# STRUCTURE-PROPERTY RELATIONSHIPS IN ORGANIC NONLINEAR OPTICAL MATERIALS

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## ABSTRACT

Tuning the degree of bond-length alternation in organic nonlinear optical materials is a powerful paradigm for the design of organic materials with large molecular hyperpolarizabilities ( $\beta$ ). Several research groups have employed this paradigm in the design and synthesis of NLO materials incorporating donor-acceptor polyenes. Increased bond-length alternation in polyenes leads to decreased barriers to rotation about C=C bonds and, hence, increased conformational flexibility. Since the degree of bond-length alternation is solvent dependent, so is the degree of conformational flexibility. In an effort to probe the influence of conformational flexibility on NLO response, we synthesized a series of simple donor-acceptor polyenes that are either conformationally flexible (**1a**, **2a**, **3a**) or rigid (**1b**, **2b**, **3b**). For each pair of molecules ZINDO sum-over-states calculations predict a larger value of  $\beta_{\mu}$  for the conformationally flexible isomer, but EFISH measurements (CHCl<sub>3</sub>) display mixed results. Various explanations for this behavior will be considered.

## **INTRODUCTION**

Significant interest exists for the design and development of materials exhibiting large second-order nonlinear optical properties due to their potential application in telecommunications, optical computing, and optical signal processing.<sup>1,2</sup> Optimizing both the thermal stability and magnitude of second-harmonic generation has been the focus of NLO research for the past decade.<sup>3,4</sup> Much of this work involved the use of organic chromophores.

Typical organic NLO compounds include donor (D) and acceptor (A) moieties connected by a  $\pi$ -conjugated linker. A common recent strategy for optimizing second-order nonlinear optical properties has involved varying the degree of bond length alternation (BLA) of the  $\pi$ conjugated bridge.<sup>5,6</sup> BLA is defined as the difference of the average carbon-carbon single and double bond lengths of the unit bridging the donor and acceptor. The BLA can be related to the contributions of two limiting resonance structures to the overall ground state electronic structure. The limiting structures refer to polyenic and zwitterionic resonance forms (Scheme 1). Complete contribution from either the polyene or zwitterion form to the ground state leads to severe bond length alternation (0.1 to -0.1 Å, respectively), which correlates to minimal electronic mixing between the donor and acceptor. Partial contribution from both resonance forms leads to a



diminished IBLAI, relating to an increase in donor/acceptor mixing. Increasing the mixing between donor and acceptor or, equivalently, decreasing the IBLAI from 0.1 to 0.05 Å has been shown to increase the hyperpolarizability,  $|\beta_{\mu}|$ . Further mixing to the point where the polyene and zwitterion forms contribute equally (BLA = 0 Å) can lead to vanishingly small hyperpolarizabilities.

Computational studies predict that the presence of a small electric field about a D- $\pi$ -A chromophore can influence the BLA parameter, which can dramatically effect  $\beta_{\mu}$ .<sup>68</sup> A simple method of experimentally altering the electric field to which a molecule is exposed is to change the solvent polarity used to dissolve the NLO chromophore. It is well known, however, that altering the solvent polarity can decrease the barrier to rotation about carbon-carbon double bonds for donor-acceptor substituted polyenes.<sup>9,10</sup> This increase in the conformational flexibility should also significantly effect the NLO properties. In an effort to probe the influence of conformational flexibility on NLO response, we synthesized a series of simple donor-acceptor polyenes that are either conformationally flexible **1a-3a** or rigid **1b-3b** (Scheme 2).



In this paper we report the computed and experimentally determined absorption spectra and NLO properties as well as the calculated dipole moments of a series of conformationally rigid and flexible chromophores. Semi-empirical computations provide structural data with which trends found in the experimental and computational hyperpolarizability measurements will be explained.

#### RESULTS

Table 1 contains the computed<sup>11</sup> and experimentally determined absorption spectra and NLO properties for compounds 1-3. The EFISH experiments show no consistent trend differentiating the conformationally rigid chromophores from their respective flexible analogs. For compounds 1-2 the rigid and flexible analogs display approximately equal  $\beta_{\mu}$  values. Compounds 3a and 3b, however, display significant and different hyperpolarizabilities. The flexible and rigid pairs with small hyperpolarizabilities (1-2) may display similar hyperpolarizabilities because of the large error inherent to the EFISH experiment (10-15%).

Semi-empirical ZINDO calculations predict larger hyperpolarizabilities for the flexible compounds relative to their respective rigid chromophores for all of the compounds studied. The ZINDO calculations do not, however, consistently predict the absolute magnitudes of the molecular hyperpolarizability. The calculated  $\beta_{\mu}$  values for **2b**, **3a**, and **3b** are significantly lower than the experimentally determined hyperpolarizabilities.

To explain the trends displayed in the ZINDO calculations, we concider conformational aspects of the AM1 optimized geometries.<sup>12</sup> The dihedral angle defined by LP-N1-C3-C4 ( $\phi_a$ ) (Scheme 3) and the BLA parameter are reported in Table 2. The dihedral angles of the bridging

| Compound | $\lambda_{\max}^{a,d}$ calc | $\lambda_{\max}^{a,g}$ expt | μ <sup>c,d</sup><br>calc | μ·β <sup>d,e</sup><br>calc | μ·β <sup>ь,e</sup><br>expt | $\beta_{\mu}{}^{d,f}$ calc | $\beta_{\mu}^{b,f}$ expt |
|----------|-----------------------------|-----------------------------|--------------------------|----------------------------|----------------------------|----------------------------|--------------------------|
| <br>1a   | 271                         |                             | 7.1                      | 29                         | 7                          | 4                          | 1                        |
| 1b       | 266                         | 233                         | 6.9                      | 14                         | 13                         | 2                          | 2                        |
| 2a       | 311                         | 331                         | 8.2                      | 98                         | 78                         | 12                         | 10                       |
| 2b       | 396                         | 339                         | 8.3                      | 50                         | 90                         | 6                          | 11                       |
| 3a       | 409                         | 381                         | 8.8                      | 230                        | 408                        | 26.                        | 46                       |
| 3b       | 394                         | 386                         | 9.5                      | 124                        | 311                        | 13                         | 33                       |

 

 Table 1. Electronic Absorption, Dipole Moment, and Nonlinear Optical Properties for Compounds 1-3.

<sup>a</sup> in units of nm; <sup>b</sup> in CHCl<sub>3</sub>; <sup>c</sup> in units of Debye (1 D = 10<sup>-18</sup> cm esu); <sup>d</sup> computed from AM1 geometry; <sup>e</sup> in units of 10<sup>-48</sup> cm<sup>6</sup>; <sup>f</sup> in units of 10<sup>-30</sup> cm<sup>5</sup> esu<sup>-1</sup>, <sup>g</sup> in hexane.

polyene chains are computed to be in a virtually planar s-trans configuration. The  $\pi$ -system of the acceptors are predicted to be co-planar with the bridging polyene moieties. Examination of the dihedral angles provides an explanation for the observed disparities in NLO response between rigid and non-rigid chromophores with identical  $\pi$ -systems.

## DISCUSSION

For all compounds, computationally predicted (ZINDO) hyperpolarizabilities are greater for the flexible relative to the rigid chromophores. Experiment corroborates these calculations for only compounds **3a** and **3b**, whereas compounds **1-2** may not follow the predicted trend due to the error associated with the EFISH experiment. Differences in the hyperpolarizability between the respective rigid and flexible pairs may arise from the ability of the flexible isomers to achieve conformations other than those shown in Scheme 2 by Z/E isomerization of the carbon-carbon double bonds and/or rotating about the carbon-carbon single bonds. Strong evidence exists for the ability of donor-acceptor polyenes to readily isomerize about the carboncarbon double bonds.<sup>9,10</sup> Hence, the flexible isomers can potentially rotate about the bridging bonds. If isomerization about single or double carbon-carbon bonds was occurring in the flexible chromophores, a decreased hyperpolarizability would be expected for those chromophores relative to the rigid compounds. Because this is the opposite of the observed trend for **3a** and **3b**, it is likely not the case, at least in CHCl<sub>3</sub> that conformational issues regarding isomerization about the bridging carbon-carbon bonds can account for the lower hyperpolarizabilities observed for the rigid chromophores.

A significant literature exists in which the BLA parameter is used to explain changes in the hyperpolarizability. Changes in the local electric field surrounding the chromophore (solvent polarity) caused variations in  $\beta_{\mu}$ , which were explained through changes in the electronic nature of the bridging bonds via the BLA parameter.<sup>5,13</sup> The rigid and flexible pairs in this study have identical donors, acceptors, and  $\pi$ -systems. Because of this, assuming no single or double bond isomerization, the rigid and flexible pairs are expected to display similar bond length alternation and, hence, similar  $\beta_{\mu}$  values. Examination of Table 2 shows that all of the compounds in this study are predicted to have approximately the same BLA parameter (ca. 0.10 Å), so differences in BLA can not account for the differences observed in  $\beta_{\mu}$ .

| Bond Length Alternation Values for<br>Compounds 1-3. |                   |                    |                   | LP - lone pair     |
|--|-------------------|--------------------|-------------------|--------------------|
| Compound   | ф <sub>а</sub> .с | BLA <sup>b,c</sup> | ¢a (Na            | <b>`</b>           |
| <b>1</b> a   | 82.9              | 0.097              |                   | ane of phenyl ring |
| 1b   | 68.5              | 0.097              | С1 н1             | C1 Ç4·C6           |
| 2a   | 81.7              | 0.097              | Ň1-Cਤ́ H3         |                    |
| 2b   | 66.9              | 0.098              | C2 C5·C7<br>H2 ,× | H2 ×               |
| 3a   | 81.2              | 0.094              | 1a-3a             | 1b-3b              |
| 3b   | 66.1              | 0.098              |                   |                    |

Cabamaa 2

| Table 2. | Compu    | ted D  | ihe | d  | ra | l Angles and |
|----------|----------|--------|-----|----|----|--------------|
| Bond 1   | Length . | Alterr | at  | io | n  | Values for   |
|          | ~        |        |     | -  | ~  |              |

in aegrees; " in A; " computed from AM1 geometry

The main structural difference between the rigid and flexible pairs is the presence of the fused cyclohexene rings used to lock the conformation of the rigid analogs. Neither severe twisting about the single or double carbon-carbon bonds of the bridge nor BLA differences can account for the observed changes in  $\beta_{\mu}$ . Examination of other conformational issues leading to electronic differences is appropriate. The AM1 optimized geometries used as input to the ZINDO calculations of  $\beta_{\mu}$  provide useful conformational information.

Analysis of the dihedral angle  $\phi_a$  (LP-N1-C3-C4) (Scheme 3, Table 2) describes the degree to which the lone pair (LP) of the amine nitrogen is displaced from the conjugated porbitals of the bridging system. The p-orbital overlap displays a  $\sin^2 \phi_a$  dependence, whereby small changes in  $\phi_{a}$  translate into large changes in computed hyperpolarizability. For the greatest amount of overlap of the lone pair with the p-orbital of C3,  $\phi_a$  should be 90°. For compounds 1a, 2a, and 3a,  $\phi_a$  ranges from 81.2 - 82.9°, whereas the rigid analogs 1b, 2b, and 3b range from 68.5 - 66.1°. The differences in p-orbital overlap of the amine lone pair with the bridging carbon p-orbitals between the rigid and flexible pairs is approximately 15%. The loss of overlap predicted for the rigid chromophores is likely the source of the decreased calculated  $\beta_{\mu}$  values for 1b, 2b, and 3b relative to 1a, 2a, and 3a. The decreased  $\phi_a$  from compounds 1b, 2b, and 3b is due to the steric repulsions between the methyl groups of the amine and hydrogens at C4 of the cyclohexene rings. This interaction is not present in 1a, 2a, and 3a, however, minimal interactions are possible between the amine methyl groups and H1.

Further studies incorporating more polar solvents are needed to elucidate the contribution of conformational relative to electronic effects on the NLO response of donor- $\pi$ -acceptor chromophores.

### EXPERIMENT

The following compounds were prepared according to literature procedures: 3-(dimethylamino)-2-cyclohexene-1-one (1b),<sup>14</sup> 5-dimethylamino-penta-2,4-dienal (2a),<sup>15</sup> 7dimethylamino-hepta-2,4,6-trienal (3a).<sup>15-17</sup> Preparations for 1a, 2b, and 3b will be described in a future publication. As a means of calibrating the EFISH apparatus, the molecular

hyperpolarizability was determined for 4-nitroaniline ( $\beta_{\mu} = 7.1 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$  in CHCl<sub>3</sub>). This compares well to previously reported values.<sup>18</sup> Molecular hypolarizabilities were determined by a concentration dependent analysis of the EFISH data. We performed all EFISH experiments at 1907 nm in chloroform.

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