Flick of a switch: The nonlinear optical (NLO) response of three \( \pi \)-conjugated azobenzene (AB) derivatives is investigated to evaluate the effect of an ethynyl-based conjugated spacer on the NLO properties of ABs. A \( \text{cis} \)-isomer-dependent increase of the NLO response, together with intrinsic structure-related high hyperpolarizability values, determined these compounds superb candidates for ultrafast switching NLO devices.
NLO Response of Photoswitchable Azobenzene-Based Materials

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The nonlinear optical (NLO) response of three $\pi$-conjugated azobenzene (AB) derivatives was investigated under picosecond laser excitation by means of the Z-scan technique to evaluate the effect of an ethynyl-based conjugated spacer on the NLO properties of ABs. All modules possessed large third-order nonlinearity, but unexpectedly it was the less extended AB derivative that exhibited the largest NLO response. This finding has been confirmed by means of DFT calculations and was attributed to a higher cis/trans ratio of the particular AB derivative in its investigated photoequilibrated state. Furthermore, the influence of the amount of cis isomer on the third-order nonlinear susceptibility $\chi(3)$ of the less extended AB derivative has been thoroughly investigated. Specifically, modulation of the NLO response has been successfully achieved by tuning the isomeric composition of the investigated photostationary state. These results highlighted the cis-dependent increase of the NLO response to support the general idea that such compounds can be used for multistep switching NLO materials.

1. Introduction

Nonlinear optical (NLO) effects generally occur when high-intensity electric fields, such as intense laser beams, interact with matter to modify its optical properties, generating new components (i.e. amplitude, phase, and polarization). NLO effects are of technological importance because they are considered promising elements for optical devices related to a plethora of applications, such as optical data storage, telecommunications, biophotonics, and nanophotonics.[2–4] As a practical example, the exponentially growing demand for information processing in various activities, ranging from commerce and education to health, government, security, and entertainment, creates a great need for high-speed operations and large transmission bandwidths.[5] The envisaged possibility of performing information processing operations entirely in the optical domain (by employing only optical devices such as optical fibers, waveguide gratings, optical amplifiers, and isolators)[6] would eliminate the need for opto–electrical–opto conversion to take place, as it does today, and therefore, the speed of electronic devices would no longer limit network throughput.[5]

Although there are several classes of materials that exhibit intrinsic large NLO responses, molecular organic materials are generally considered to be the most promising candidates for optoelectronic and photonic applications.[8] This trend is further supported by the great synthetic versatility exhibited by the molecular organic materials, which ultimately allows fine-tuning of their linear optical properties, and consequently, of their optical nonlinearities. Although the emphasis was initially focused on the preparation of such compounds with constantly larger optical nonlinearities, recently there has been significant interest in the reversible switching or modulation of their NLO properties achieved by protonation/deprotonation, oxidation/reduction, or photoisomerization sequences.[5,9]

One class of organic compounds that could play a crucial role in the fabrication of novel materials exhibiting enhanced “switching” NLO properties are molecular switches (MSs).[10] These are nanoscale molecular machines able to reversibly transmute, upon assimilation of an external stimuli (light, temperature, pH, cations, etc.), between two or more states, possessing different readable properties (optical, electrical, magnetic, etc.).[11] Among the many available MSs, azobenzene (AB) and its derivatives represent one of the most studied organic switchable molecular materials. Its characteristic trans–cis photoisomerization has been extensively studied since the discovery of AB in late 1930s[12] and, thereafter exploited, among other things, for many optoelectronic applications.[13] AB molecules can exist in two geometric isomers: the thermodynamically more stable trans form and the highly energetic cis isomer. As shown schematically in Figure 1, the two isomers...
can be easily interconverted under illumination with either UV or Vis light; the cis–trans isomerization is also induced by thermal stimulation (Figure 1). It must be emphasized that, in the case of substituted ABs, it is very difficult to exclusively obtain one of the two isomers, and more commonly both isomers coexist in different ratios in a photostationary state (PSS).[14]

Accompanied by a dramatic conformational change, stimuli-induced trans–cis isomerization has been chosen as an effective molecular articulation to induce or mimic movements at the molecular, nanoscopic, and microscopic level.[15] Moreover, these geometric changes, together with electronic and thermal factors,[16] are the three key parameters that influence the remarkably large third-order nonlinear susceptibility, \( \chi^{(3)} \), of ABs.[17] Indeed, in asymmetric push–pull ABs, the distance between the two phenyl rings is reduced when passing from the trans to the cis configuration, severely lessening the molecule’s dipole moment and consequently its polarizability; thus providing large values of nonlinearity.[16] Further modulation of the NLO properties of AB can be obtained by derivatization upon careful choice of the substituents.[17–23] Typically, the preparation of π-conjugated organic backbones with electron-donating moieties is of particular interest because, upon extension of the conjugation length and increasing the electron density of the molecular system, the second hyperpolarizability, \( \gamma \), which expresses the strength of the third-order nonlinearity per molecule, increases considerably. Recently, materials based on ABs that possess a high density of polarizable electrons, long conjugation lengths, and small HOMO–LUMO gaps[24,25] have also been developed for optical switching applications,[17,18] whereas other similar materials have been developed for optical limiting applications.[19] 3D microfabrication, and two-photon microscopy.[20] Much about the third-order optical nonlinearities of AB compounds has been reported in the literature,[22,23] but, to the best of our knowledge, modulation of the NLO response of an AB derivative upon triggering of the cis/trans composition has not yet been studied.

Herein, we report new results obtained from the Z-scan investigation of the NLO properties of three electronically rich AB derivatives, namely, molecules 1, 2, and 3, the structures of which are depicted in Figure 2. Specifically, our solution studies have probed the structure–property relationships that govern the nonlinearity of these compounds, and ultimately reveal the influence of the cis/trans composition of the analyzed photostationary state (PSS) on their third-order NLO response. Moreover, complementary investigations of some poly(methyl methacrylate) (PMMA) thin films doped with AB molecule 1 were also conducted, which confirmed, even in the solid state, the very large third-order NLO response of this compound.

**Experimental Section**

**Z-Scan Basics**

The NLO properties of the AB-based molecules 1–3 have been systematically investigated by using Z-scan technique, employing 35 ps, 532 nm (Vis) and 1064 nm (IR) laser pulses from a mode-locked Nd:YAG laser, operating at a repetition rate of 10 Hz. The Z-scan technique has been employed because of its experimental simplicity and because it allows the simultaneous determination, from a single measurement, of the sign and magnitude of the nonlinear absorption and refraction of a sample, which are related to the imaginary and real parts of the third-order susceptibility, \( \chi^{(3)} \), respectively. In the Z scan,[24] the measurement of the transmittance \( T \) of a sample, as it moves along the laser propagation direction of a focused laser beam, is performed in two different ways: 1) just after the sample, where all the transmitted laser light is collected and measured; or 2) after the transmitted laser beam has passed through a small aperture placed in the far field. The former measurement is known as a “open-aperture” Z scan, whereas the latter is known as a “closed-aperture” Z scan. From the former measurement, the magnitude of the nonlinear absorption coefficient, \( \beta \), of the sample, which is related to the imaginary part of the third-order susceptibility \( |\text{Im} \chi^{(3)}| \), can be determined by fitting the open-aperture Z-scan recording with Equation (1):

\[
T = 1 + \frac{\beta \text{L}_{at}}{(1 + z^2/\text{D}^2)} \left( m + 1 \right)^{m/2}
\]  

\[ (m+1)^{m/2} \]  

Figure 1. Representation of the stimuli-induced trans–cis isomerization reaction of AB.

Figure 2. Chemical structures of the investigated AB-based switches 1–3.
in which \( T \) is the normalized transmittance; \( I_0 \) is the peak on-axis irradiance of the laser beam at the focus; \( m \) is an integer; and \( L_{\text{eff}} = \{1 - \exp(-\alpha L)/\alpha \} \), in which \( \alpha \) is the linear absorption coefficient at the laser wavelength and \( L \) denotes the physical length of the sample (i.e. the thickness of the cell, which was 1 mm). In addition, the presence of a transmittance minimum or maximum at the open-aperture Z-scan recording indicates the sign of the nonlinear absorption coefficient, \( \beta \), which corresponds to reverse saturable absorption (RSA, \( \beta > 0 \)) or saturable absorption (SA, \( \beta < 0 \)) respectively.

By dividing the closed-aperture Z scan by the corresponding open-aperture one, the “divided” Z scan can be obtained, from which, under some conditions (i.e. weak nonlinear absorption) and the real part of the third-order susceptibility, Re\( \chi^{(3)} \), can be determined. A divided Z scan can exhibit either a postfocal minimum (valley) followed by a postfocal maximum (peak) or a postfocal maximum (peak) followed by a postfocal minimum (valley), indicating positive or negative Re\( \chi^{(3)} \), with the sample acting as a positive (focusing) or negative (defocusing) lens, respectively. The nonlinear refractive parameter, \( \gamma' \), can thus be obtained by using Equation (2):

\[
\gamma' = \frac{\Delta T_{\text{p}}}{T - e^{-\gamma' I_0} 0.812 \pi \alpha L (1 - S)^{3/2}}
\]

in which \( I \) is the laser wavelength, \( \Delta T_{\text{p}} \) is the difference between the peak and the valley of the normalized transmittance, \( S \) is the linear transmittance of the aperture (defined as \( S = 1 - \exp(-2r_a^2/w_a^2) \)); \( r_a \) is the radius of the aperture and \( w_a \) is the beam radius at the aperture. The quantities \( \alpha, I_0 \), and \( L \) are the same as those previously defined.

The nonlinear refractive parameter, \( \gamma' \), is related to the refractive index, \( n \), through Equation (3):

\[
n = n_0 + \gamma' I
\]

in which \( n_0 \) is the linear index of refraction and \( I \) is the irradiance of the laser beam in the sample.

Having determined the NLO parameters \( \gamma' \) and \( \beta \), we can easily calculate the real and imaginary parts of the third-order susceptibility, \( \chi^{(3)} \), according to Equation (4):

\[
\text{Re} (\chi^{(3)}) (\text{esu}) = \frac{10^{-24} c^2}{480 \pi^2} \gamma' (\text{cm}^3\text{W}^{-1})
\]

\[
\text{Im} (\chi^{(3)}) (\text{esu}) = \frac{10^{-24} c^2}{96 \pi^2 \omega} \beta (\text{cm}^3\text{W}^{-1})
\]

in which \( \omega \) (in \( \text{s}^{-1} \)) is the frequency of the laser light, \( c \) (in \( \text{cm} \text{s}^{-1} \)) is the speed of light and \( n_0 \) is the linear refractive index.

Because the third-order susceptibility, \( \chi^{(3)} \), is a concentration-dependent quantity, the NLO response of a molecule is better described in terms of its second hyperpolarizability, \( \gamma \), which is a molecular constant, independent of the concentration revealing the nonlinearity per molecule [Eq. (5)]:

\[
\gamma = \frac{\chi^{(3)}}{N n_0^2}
\]

in which \( N \) is the number of molecules per unit volume; \( L \) is the Lorentz–Lorentz local field correction factor, which is defined as \( L = (n_0^2 + 2)/3 \); and \( n_0 \) is the refractive index of the solvent.

Materials

Molecules 1–3 were synthesized according to reported procedures.\(^{23}\) The solvents used for the preparation of the solutions and PMMA were purchased from Sigma Aldrich and used without further purification.

UV/Vis Absorption

Absorption spectra were recorded with a PerkinElmer 1950 UV/Vis spectrophotometer. Emission spectra were obtained with an Edinburgh FLS920 spectrometer (continuous 450 W Xe lamp), equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185–850 nm).

Photoisomerization

Irradiation experiments of AB units were performed by using a 150 W xenon lamp model LS8521, an arc lamp power supply model LSN1, and a lamp housing model LSH102; all provided by LOT ORIEL. The excitation wavelength was selected by means of CVI Melles Griot optical bandpass interference filters [full-width at half maximum (FWHM): (10 ± 2) nm]. All measurements were performed in spectroscopy grade cyclohexane (CHX), used without further purification, and under ambient atmosphere at room temperature.

NLO Measurements

The NLO response of AB derivatives was investigated both in the Vis and the IR using the fundamental and the second harmonic outputs at 1064 and 532 nm, respectively, of a 35 ps mode-locked Nd:YAG laser, operating at a repetition rate of 10 Hz. A detailed description of the experimental setup and procedure for the analysis of the Z-scan recordings is presented elsewhere.\(^{25}\) All samples were placed in 1 mm thick quartz cells. In order to determine accurately the nonlinear absorptive and refractive parts of the third-order susceptibility, \( \chi^{(3)} \), Z-scan measurements of different concentration samples were performed at various incident laser energies.

DFT Calculations

Calculations were performed by using the Gaussian 03 package.\(^{26}\) Geometry optimizations were conducted by DFT using Becke’s three-parameter exchange functional,\(^{27}\) the Lee–Yang–Parr correlation functional\(^{28}\) (B3LYP), and the 6-31G basis set. In geometry optimizations, every bond length, bond angle, and dihedral angle was allowed to relax, free from constraints. The nature of the stationary points (cis and trans isomers) was confirmed by vibrational frequency analysis. The dipole moment, \( \mu \), and second-order hyperpolarizability, \( \gamma \), were calculated on the optimized geometries at the B3LYP/6-31G and HF/3-21G levels of theory, respectively. The dipole moments (\( \mu \)) were also calculated by using the B3LYP/HF/MP2 methods with 6-31G/3-21G/6-31G* basis sets, and first- (\( \beta \)) and second-order (\( \gamma \)) hyperpolarizabilities were also calculated at the B3LYP-MP2/6-31G* level of theory for the geometry-optimized model compounds AB, C1, and C2.
2. Results and Discussion

Compounds 1 and 2 are characterized by an AB core surrounded by two electron-rich alkylated anilines through either one or two ethynyl spacers, whereas molecule 3 laterally exposes two zinc–porphyrin termini.24 These structures were employed because it is well established that, upon increasing a molecule’s planarity and rigidity, its third-order susceptibility results are enhanced, as a direct consequence of the increase in electron delocalization, and hence, enhancement of the molecule’s polarizability.24 All modules were synthesized by transition-metal catalyzed cross-coupling reactions between the ethynyl-bearing ABs and the desired π-conjugated moiety, following synthetic protocols previously reported.24 In their thermally equilibrated state, compounds 1–3 mainly exist as trans isomers.24

Reliable quantitative estimation of the cis and trans isomers in the PSSs is impeded because the weak features of the cis isomers are substantially masked by the strong absorption envelope derived from the highly conjugated ethynyl–phenyl molecular skeleton.24 Subsequently, upon irradiation at the maximum of the intense π–π* absorption feature that is characteristic of the trans isomer (the UV/Vis/near-infrared (NIR) absorption spectra of molecules 1–3 are reported in Figure 3;[24] λmax ≈ 450 nm for 1 and 2; 360 nm for molecule 3), all molecules undergo trans → cis photoisomerization to reach a cis-enriched PSS (cis-PSS); thus indicating that the bulky and π-delocalized appendages do not prevent photochemical isomerization of the AB core.24 This process was fully reversible through both photochemical and thermal activation (ca. 120 min in the dark).24

As discussed in a previous report,24 CH2Cl2 prevents effective isomerization of the AB core. Therefore, studying the NLO response of AB derivatives 1–3 in CH2Cl2 allows evaluation of the response of thermally equilibrated trans-PSS with a cis/trans ratio that is only dictated by the relative stabilities of the two isomers; this minimizes the possibility of undesired photoisomerization occurring, which would possibly affect the NLO response of the molecule. On the contrary, CHX is the best solvent for efficient modulation of the cis/trans ratio through photochemical stimulation.24

2.1. NLO Measurements

2.1.1 Experimental Results

The AB derivatives 1–3 were dissolved in CH2Cl2 at different concentrations, and the as-prepared solutions were studied systematically by means of the Z-scan technique. To check for possible contributions to the NLO response of the solutions arising from the solvent, the NLO response of CH2Cl2 was measured separately. It was found that CH2Cl2 exhibited a negligible NLO response under visible excitation and a measurable response under IR excitation, at least for the range of incident laser energies used to study the solutions. In particular, upon excitation at λ = 1064 nm, a valley–peak configuration was observed, as indicated by the shape of the divided Z scans presented in Figure 5, suggesting positive-sign refractive nonlinearity. As a result, the nonlinear refractive parameter, γ', of CH2Cl2 was determined to be 0.25×10−18 m2/W,[29] which corresponded to a χ(3) value of 0.32×10−13 esu that was in very good agreement with the χ(3) values of 0.22×10−13 and 0.48×10−13 esu reported by others.[31,32]

Some representative open-aperture and divided Z scans of the AB derivatives 1–3, obtained under Vis (532 nm) and IR (1064 nm) laser excitation, are shown in Figures 4 and 5, respectively. In Figure 4a, the open-aperture and divided Z scans of a 0.10 mM solution of derivative 1 in CH2Cl2 are presented; these were obtained by using 0.17 μJ (corresponding to an intensity of 1.01 GW cm−2) 532 nm laser excitation. As shown, the open-aperture recording exhibited a transmission minimum that was indicative of RSA behavior (i.e. β > 0), whereas the corresponding divided Z scan exhibited a peak–valley transmission configuration, suggesting negative refractive nonlinearity (i.e. Reχ(3) < 0). The negative Reχ(3) value can be understood considering one-photon contributions in a two-level system, in which the excitation frequency lies below the resonance frequency.33 In fact, the theoretical description of a two-level system predicts positive Reχ(3) for excitation frequencies above the main resonance frequency and negative Reχ(3) for excitation frequencies below the resonance frequency.33 Similar behavior has been reported elsewhere.[34] Similarly, in Figure 4b and c, the Z-scan recordings of 0.38 and 0.26 mM solutions of AB molecules 2 and 3, respectively, in CH2Cl2 are presented. Molecule 2 exhibited negligible NLO absorption and negative refractive nonlinearity (i.e. peak–valley configuration) similar to molecule 1, whereas molecule 3 exhibited a sizeable NLO absorption and positive refractive nonlinearity (i.e. valley–peak configuration). The sign change of Reχ(3) suggests that the resonance frequency of molecule 3 should be lower than the excitation frequency employed.6,31

Furthermore, the NLO response of AB molecules 1–3 was studied by using IR (1064 nm) laser excitation. In this case, molecules 1 and 3 exhibited negligible NLO absorption, as in—

![Figure 3. UV/Vis/NIR optical absorption spectra of solutions of molecules 1 ( ), 2 ( ) and 3 ( ) in CH2Cl2 at the same concentration of 0.14 mM.](Image)
The nonlinear absorption coefficient, \( \beta \), of AB molecules 1–3 has been determined by fitting the open-aperture Z-scan recordings with Equation (1). The corresponding imaginary part of the third-order nonlinear susceptibility, \( \Im g \), has been calculated by using Equation (4b). Next, from the slope of the straight line, which corresponded to the linear best fit of the values of the \( \Delta T_{p,v} \) parameter plotted versus the incident laser energy, the nonlinear refractive parameter, \( \gamma' \), was obtained (see also Figure S1 in the Supporting Information). Then, using Equation (4a), the corresponding real part of the third-order nonlinear susceptibility, \( \Re g \), was calculated. From the values of \( \Re g \) and \( \Im g \), using Equation (5), the second hyperpolarizability, \( \gamma \), was calculated for both excitation wavelengths. The \( \gamma \) values determined are given in Table 1, while the values of \( \Re g \) and \( \Im g \) are shown in Table S1.

As mentioned in the Introduction, it is generally known that AB compounds are characterized by important optical nonlinearities. The AB derivatives studied herein follow this general trend and exhibit large optical nonlinearities that exceed those reported in the literature for similar systems, ranging from \( 10^{-28} \) (for IR excitation) to \( 10^{-26} \) esu (for Vis excitation; see Table 1), with molecule 1 possessing the largest second hyperpolarizability (\( \gamma \)) value. In addition, they all exhibited significantly larger optical nonlinearities in the Vis than in the IR region. To facilitate comparison, the ratios of the hyperpolarizability values in the Visible and IR regions, \( \gamma_{532}/\gamma_{1064} \), are also included in Table 1. Thus, second hyperpolarizability ratios as large as 1864, 2966, and 1400 have been obtained for mole-

| Table 1. Second hyperpolarizability (\( \gamma \)) values of AB derivatives 1–3 dissolved in CH\(_2\)Cl\(_2\) determined under 35 ps, 532 and 1064 nm laser excitation. |
|---------------------------------|-----------------|-----------------|
|                                | 532 nm \( \gamma \times 10^{-36} \) esu | 1064 nm \( \gamma \times 10^{-36} \) esu | \( \gamma_{532}/\gamma_{1064} \) |
| 1                              | 6.90 ± 0.83     | 3.70 ± 0.80     | 1864             |
| 2                              | 2.67 ± 0.30     | 0.90 ± 0.10     | 2966             |
| 3                              | 0.56 ± 0.08     | 0.40 ± 0.10     | 1400             |

The nonlinear absorption coefficient, \( \beta \), of AB molecules 1–3 has been determined by fitting the open-aperture Z-scan recordings with Equation (1). The corresponding imaginary part of the third-order nonlinear susceptibility, \( \Im g \), has been calculated by using Equation (4b). Next, from the slope of the straight line, which corresponded to the linear best fit of the values of the \( \Delta T_{p,v} \) parameter plotted versus the incident laser energy, the nonlinear refractive parameter, \( \gamma' \), was obtained (see also Figure S1 in the Supporting Information). Then, using Equation (4a), the corresponding real part of the third-order nonlinear susceptibility, \( \Re g \), was calculated. From the values of \( \Re g \) and \( \Im g \), using Equation (5), the second hyperpolarizability, \( \gamma \), was calculated for both excitation wavelengths. The \( \gamma \) values determined are given in Table 1, while the values of \( \Re g \) and \( \Im g \) are shown in Table S1.

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Contrary to molecules 1 and 3, molecule 2 exhibited both NLO absorption and refraction, as seen from the respective Z-scan recordings shown in Figure 5b. In detail, molecule 2 exhibited RSA behavior, which was explained in terms of two-photon excitation, whereas it exhibited the opposite sign of NLO refraction compared with the solvent; the latter exhibited a positive sign for NLO refraction. This is nicely depicted by the divided Z scans shown in Figure 5b, for which the \( \Delta T_{p,v} \) value of the solution of molecule 2 was reduced relative to that of the solvent, as should be expected when the solute and solvent have opposite signs of refractive nonlinearities.
molecules 1–3, respectively; this indicates that resonance enhancement can drastically affect the NLO response.

Moreover, upon increasing the conjugation length and bulkiness of the termini of the AB core, the second hyperpolarizability of derivatives 1–3 exhibited a clear decrease. This finding is in contrast to the results reported in previous works on AB-based push–pull systems,[23] in which increasing the conjugation length between the donor and acceptor groups resulted in larger second hyperpolarizability, \( \gamma \), values.

### 2.2. Theoretical Calculations

To rationalize the experimental data obtained for the NLO properties of AB derivatives 1–3, the dipole moment (\( \mu \)), first (\( \beta \)) and second hyperpolarizability (\( \gamma \)), \( \Delta H \), and \( \Delta G \) of the cis–trans isomerization equilibrium of reference compound AB and the \( \pi \)-conjugated substructure cores of 1–3 (bearing an ethynyl or a diyne spacing group, respectively, namely, C1 and C2; Figure 6) were modeled by DFT calculations at the B3LYP/6-31G level of theory, and their values are reported in Table 2. Compounds C1 and C2 were chosen as model compounds for molecules 1 and 2 because we can reasonably assume that the peripheral hexyl substituents negligibly influence the electronic properties of the AB \( \pi \)-conjugated cores.

As expected, for all the three investigated model compounds, AB, C1, and C2, the cis isomer exhibited a higher dipole moment, \( \mu \), than that of its trans isomer.[8] Furthermore, a sharp increase in the molecular dipole moment was detected, in accordance with an increase in the conjugation on going from AB to C2. The relevant difference in the calculated dipole moments in the trans–cis isomerization for all the model compounds under study was also confirmed by computing the dipole moment, \( \mu \), with different functionals (B3LYP/HF/MP2) and basis sets (6-31G/3-21G/6-31G*), as reported in Table 3. Despite the slight overestimation of the values at the B3LYP/6-31G method, comparing these results with those obtained by using a polarized basis set with d functions added to heavy atoms, the trend is always verified. This confirms the accuracy of the values calculated at the B3LYP/6-31G level of theory.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Open-aperture (left) and divided (right) Z scans of some solutions of AB derivatives 1–3 in CH_2Cl_2, excited by 1064 nm, 35 ps laser light: a) 1 (4.30 mM, 9.5 \( \mu \) J), b) 2 (9.30 mM, 15.10 \( \mu \) J), and c) 3 (20.80 mM, 13.10 \( \mu \) J).

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Modeled reference core structures AB, C1, and C2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \mu ) [D]</th>
<th>( \beta ) ( \times 10^{-36} ) esu</th>
<th>( \Delta H ) [kcal mol(^{-1})]</th>
<th>( \Delta G ) [kcal mol(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>trans</td>
<td>0.02</td>
<td>130.67</td>
<td>−15.58</td>
</tr>
<tr>
<td></td>
<td>cis</td>
<td>3.92</td>
<td>320.80</td>
<td>−16.24</td>
</tr>
<tr>
<td>C1</td>
<td>trans</td>
<td>0.09 ( \times 10^2 )</td>
<td>−164.10</td>
<td>−16.24</td>
</tr>
<tr>
<td></td>
<td>cis</td>
<td>3.22 ( \times 10^1 )</td>
<td>290.31</td>
<td>−70.01</td>
</tr>
<tr>
<td>C2</td>
<td>trans</td>
<td>0.65 ( \times 10^2 )</td>
<td>−138.45</td>
<td>−70.01</td>
</tr>
<tr>
<td></td>
<td>cis</td>
<td>37.11 ( \times 10^1 )</td>
<td>199.45</td>
<td>−70.01</td>
</tr>
</tbody>
</table>
Instead, when it came to evaluation of the second hyperpolarizability values, the data obtained did not follow the previous conjugation-related trend. Again, the cis and trans isomers of the three model compounds exhibited exceedingly different values. But in contrast to the dipole moment, in this case it was the trans isomer presenting higher \( \gamma \) values.

Similarly to the dipole moment, \( \beta \), the second hyperpolarizability, \( \gamma \), was further investigated by using different functionals (B3LYP/MP2) and polarized basis set (6-31G*), as reported in Table 4. In addition, to unravel the overturned behavior of \( \gamma \), the first hyperpolarizability, \( \beta \), was also calculated for the three model compounds. These analyses confirm the overestimation of both hyperpolarizabilities at the B3LYP level compared with the MP2 level, even when a polarized basis set is used. The performance of different levels of theory is consistent with that reported by Champagne et al.,\(^{[37]}\) furthermore, the values reported herein are within the same range as those reported in the literature for similar molecules.\(^{[38]}\) The unexpected trend for the hyperpolarizability \( \gamma \) between the cis and trans isomers is also observed at higher level of theory. These contradictory results can be explained by the nature of the calculations performed. By computing the electronic contributions only, the more computationally demanding vibrational contributions were overlooked. These vibrational contributions have a fundamental weight in the total value of the calculated hyperpolarizability.\(^{[39]}\) Hence, if we consider the vibrational effects, the trend may be in agreement with other calculated (hyper)polarizability values and experimental data.

On the other hand, by analyzing \( \beta \) for molecule AB, the value of the cis isomer is again higher, but in the same order of magnitude as the corresponding trans isomer. On the contrary, the calculated values for the cis isomers of molecules C1 and C2 are one order of magnitude higher than their trans isomers. Surprisingly, model compound C1 presents the highest cis–trans difference in \( \beta \) values among all the investigated molecular references. An explanation of this phenomenon can be found in the estimated \( \Delta H \) and \( \Delta G \) values of the cis–trans isomerization equilibrium. Indeed, although in all cases the trans isomer is more stable than the cis isomer, compound C1 has a small difference in energy between the two isomeric forms, namely, \(-16.24 \text{ kcal mol}^{-1}\), which is very similar to \(-15.58 \text{ kcal mol}^{-1}\) for reference AB, relative to \(-70.01 \text{ kcal mol}^{-1}\) for C2. The value of \( \Delta G \) indicates that the three trans–cis isomerizations are thermodynamically unfavored and display the same trend as that observed for \( \Delta H \) (Table 2). It is straightforward to assume that both the peculiar NLO and photochemical\(^{[20]}\) performances of compound C1 can be ascribed to the higher relative stability of cis-C1.

To determine how the structures of these derivatives influenced the calculated physicochemical properties, geometrical parameters such as bonds length, angles (\( \alpha \)), dihedral angle (\( \phi \)), and the distance between the centroids of the two phenyl rings (\( d \)) were calculated for the optimized geometries of the three model derivatives, as outlined in Figure 7 and summarized in Table 5.

Looking at the geometrical parameters calculated for the optimized structures, the higher isomer stability of cis-C1 can be explained by the smaller dihedral angle, \( \Phi_{\text{CONN}} \), which, to

<table>
<thead>
<tr>
<th>Compound</th>
<th>B3LYP/6-31G*</th>
<th>MP2/6-31G*</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis</td>
<td>0.5169</td>
<td>20.64</td>
</tr>
<tr>
<td>trans</td>
<td>0.83 x 10^-1</td>
<td>0.19 x 10^-1</td>
</tr>
<tr>
<td>C1</td>
<td>130.66</td>
<td>31.38</td>
</tr>
<tr>
<td>cis</td>
<td>34.09</td>
<td>56.90</td>
</tr>
<tr>
<td>trans</td>
<td>244.33</td>
<td>167.68</td>
</tr>
</tbody>
</table>

Figure 7. Representation of the geometrical parameters calculated for the optimized geometries of the molecular derivatives. The angle, \( \alpha \), between the three atoms is labeled. The arrows around the bond represent the four-atom dihedral angle, \( \phi \). Finally, the distance (\( d \)) between the centroids (grey dots) of the phenyl rings is also indicated with a dotted line.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bonds [Å]</th>
<th>( \alpha ) [D]</th>
<th>( \phi ) [D]</th>
<th>( d ) [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>1.45</td>
<td>1.27</td>
<td>115.76</td>
<td>–179.96</td>
</tr>
<tr>
<td>cis</td>
<td>1.43</td>
<td>1.29</td>
<td>125.07</td>
<td>–11.02</td>
</tr>
<tr>
<td>trans</td>
<td>1.42</td>
<td>1.28</td>
<td>115.23</td>
<td>–179.92</td>
</tr>
<tr>
<td>C1</td>
<td>1.44</td>
<td>1.27</td>
<td>125.25</td>
<td>–13.45</td>
</tr>
<tr>
<td>cis</td>
<td>1.44</td>
<td>1.27</td>
<td>115.26</td>
<td>–13.43</td>
</tr>
<tr>
<td>trans</td>
<td>1.36</td>
<td>1.35</td>
<td>115.21</td>
<td>–179.95</td>
</tr>
<tr>
<td>C2</td>
<td>1.44</td>
<td>1.27</td>
<td>125.26</td>
<td>–65.67</td>
</tr>
<tr>
<td>cis</td>
<td>1.44</td>
<td>1.27</td>
<td>115.26</td>
<td>–77.01</td>
</tr>
</tbody>
</table>

Table 5. Calculated geometrical parameters of bond length, angle (\( \alpha \)), four-atom dihedral angle (\( \phi \)), and the phenyl-phenyl distance (\( d \)) in the cis-trans isomers for model compounds AB, C1, and C2.
together with a longer distance between the phenyl rings, describes a typical cis-centered, shifted AB core orientation. This is reflected in the smaller dihedral angles, $\phi_{CCNN}$ measured around the N–C=O bond for cis-C1.

Figure 8. Licorice representation of compounds cis-C1 and -C2. The core of C2 preferably adopts a face-to-face orientation and displays a typical shifted AB core orientation. This is reflected in the smaller dihedral angles, $\phi_{CCNN}$ measured around the N–C=O bond for cis-C1.

The more stabilized geometry adopted by cis-C1 is not envisaged in cis-C2, in which a face-to-face orientation might explain the lower stability of this isomer. Thus, it can be speculated that the impressive value of the nonlinearity measured for compound 1 could be attributed to the higher relative stability of its cis isomer. It is reasonable to expect that the initial thermally equilibrated PSS of compound 1 presents a higher cis/trans ratio if compared, for example, to that of molecule 2. This is also confirmed by the low $\Delta H$ value for 1, which resembles that of AB and indicates a very small difference in energy between the two isomers, and probably a low energy barrier for their interconversion. Thus, because isomer cis-1 is characterized by higher nonlinearity, the impressively high NLO response of molecule 1 might be explained by a higher amount of cis isomer in its PSS, as compared to the other two AB derivatives investigated. These results clearly indicate that, through photochemical control of the concentration of cis isomer in the sample, modulation of the NLO properties of the molecule can be achieved.

2.3. Modulation of the NLO Response Induced by the Photoisomerisation Process

To study the relative contribution of each of the cis and trans isomers on the NLO response, further experiments with molecule 1 were performed. During these experiments, photochemical cis-enriched PSSs were generated and the NLO response of the solution was measured. More specifically, molecule 1 was dissolved in CHX, which is a solvent known to allow the strongest modulation of the trans–cis population when the solution is irradiated with 460 or 310 nm light. For this purpose, a continuous wave (CW) xenon arc lamp was employed as the light source and bandpass filters were used to obtain the 460 and 310 nm radiations needed to induce the cis- and trans-PSS states, respectively (see Figure S3).

By irradiating the solutions of molecule 1 in CHX with 460 nm light, the 460 nm band of the UV/Vis absorption spectrum decreased until the population of the cis isomer reached the PSS (i.e. attaining a cis-enriched PSS state, herein referred to as cis-PSS). This implies that the population of the trans isomer has attained a minimum concentration. In contrast, when the solution was irradiated with 310 nm light, the 460 nm band was observed to increase gradually as the 310 nm band decreased; this indicated the return of molecule 1 to its initial trans-enriched PSS (i.e. the trans-PSS state). Z-scan measurements of solutions of trans- and cis-PSS have thus been performed (time-dependent UV/Vis measurements revealed that no changes to the UV/Vis profile were observed during the typical timescale of the Z-scan measurement).

Similar experiments, performed with solutions of 1 in CH$_2$Cl$_2$, did not exhibit any modification of the intensity of the 460 nm band, although various irradiation conditions were tested; this confirmed that trans–cis isomerization was apparently hindered in this solvent.

Some open-aperture and divided Z scans of solutions of 1 in CHX for cis- (Figure 9a) and trans-PSS (Figure 9b) are depicted in Figure 9. Negligible NLO absorption was found, in contrast to the case of solutions in CH$_2$Cl$_2$, although the divided Z scans...
data exhibited a peak-valley configuration, as in the case of solutions in CH$_2$Cl$_2$; this suggested a negative value for Re$^\gamma$, which would correspond to self-defocusing behavior. The dependence of the $\Delta T_{p-s}$ parameter for cis- and trans-PSS solutions of molecule 1 as a function of the incident laser energy is shown in Figure 10. It becomes evident that the cis-PSS solution exhibited a greater NLO response than the trans-PSS one.

Table 6 provides a summary of the values of the third-order nonlinear susceptibility, $\chi^{(3)}$, and second hyperpolarizability, $\gamma$, of 1 in CH$_2$Cl$_2$ and in its cis- and trans-PSS forms in CHX, as determined by using 35 ps, 532 nm laser excitation. Initially, molecule 1 was considered to be in the trans-PSS in both solutions before being irradiated with 460 nm light. Comparing the $\chi^{(3)}$

tions, and therefore, a larger NLO response. This situation is further supported by experimental evidence of a 53-fold enhancement of the second hyperpolarizability values of molecule 1 in CH$_2$Cl$_2$ compared with those obtained in CHX (i.e. $\gamma_{\text{trans-PSS in CH}_2\text{Cl}_2}/\gamma_{\text{trans-PSS in CHX}} \approx 53$), under 532 nm laser excitation, as reported in Table 7. The observed enhancement should reflect directly the effect of absorption on the observed NLO response because all other parameters (such as cis/trans ratio, excitation wavelength, and concentration), which could potentially influence the NLO response, have remained unchanged for both solutions. Thus, it is important that, under 1064 nm laser excitation (i.e. in the absence of any absorption for both solvents), the second hyperpolarizability values of 1 had same magnitude (Table 7). This experimental evidence further suggests that both the nonlinear absorption and the 53-fold enhancement of the second hyperpolarizability in CH$_2$Cl$_2$ could be attributed to the more resonant situation that resulted from the spectral shift of the UV/Vis absorption spectrum of 1 in the chlorinated solvent.

![Figure 10. Variation of the $\Delta T_{p-s}$ parameter of molecule 1 in CHX as a function of laser energy.](image)

![Figure 11. UV/Vis absorption spectra of 1 in CHX (---), in CH$_2$Cl$_2$ (-----), spin-coated on glass substrate (----), and doped in PMMA (----). The vertical arrow indicates where laser excitation occurs.](image)

| Table 6. Third-order nonlinear susceptibility, $\chi^{(3)}$, along with its real and imaginary components, and the corresponding second hyperpolarizability, $\gamma$, of 1 in CH$_2$Cl$_2$ and CHX, as determined under 35 ps, 532 nm laser excitation. |
|---------------------------------|------------------|-----------------|-----------------|-----------------|
|                                | Re$^\gamma \times 10^{-15}$ esu | Im$\gamma \times 10^{-15}$ esu | $\chi^{(3)} \times 10^{-15}$ esu | $\gamma \times 10^{-30}$ esu |
| CH$_2$Cl$_2$                  | $-26.4 \pm 1.94$  | $13.58 \pm 2.03$ | $29.71 \pm 2.81$ | $6.90 \pm 0.83$  |
| trans-PSS in CHX              | $-0.49 \pm 0.02$  | $-0.49 \pm 0.02$ | $0.12 \pm 0.01$  | $0.01 \pm 0.00$  |
| cis-PSS in CHX                | $-0.70 \pm 0.03$  | $0.70 \pm 0.03$  | $0.17 \pm 0.01$  | $0.01 \pm 0.00$  |
| (a) The second hyperpolarizability, $\gamma$, of cis-PSS was calculated by assuming the same concentration of 0.22 mM as that for the trans-PSS solution. |

| Table 7. Second hyperpolarizability values of 1 in CH$_2$Cl$_2$ and CHX under 532 and 1064 nm laser excitation conditions. |
|-------------------------------------------------|------------------|-----------------|-----------------|-----------------|
|                                                | Re$^\gamma$      | Im$\gamma$      | $\gamma$        | $\gamma_{532/1064}$ |
| 532 nm                                         | CH$_2$Cl$_2$     | $0.13 \pm 0.01$ | $0.13 \pm 0.01$ | 1865            |
|                                                | CHX              | $0.13 \pm 0.01$ | $0.13 \pm 0.01$ | 38              |
| 1064 nm                                        | CH$_2$Cl$_2$     | $3.7 \pm 0.8$   | $3.7 \pm 0.8$   | $3.4 \pm 0.14$  |
|                                                | CHX              | $3.4 \pm 0.14$  | $3.4 \pm 0.14$  | $3.4 \pm 0.14$  |
| (a) $\times 10^{-36}$ esu, (b) $\times 10^{-33}$ esu. |
To further investigate the NLO response of AB derivatives 1–3 and to search for any effects related to cis/trans isomerization, thin films of 1-doped PMMA on glass substrates were prepared by spin coating. The Z-scan measurements were then performed under both IR and Vis laser excitation. The as-prepared films were characterized by a homogeneous thickness of 3–3.5 μm; the UV/Vis optical absorption spectra are shown in Figure 11. The spectra of the thin films were redshifted relative to the corresponding spectra of solutions in CH₂Cl₂. The maximum of the main band of the films was closer to the laser excitation wavelength at 532 nm; thus a more efficient enhancement was expected to occur. Furthermore, the linear absorption of the films was almost the same as that of the solution of 1 in CH₂Cl₂ (see Figure 11).

Interestingly, the third-order nonlinear susceptibility values determined under 532 nm laser excitation were significantly smaller than those obtained from the similar absorption solutions in CH₂Cl₂, and a negligible NLO response was observed under IR laser excitation. To have a better comparison of the NLO response of the films and the solutions in CH₂Cl₂ and CHX, the quantity $\chi''/\alpha_0$ was used, which was the linear absorption coefficient of the sample at the laser wavelength because it accounted for any variation in the absorption between the films and solutions. The results are summarized in Table 8. By comparing the $\chi''/\alpha_0$ values of 1 in the two solvents, the trans-PSS sample in CHX exhibited a lower nonlinearity than that of cis-PSS, although when dissolved in CH₂Cl₂, it exhibited the highest value of $\chi''/\alpha_0$. This evidence suggests that the enhancement of the NLO response of molecule 1 in CH₂Cl₂ can be understood in terms of the more resonant conditions due to the spectral shift of the solvent. The lowest values of $\chi''/\alpha_0$ have been found for the PMMA-doped films, which is in agreement with what is generally considered, namely, that the NLO response of an organic molecule is significantly reduced when the molecule is placed in a solid matrix, as a consequence of interactions between the matrix and the molecules or between the molecules themselves (quenching of the triplet state(s)).

As discussed in the Introduction, third-order NLO materials are very attractive because they are candidates for optical signal processing applications, in which molecules performing data processing operations will eliminate the need for optoelectrical–opto conversion. In this respect, there are two figures of merit that should be optimized for a material to be attractive for devices based on the ultrafast, third-order NLO response [Eq. (6)]:

$$W = \Delta n/(\alpha \lambda) > 1, \quad T = (\beta \lambda)/|\gamma'| < 1 \quad (6)$$

in which $\Delta n = |\gamma'|$ is the induced index change, $\alpha$ is the linear absorption coefficient (in units of inverse length), $\lambda$ is the excitation wavelength, $\beta$ is the nonlinear absorption coefficient, and $\gamma'$ is the nonlinear refractive parameter. The first condition ($W > 1$), implies that the linear absorption must be relatively weak compared with nonlinearity, whereas the last condition ($T < 1$), implies that the nonlinear absorption must be weak compared with nonlinear refraction. For molecule 1 in CH₂Cl₂, $W = 0.4$ and $T = 11.2$, whereas for solutions in CHX $W = 2.24$ and $T = 0$. Therefore, in the case of solutions of molecule 1 in CHX, both figures of merit are fulfilled; thus validating the true potential of this material to be used in molecular-based devices.

### 3. Conclusions

Three novel π-conjugated AB-based molecules were investigated by the Z-scan technique with 35 ps laser excitation both in the Vis and IR regions. All three AB derivatives exhibited very large optical nonlinearities at both excitation wavelengths, both in solution and in the form of thin films. The second hyperpolarizability values were 10⁻¹⁰ and 10⁻¹¹ esu under 35 ps laser excitation at 532 and 1064 nm, respectively. Furthermore, photoswitching-induced modulation of the NLO response of 1 was demonstrated by irradiating a solution of 1 in CHX at $\lambda = 460$ nm. As a result, an enhancement of the third-order susceptibility value was attained in the presence of cis-PSS, relative to trans-PSS, which indicated the important role of the cis–trans isomerization equilibrium on the NLO response of the AB derivatives. The large optical nonlinearities of molecules 1–3 make them potential candidates for several optoelectronic and photonic applications and, in particular, for ultra-fast switching applications.

### Acknowledgements

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Table 8. The $\chi''/\alpha_0$ values of 1 in solution and as a thin film under 35 ps, 532 nm laser excitation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Re \chi''$ (10⁻¹² esu)</th>
<th>$\Im \chi''$ (10⁻¹² esu)</th>
<th>$\chi''$ (10⁻¹⁴ esu)</th>
<th>$\gamma'$ (10⁻¹⁵ esu)</th>
<th>$\chi''/\alpha_0$ (10⁻¹⁰ esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂Cl₂ (1)</td>
<td>-2.01 ± 0.18</td>
<td>0.93 ± 0.08</td>
<td>2.21 ± 0.19</td>
<td>0.016 ± 0.001</td>
<td>25.7 ± 1.5</td>
</tr>
<tr>
<td>trans-PSS in CHX (3)</td>
<td>-0.049 ± 0.002</td>
<td>-</td>
<td>0.049 ± 0.002</td>
<td>0.00038 ± 0.00001</td>
<td>5.71 ± 0.32</td>
</tr>
<tr>
<td>cis-PSS in CHX (3)</td>
<td>-0.070 ± 0.002</td>
<td>-</td>
<td>0.070 ± 0.002</td>
<td>0.00054 ± 0.00002</td>
<td>7.40 ± 0.32</td>
</tr>
<tr>
<td>PMMA on glass</td>
<td>-20.8 ± 4.6</td>
<td>-</td>
<td>20.8 ± 4.6</td>
<td>-0.142 ± 0.031</td>
<td>1.2 ± 0.3</td>
</tr>
<tr>
<td>on glass</td>
<td>-21.1 ± 1.6</td>
<td>-</td>
<td>21.1 ± 1.6</td>
<td>-0.144 ± 0.011</td>
<td>1.2 ± 0.1</td>
</tr>
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</table>

[a] 0.14 mm; [b] 0.22 mm.
Keywords: azobenzenes · density functional calculations · nonlinear optical properties · nonlinear absorption · nonlinear refraction


The UV/Vis/NIR optical absorption spectra of the solutions were periodically measured to ensure that no degradation occurred due to laser irradiation.