BAC1 was found to be soluble in several other polar and non polar solvent (chloroform, methanol, ethanol, 1,4-dioxan,

environment, and external optical and electric fields. Benzylic amide [2]catenanes (BACs) form a family of newly synthesised catenanes derived in one step from 1,3-dicarbonyl compounds and benzylic diamines.[3, 5-7] In view of their ease of preparation and tolerance to structural variations, BACs appear to be an ideal backbone onto which functional groups and subunits can be attached and the special dynamic properties of catenanes exploited to get artificial materials with useful electronic or optical properties (e.g. switchable dipole moment and susceptibility). The isophthaloyl [2]catenane[3] (BAC1) is the smallest interlocked ring system yet isolated. It consists of two identical, interlocked, 26-membered macrocyclic rings with an internal cavity of 46 Å. X-ray spectroscopy of single crystals of BAC1 showed that the solid state structure is dominated by an array of inter- and intramolecular hydrogen bonds and π-stacks of four aromatic rings. Unlike in the solid state, in polar solvents the intermacrocyclic hydrogen bonds are weakened and fast circumrotation of one macrocyclic ring through the other occurs.[5,6] Exploitation of the interlocked architecture can also take advantage of the presence of a large number of chromophores (up to eight) in relative orientations and with interactions that are unique to benzylic amide catenanes.

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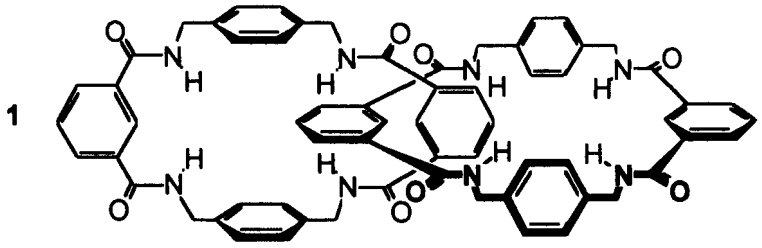


FIGURE 1 Chemical structure of Benzylic amide [2]catenane 1

acetonitrile, tetrahydrofuran) with a maximum concentration of only 0.1-0.5 g/l; therefore, solutions in DMSO were chosen for use in the optical measurements.

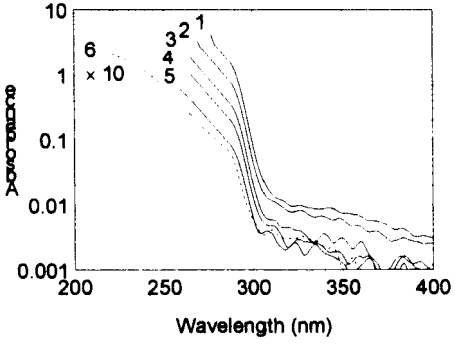


FIGURE 2 Absorption spectra of BAC1 solutions in DMSO (semilogarithmic scale). The spectra 1-5 were recorded in solutions with a concentration of 7.5, 4.0, 1.5, 0.88, and 0.36 g/l respectively. The dashed line (6) is the spectrum of a solution in methanol with a concentration of about 0.04 g/l; the optical density of 6 is multiplied by a factor 10.

Absorption spectra of the solutions were recorded in transmission by use of a Perkin Elmer Lambda 19 spectrophotometer and HELLMA fused silica cells with an optical path length of 1 mm. The refractive index of BAC1 solutions in DMSO was measured by a PROLABO Abbe refractometer which could be operated both with white light and monochromatic light. In particular, we used the wavelengths λ = 543, 594, 604, 612 and 633 nm emitted by a Research ElectroOptic Inc. tunable Helium-Neon laser system.

Third harmonic generation measurements were performed at the fundamental

wavelength of λ_ω = 1064 nm by using 13 ns pulses emitted by a Quantel Nd:Yag laser Model YG 481 at a repetition rate of 10 Hz. Solutions and solvents were held in a 1.5° wedge shaped cell with two 2-cm-thick fused silica windows. The special design of the cell permitted to neglect the contribution of air to the generation of harmonic light in accordance with the principle of harmonic generation by focused Gaussian beams in an infinite medium.[8c,10a] A detailed description of the experimental setup is given in Reference 10a. The solution and solvent $\chi^{(3)}$ values were calibrated with THG measurements on acetone done in the same conditions assuming $\gamma_{\text{aceton}} = 4.69\times10^{-14}$ esu from Reference 8c. Hereafter, the second hyperpolarizability and third order susceptibility are given in accordance with the second convention recommended in Reference 10b.

LINEAR AND NONLINEAR OPTICAL PROPERTIES OF CATENANE SOLUTIONS

The absorption spectra of solutions of BAC1 at different concentrations in DMSO are shown in Figure 2. The main absorption peak was located beyond the transparency range of the solvent. A shoulder of the main band was found at 290 nm. Further (but not exhaustive) information on the position of the main absorption peaks were obtained from solutions of BAC1 in methanol the spectrum of which is also shown in Figure 2. The refractive index n of some BAC1 solutions in DMSO is shown as a function of the wavelength in Figure 3. The continuous lines are the fitted Sellmeier curves of the general equation

$$n^2 = n_\infty^2 + \frac{q}{\lambda^2 - \lambda_{max}^2} \qquad (1)$$

Here, n_∞, is the refractive index at infinite wavelength and λ_{max} is the wavelength of the absorption maximum. The parameters of the fitting are listed in Table I.

TABLE I Parameters of the Sellmeier curves which fit the experimental indices of BAC1 solutions with the measured value of $\Delta n = n_{3\omega} - n_\omega$.

C (g/l)	n_∞	q (nm^2)	λ_{max} (nm)
0	1.465 ± 0.001	10100 ± 300	233 ± 4
30 ± 4	1.467 ± 0.001	10500 ± 1200	235 ± 20
200 ± 30	1.477 ± 0.001	15000 ± 1000	190 ± 12

It is worth noting that the measured refractive indices were not sufficient to calculate the Sellmeier dispersion curves with the necessary accuracy, particularly in the short wavelength region. However, we achieved additional data on dispersion from the knowledge of the difference $\Delta n = n_{3\omega}-n_{\omega}$ between the refractive index of the solutions at the third harmonic wavelength ($\lambda_{3\omega}$ = 355 nm) and fundamental wavelength (λ_{ω} = 1064 nm). The refractive index difference Δn was determined from THG measures with a precision of $\sim 10^{-4}$. Hence, the Sellmeier dispersion curve of catenane solutions was calculated as that one which fitted the experimental indices for the measured value of Δn, as shown in Figure 3 in the case of the solutions with concentration C = 30 and 200 g/l and the pure solvent.

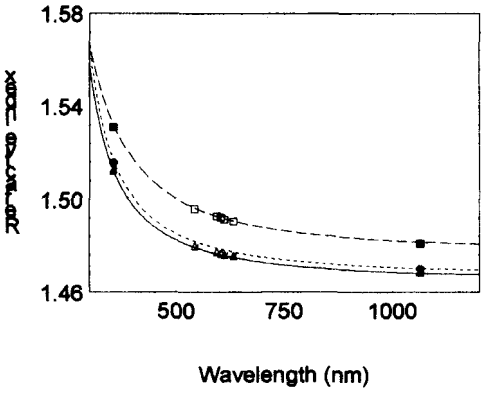


FIGURE 3 Index of refraction of DMSO and two solutions of BAC1 in DMSO as a function of the wavelength. Empty symbols (triangles, circles, and squares) are the values measured with a precision of 10^{-3} using a limiting angle refractometer; filled symbols (triangles, circles and squares) correspond to the refractive indices n_{ω} and $n_{3\omega}$ at the fundamental wavelength (1064 nm) and the harmonic wavelength (355 nm); lines (continuous, short dashed and dashed) are the Sellmeier curves which fit the experimental points for the measured difference $\Delta n = n_{3\omega}-n_{\omega}$ in the case of DMSO and two solutions of BAC1 with C = 30 and 200 g/l, respectively.

In Figure 4 the refractive index of BAC1 solutions in DMSO is plotted as a function of the concentration at the wavelengths λ = 355, 543, 633, and 1064 nm. We extrapolated the refractive index of BAC1 in the solid state from the curves in Figure 4 by using the Clausius-Mossotti equation

$$\frac{\varepsilon_{SOL}(\omega)-1}{\varepsilon_{SOL}(\omega)+2} \approx \frac{4\pi}{3}\left(N_{DMSO}\alpha_{DMSO} + N_{BAC1}\alpha_{BAC1}\right) \qquad (2)$$

with ω the frequency, $\varepsilon_{SOL}(\omega)$ the dielectric constant of the solution, and $\alpha_{DMSO,BAC1}$ the polarizability of the molecules of DMSO or BAC1. In the range of optical frequencies and far away from resonances we assumed $\varepsilon_{SOL}(\omega) = n^2(\omega)$, and indicated with α the merely electronic contribution to the molecular polarizability. The density number

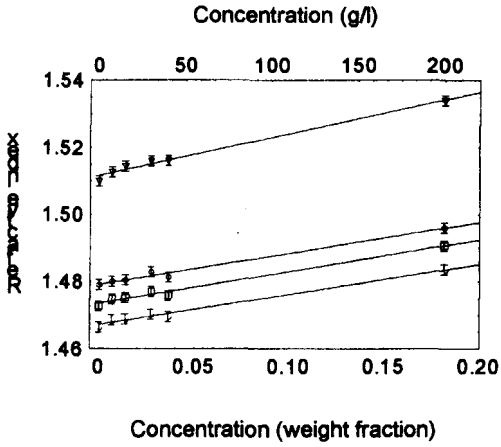


FIGURE 4 Index of refraction of solutions of BAC1 in DMSO as a function of concentration at different wavelengths λ. Diamonds and squares are the values determined from the refractive index measurements at λ = 543 nm and 633 nm, respectively; triangles and circles are the refractive indices at λ = 355 nm and 1064 nm, as derived from the fitting of the Sellmeier curve to the experimental values; the continuous lines are a visual guide. $N_{DMSO,BAC1}$ was calculated by assuming the density of BAC1 d_{BAC1}= 1.354 g/cm^3 at room temperature.[5] The extrapolated refractive index of BAC1 in the solid state resulted to be 1.62 in the visible and near infrared region, in substantial agreement with the value measured in thin films.[11]

The output of the THG experiment was given by the composition of three contributions due to the thick windows of the wedge shaped cell that possesses a third order susceptibility $\chi^{(3)}_{FS}$ and to the solution whose third order susceptibility was given by

$$\chi_S^{(3)} = N_{DMSO} F_{DMSO} \gamma_{DMSO} + N_{BAC1} F_{BAC1} \gamma_{BAC1} \qquad (3).$$

In Eq. 3 the abbreviation $\chi^{(3)} \equiv \chi^{(3)}(-3\omega;\omega,\omega,\omega)$ was adopted for the third order susceptibility. Here, N is the number density, and F is the global field factor with $F = \left(\frac{n_{3\omega}^2+2}{3}\right)\left(\frac{n_{\omega}^2+2}{3}\right)^3$. The subscript FS, S, DMSO, and BAC1

indicate fused silica, the solution, the solvent DMSO, and the molecule BAC1, respectively.

With translating the cell perpendicularly to the beam propagation direction, the path length in the liquid compartment L(x) changed as a function of the displacement x, the initial position L_0, and the wedge angle δ according to the relation:

$$L(x) = L_0 + 2x\,tg\frac{\delta}{2} \qquad (4).$$

Due to the refractive index mismatch between the fundamental and harmonic wave in the solution, the harmonic field varied with x giving rise to Maker fringes. Typical Maker fringes originated from catenane solutions are shown in Figure 5.

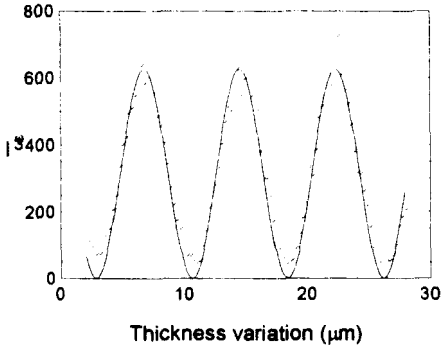


FIGURE 5 Harmonic intensity variation as a function of translation generated from a solution with concentration of 40 g/l. The solution was held in a liquid cell with thick windows. Circles are experimental points, the continuous line is the theoretical curve which fits the experimental data.

The harmonic intensity as a function of the displacement of the wedge shaped cell was recorded for several solutions with different concentration. After each acquisition the harmonic light generated in the pure solvent was measured as a reference for the calibration of the maximum amplitude of the interference fringes. The normalised harmonic intensity versus the concentration is plotted in Figure 6.

Within the same assumptions made in Ref. 10a the normalised harmonic intensity can be written as:

$$\frac{I_{3\omega}(C)}{I_{3\omega}(C=0)} = \frac{1}{\beta^2}\frac{\left|\left\{A + B(C)\left[\frac{C\gamma^{Re}_{BACl}}{M_{wBACl}} + \frac{\gamma_{DMSO}}{M_{wDMSO}}\right]\right\}\right|^2 + C^2\left[\frac{\gamma^{Im}_{BACl}}{M_{wBACl}}B(C)\right]^2}{\left[A + B(0)\frac{\gamma_{DMSO}}{M_{wDMSO}}\right]^2} \quad (5).$$

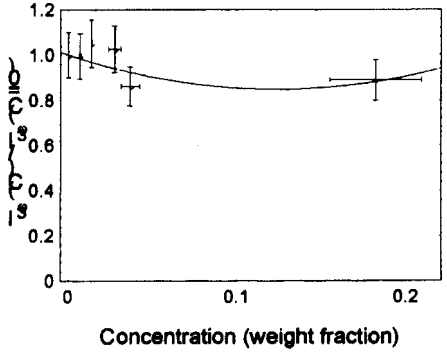


FIGURE 6 Normalised harmonic intensity as a function of the concentration: circles are experimental points, the continuous line is the theoretical curve which fits the experimental data.

In Eq. 5 the symbols are defined as following:
C is the concentration; M_w is the molecular weight; $\gamma^{Re} = Re(\gamma)$ and $\gamma^{Im} = Im(\gamma)$;

$A = t^{CS}_{3\omega}t^{SC}_{3\omega} - \alpha\beta e^{i\Delta\varphi}\left\{t^{CS}_{\omega}t^{SC}_{\omega}\right\}^3$ with $\alpha = e^{3\omega k_{\omega}L(x)/c}$ and $\beta = e^{3\omega k_{3\omega}L(x)/c}$;

$$B(C) = \frac{F(C)d(C)N_A}{(1+C)\chi^{(3)}_{FS}}\left[\alpha\beta e^{i\Delta\varphi} - 1\right]\left(t^{SC}_{\omega}\right)^3 t^{SC}_{3\omega}\frac{(\Delta\varepsilon)_{FS}}{(\Delta\varepsilon)_S}.$$

Here, $F(C) = \left(\frac{n_{\omega}(C)+2}{3}\right)^3\left(\frac{n_{3\omega}(C)+2}{3}\right)$ is the product of the Lorenz-Lorentz field factors, d(C) is the density, N_A is the Avogadro number, t is the transmission coefficient, k is the imaginary part of the refractive index, c is the speed of light, $\Delta\varphi$ is the phase mismatch between the harmonic and fundamental waves being $\Delta\varphi = 2\pi L(x)\left(\frac{3n_{\omega}\cos\vartheta_{\omega}}{\lambda_{\omega}} - \frac{n_{3\omega}\cos\vartheta_{3\omega}}{\lambda_{3\omega}}\right)$, θ is the propagation angle, and the relation $\Delta\varepsilon = (n_{3\omega} - n_{\omega})(n_{3\omega} + n_{\omega})$ is valid. The subscripts FS and S refer to fused silica and solution, ω and 3ω to the fundamental and the third harmonic wavelength, respectively. The superscripts SC and CS indicate the interface between solution and cell.

The curve in Equation 5 was fitted to the experimental data. From the fitting procedure we evaluated $\gamma^{Re}_{BAC1} = (6.5 \pm 0.7) \times 10^{-35}$ esu and $\gamma^{Im}_{BAC1} \sim 0$. As expected, the imaginary part of the hyperpolarisability was found to be zero; indeed, ω and 3ω were far from the absorption zone and even two photon resonance could be ruled out. We calculated the corresponding macroscopic susceptibility $\chi^{(3)}_{BAC1}$ in the case of an isotropic bulk medium from the relation $\chi^{(3)}_{BAC1} = N_{BAC1} F_{BAC1} \gamma_{BAC1}$. It resulted to be $\chi^{(3)}_{BAC1} = (2.9 \pm 0.3) \times 10^{-13}$ esu. This corroborates well with the data measured in thin films at the same wavelength ($\chi^{(3)}_{BAC1} = (3.4 \pm 0.3) \times 10^{-13}$ esu).[11]

Finally, we compared the measured value of γ_{BAC1} to that one evaluated by using an additivity model of bond hyperpolarizabilities.[8] The second order hyperpolarisability of the single bonds in BAC1 at the wavelength of 1064 nm is given in Table II.

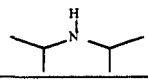
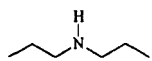
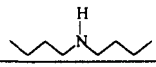
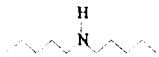
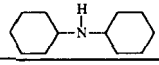
The hyperpolarisability of the bonds C-N, $\gamma_{C\text{-}N}$, and N-H, $\gamma_{N\text{-}H}$, was evaluated as an average value from the solvents listed in Table III. The refractive index of the solvents in Table III was determined by following the same procedure used for BAC1 solutions and DMSO. From the summation of the hyperpolarisability of the single bonds in BAC1 we obtained $\gamma^{Re}_{BAC1} = (6.8 \pm 0.9) \times 10^{-35}$ esu in a quite good agreement with the experimental value.

TABLE II Average bond hyperpolarisability of single bonds at λ = 1064 nm

Bond	γ ($\times 10^{-36}$ esu)
C — H	0.05±0.04 [a]
C — C	0.32±0.42 [a]
C = C	1.03±1.52 [a]
C — N	0.36±0.54 [b]
C = O	0.82±1.10 [a]
N — H	1.97±0.60 [b]

[a] Reference 9c. [b] Measured in this work and calibrated with acetone: the approximation $\gamma_{C-N} \sim \gamma_{C=N}$ was made; γ_{N-H} was evaluated as an average value from a sequence of amines.

TABLE III List of the solvents used to determine the bond hyperpolarizabilities $\gamma_{C\text{-}N}$ and $\gamma_{N\text{-}H}$. The optical parameters were measured at the wavelength λ_ω= 1064 nm. n_ω is the refractive index and L_c is the coherence length defined as $L_c = \frac{\lambda_\omega}{6(n_{3\omega} - n_\omega)}$. The parameters of DMSO determined in the present study are also listed.

Solvent	Chemical structure	n_ω $\pm 5\times10^{-4}$	L_c (μm) $\pm 1\times10^{-3}$	$\frac{\chi^{(3)}}{\chi^{(3)}_{acetone}}$ [a]	$\chi^{(3)}\times10^{-14}$ esu ±10%	$\gamma\times10^{-36}$ esu ±10%
Acetonitrile	$H_3C-C\equiv N$	1.3287	7.311	0.51	2.40	0.83
Diisopropyl-amine		1.3838	6.163	1.44	6.74	5.36
Dipropyl-amine		1.3953	5.896	1.45	6.81	5.06
Dibutyl-amine		1.4096	6.144	1.40	6.56	5.81
Dipentyl-amine		1.4185	5.725	1.35	6.33	6.52
Dicyclohexyl-amine		1.4766	5.179	1.52	7.11	6.09
Dimethyl-sulphoxyde		1.4684	4.032	2.21	10.4	6.81

[a] From Reference 8c $\chi^{(3)}_{aceton}$= 4.69*10^{-14} esu

PREDICTION OF THE SECOND ORDER HYPERPOLARISABILITY OF CATENANES BY USING QUANTUM CHEMISTRY CALCULATIONS

For a system of the size and the nature of BAC1 quantum chemical calculations are still very demanding. The low symmetry and the 136 atoms of the structure do not allow the consistent exploration of the many torsional degrees of freedom of the molecule. It was therefore decided to use the X-ray structure[5] and a non

standard ab initio method[9] that has already proved to be valuable in many cases.[12-15] The model is derived from the Sum Over States description of non linear optical properties. In principle, it would require the energies and wavefunctions of a manifold of electronically excited states. In practice, one has to make compromises.[16] A practical possibility is to limit the molecular Hamiltonian to one-electron, non interacting terms. The approximation usually referred to as a tight binding model replaces the electronic states with molecular orbitals. This approach can use orbitals obtained solving the Hartree-Fock equations.[9] The expression for a fully diagonal component of the static second hyperpolarisability $\tilde{\gamma}$ obtained within this approximation reads

$$\tilde{\gamma}_{wwww} = 24\sum_{i,a}\left(\sum_{j} c_{ia} V_{ij} c_{ja} - \frac{1}{E_{ia}}\left[V_{ia} - O_{ia}\right]^2\right) \tag{6}$$

where

$$c_{jb} = \frac{\langle j|\mu_w|b\rangle}{\Delta E_{jb}} \tag{7}$$

$$O_{ia} = \sum_{j} \frac{\langle i|\mu_w|j\rangle\langle j|\mu_w|a\rangle}{\Delta E_{aj}} \tag{8}$$

$$V_{ia} = \sum_{b} \frac{\langle i|\mu_w|b\rangle\langle b|\mu_w|a\rangle}{\Delta E_{ib}} \tag{9}$$

with m_w the w th Cartesian component of the dipole moment, $|i\rangle$, $|j\rangle$ occupied MOs, and $|a\rangle$, $|b\rangle$ unoccupied (virtual) MOs.

The *ab initio* calculations were performed at the Hartree-Fock level with the Gaussian92 program[17] in conjunction with the 6-31G* set of atomic orbitals.[18] The choice of this procedure is based on the much higher efficiency of this part of the Gaussian code with respect to the calculations of Density Functional based wavefunctions. To advantage of the model is, e.g., its success in the simulation of the scaling, with the molecular size, of the second order hyperpolarisability of fullerenes[12] and polyacetylene oligomers.[14] While this procedure can be derived systematically from the Hartree-Fock approximation,[9a] we prefer to think of it in terms of the tight binding model — of which the Extended Hückel is a prime example — where only one-electron terms are retained. As such, it is a rather drastic approximation, and because of the qualitative understanding sought, the calculation is limited to the diagonal elements (work to extend the program to the off diagonal terms is in progress). It must be emphasised that the calculations are meant only to provide an order of magnitude of the response rather than its exact value. The calculated values are $\tilde{\gamma}_{xxxx} = 3.7 \times 10^{-35}$ esu, $\tilde{\gamma}_{yyyy} = 3.3 \times 10^{-35}$ esu, $\tilde{\gamma}_{zzzz} = 1.3 \times 10^{-35}$ esu which gives $\tilde{\gamma}_{diag} = 1.7 \times 10^{-35}$ esu. This value should be compared to the experimental

result of $\gamma = 6.5 \times 10^{-35}$ esu.

It appears that the model underestimates the experimental value. This is not surprising because of the neglection of the off diagonal terms and the well-known tendency of Hartree-Fock theory to overestimate the energy gaps in Equations 6 to 9.

CONCLUSION

The second order hyperpolarisability of BAC1, a benzylic amide catenane, was found to be $\gamma = (6.5 \pm 0.7) \times 10^{-35}$ esu by THG experiments performed at the fundamental wavelength $\lambda_\omega = 1064$ nm. The pure electronic contribution to the nonlinearity was measured because THG originates only from coherent effects having a response time corresponding to optical frequencies. The location of the fundamental and harmonic wavelengths with respect to the absorption spectrum of BAC1 ruled out the possibility of an enhancement due to one, two or three photon resonance. Therefore, the measured value is thoroughly nonresonant and can be taken as a reference in the whole transparency region.

Although BAC1 is a molecule with a complex topology, the value of γ predicted by a simple bond-additivity model of the second order hyperpolarisability is in good agreement with the measured one, thus allowing the straightforward prediction of the order of magnitude of the hyperpolarizability of other catenanes in the same class.[7] Procedures based on quantum chemistry methods are being developed to provide a deeper understanding of the optical properties of catenanes. The static value of the third order susceptibility calculated in the frame of a Sum Over Molecular Orbitals description resulted to be a factor four less than the experimental one. A lower value of the static susceptibility was expected because of the optical dispersion. However, we believe that our result is affected by the intrinsic limitation of the applied theory and the semplification made by neglecting the out of diagonal terms of the susceptibility tensor.

The nonresonant value of the second order hyperpolarizability of BAC1, $\gamma_{CS_2} = 6.5 \times 10^{-35}$ esu, is more than one order of magnitude larger than that of carbon disulphide (CS_2), being $\gamma_{CS_2} = 4.4 \times 10^{-36}$ esu the nonresonant value reported in ref. 8b; with lower wavelength cut-off, the corresponding macroscopic third order susceptibility of BAC1, $\chi^{(3)}_{BAC1} = 2.9 \times 10^{-13}$ esu, is also larger than the one of CS_2 ($\chi^{(3)}_{CS_2} = 2.28 \times 10^{-13}$ esu)[8b]. This suggests an application of BAC1 in laboratory studies. Indeed, CS_2 is currently used as a reference or test $\chi^{(3)}$-medium in laboratory applications despite it is highly toxic. The main advantage found in using CS_2 is the coexistence of an interesting nonresonant $\chi^{(3)}$ value with a large tansparency range. BAC1 has an even wider region of transparency in the UV-visible, due to the large band-gap, and a comparable $\chi^{(3)}$ value. Furthermore, BAC1 can be used both in highly concentrate solutions and in thin films of good optical quality,[11] what may be also advantageous in laboratory applications; in contrast, CS_2 is liquid at room

temperature.

Nevertheless, catenanes are mainly expected to be employed as swithcable holding element for NLO active molecules. Since the tailorability of benzylic amide catenanes was already demonstrated,[7] in the future the substitution or addition of real chromophores to the interlocked frame fragments of these ring molecules will introduce low lying excited states and increase their second order hyperpolarizability to a level of interest for device applications.

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