

## The First Molecular Electronic Hyperpolarizabilities of Highly Polarizable Organic Molecules: 2,6-Di-*tert*-butylindoanilines

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The first molecular hyperpolarizabilities ( $\beta$ ) of a series of 2,6-di-*tert*-butylindoanilines, measured by electric-field-induced second harmonic generation, are somewhat more sensitive to donor strength than was found for analogously substituted nitrostilbenes, and dimethylindoaniline has a  $\beta$  roughly twice that of its 2,6 di-*tert*-butylated analogue, measured in chloroform; solvatochromic measurements on the former compound suggest that this decrease in hyperpolarizability is consistent with a bound-solvent effect.

Organic compounds hold considerable potential for nonlinear optical materials.<sup>1-4</sup> In order to realize this potential, it is necessary to prepare highly nonlinear molecules for incorporation into materials. Using a two-state model,<sup>5,6</sup> it was recently shown that there is an optimal combination of donor and acceptor strengths for a given bridge that will maximize the first molecular electronic hyperpolarizability ( $\beta$ ).<sup>7</sup> The peaked dependence of  $\beta$  on the difference in coulomb energies of the end groups, normalized by the coupling within the bridge orbitals [ $(\alpha_A - \alpha_D)/|t|$ ] for a generic 4-orbital  $\pi$ -system, is shown in Fig. 1. Here, small  $(\alpha_A - \alpha_D)/|t|$  represents strong mixing of donor and acceptor orbitals *via* the bridge, while large  $(\alpha_A - \alpha_D)/|t|$  represents the decoupling of these orbitals from the bridge. Thus, qualitatively, there are *strong* donors and acceptors on the left and *weak* donors and acceptors on the right. It is important to note that the detailed shapes of the plots will be system-dependent. However, the plot shown in Fig. 1 should capture the essential characteristics of donor-acceptor polyene-like molecules. To date, molecules with sufficiently strong donors and acceptors have not been synthesized to reach the peak of the  $\beta$  curve. We are therefore developing synthetic strategies that will lead to molecules where  $\beta$  is optimized by tuning the degree of bond alternation in the  $\pi$ -electron system between the donor and acceptor.<sup>7</sup> Implementation of this strategy relies on the realization that molecules such as stilbenes, with strongly aromatic end groups, will not have the correct balance of the two limiting charge-transfer resonance forms in the ground state to achieve the degree of bond alternation required to optimize  $\beta$ . This is due to the energetic price associated with the loss of

aromaticity in the charge-separated form. Accordingly, we examined dimethylindoaniline **1**, which has an aromatic and a quinone ring each in the canonical ground and charge-transfer (CT) excited states. A surprisingly high  $\beta$  of  $190 \times 10^{-30}$  esu was found.<sup>7</sup> We therefore sought to explore this class of materials further in order to understand better the role of the  $\pi$ -electron system in determining the hyperpolarizability of organic molecules.<sup>7</sup>

Here we report on the nonlinearities of a series of 2,6-di-*tert*-butylated compounds related to **1**, in which the donor and the conjugation path was varied. The *tert*-butyl derivatives (described in Table 1) were easier to synthesize than the parent indoaniline dyes and so were chosen for this study. The dyes were prepared by boron trifluoride-diethyl ether-catalysed condensation of 2,6-di-*tert*-butylbenzoquinone with the appropriately *para*-substituted aniline in tetrahydrofuran (THF), as described in the literature.<sup>8</sup> Dyes **2-7** were known<sup>8</sup> and the extended dyes, **8**<sup>†</sup> and **9**,<sup>†</sup> were prepared analogously (Scheme 1).

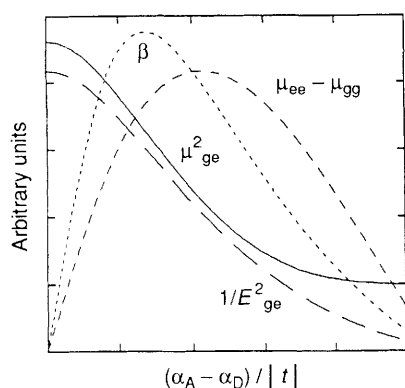
<sup>†</sup> Characterizing data, for **8**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.50 (d, *J* 8.4 Hz, 2H), 7.41 (d, *J* 8.8 Hz, 2H), 7.06 (d, *J* 16.3 Hz, 1H), 7.03 (d, *J* 2.5 Hz, 1H), 6.91 (d, *J* 15.8 Hz, 1H), 6.90 (d, *J* 2.6 Hz, 1H), 6.88 (d, *J* 8.2 Hz, 2H), 6.71 (d, *J* 8.8 Hz, 2H), 2.97 (s, 6H), 1.32, 1.20 (s, 9H).

For **9**: <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$  7.64 (d, *J* 8.3 Hz, 2H), 7.55 (d, *J* 8.6 Hz, 2H), 7.24, 7.13 (d, *J* 16.4 Hz, 1H), 7.02 (d, *J* 2.6 Hz, 1H), 6.97 (d, *J* 2.7 Hz, 1H), 6.96 (d, *J* 8.0 Hz, 2H), 6.94 (d, *J* 8.4 Hz, 2H), 3.82 (s, 3H), 1.34, 1.21 (s, 9H).

Satisfactory elemental analyses were obtained.

**Table 1** Optical data for compounds of the form R-N=(2,6-Bu<sup>t</sup><sub>2</sub>C<sub>6</sub>H<sub>2</sub>=O-4) measured in chloroform

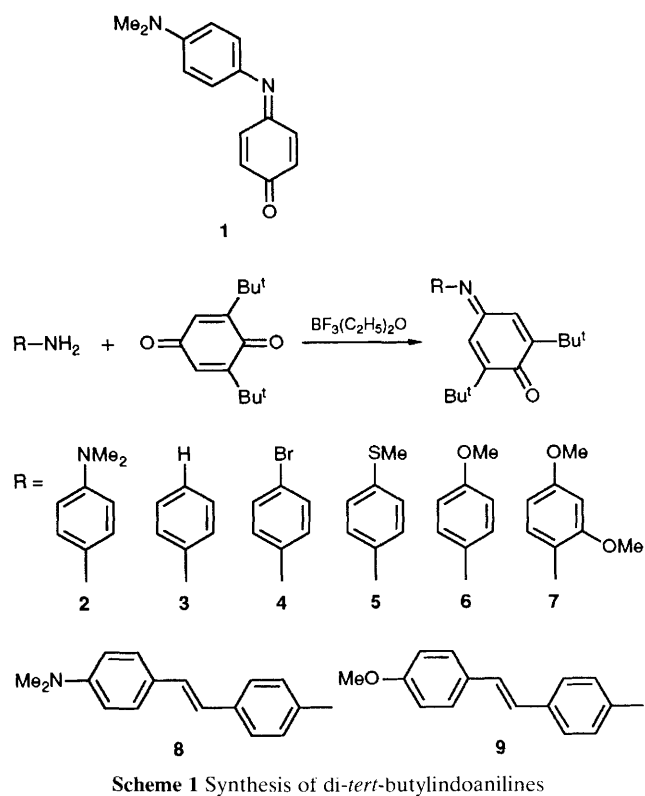
R	Comp.	$\lambda_{\max}/\text{nm}$	$\mu/10^{-30}\text{esu}$	$\beta/10^{-30}\text{esu}$	$\beta_0/10^{-30}\text{esu}$
4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	<b>2</b>	558	3.9	78	47
Ph	<b>3</b>	428	1.5	5.9	4.5
4-BrC <sub>6</sub> H <sub>4</sub>	<b>4</b>	432	1.3	13	9.9
4-MeSC <sub>6</sub> H <sub>4</sub>	<b>5</b>	476	2.3	16	11
4-MeOC <sub>6</sub> H <sub>4</sub>	<b>6</b>	469	2.4	17	12
2,4-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	<b>7</b>	498	3.4	19	13
4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> - CH=CH	<b>8</b>	512	3.7	116	77
4-MeOC <sub>6</sub> H <sub>4</sub> - CH=CH	<b>9</b>	497	2.6	48	33



**Fig. 1** Plots illustrating the dependence of the change in dipole moment, ( $\mu_{ee} - \mu_{gg}$ ), the transition dipole moment, ( $\mu_{ge}^2$ ), and the energy gap, ( $1/E_{ge}^2$ ), between the lowest unoccupied molecular orbital and the highest occupied molecular orbital, as well as  $\beta$ , upon  $(\alpha_D - \alpha_A)/|t|$  derived from molecular orbital calculations on a 4-orbital system consisting of donor, acceptor, and two bridges. For  $(\alpha_A - \alpha_D)/|t| = 0$  the  $\pi$ -electrons are symmetrically distributed in both the ground and excited state as in a symmetric cyanine chromophore or a neutral chromophore substituted with strong donors and acceptors, such that the  $\pi$  electron density is equally shared between the donor and acceptor. Moderate  $(\alpha_A - \alpha_D)/|t|$  corresponds to a somewhat unsymmetrical cyanine dye, or to a chromophore with donor and acceptor substituents of moderate strength in which asymmetry is introduced in the ground and excited state wave functions. Large  $(\alpha_A - \alpha_D)/|t|$  corresponds to chromophores with very weak donor and acceptor groups in which the bridge-mediated donor-acceptor orbital mixing decreases, such that the strongly allowed transition has mostly bridge character.

Measurements of  $\beta$  and  $\beta_0$  (corrected for dispersive enhancement using the two-state model<sup>5,6</sup>) for the di-*tert*-butylindoanilines measured using DC electric field-induced second harmonic generation (EFISH)<sup>9,10</sup> in chloroform are shown in Table 1. As expected, the magnitude of  $\beta$  and  $\beta_0$  increases with increasing donor strength. Whereas  $\beta_0$  for di-*tert*-butylindoanilines ranges from 4.5 to  $47 \times 10^{-30}$  esu for the compounds **2-7** the  $\beta_0$  for the analogously substituted nitrostilbenes range from 10 to  $56 \times 10^{-30}$  esu.<sup>10</sup> Thus, in going from no donor to dimethylamino as the donor,  $\beta$  for the former series increases by a factor of 10.4 whereas for the latter series it only increases by a factor of 5.6. The greater sensitivity of  $\beta_0$  to donor strength for the former series is consistent with the notion that the degenerate nature of the indoaniline bridge will lead it to polarize more in the presence of an electric field. In this case an internal electric field is created by substitution with donors (and acceptors).

In an attempt to probe the effect of increased conjugation length on  $\beta$  for this series of compounds we synthesized the



dimethylaminophenylvinyl compound, **8**. Surprisingly, **8** absorbs light at higher energy than the less highly conjugated **2**. The simple electron-in-a-box model predicts the opposite: the longer molecule should absorb at the lower energy. Despite the reversed trend in absorption of light, **8** still shows the higher nonlinearity. An inverse transparency-nonlinearity tradeoff is unusual in systems which differ only in conjugation length. In the context of the two-state model, these results imply that **8** has a much larger product of  $(\mu_{ee} - \mu_{gg})(\mu_{ge}^2)$  than does **2**. Given the increased length and number of  $\pi$ -electrons in the former molecule this result should not be surprising, but it illustrates that enhanced nonlinearity need not necessarily be accompanied by loss of transparency.

The relative contribution of the neutral and CT resonance forms to the ground and excited state wave functions can be tuned by solvent.<sup>7,11</sup> Thus, the ground state of **1** in a nonpolar solvent favours the neutral, bond-alternated form, while in polar solvents the CT form will contribute more equally and lead to a polar, less bond-alternate (*i.e.* more cyanine-like), ground state. In terms of the plots shown in Fig. 1,  $(\alpha_D - \alpha_A)/|t|$  decreases with decreasing bond alternation, reflected experimentally by the longer  $\lambda_{\max}$  of **1** in more polar solvents. Therefore, we expected  $\beta$  to increase with decreasing  $(\alpha_D - \alpha_A)/|t|$  (increasing  $\lambda_{\max}$ ) and then possibly decrease if  $(\alpha_D - \alpha_A)/|t|$  becomes sufficiently small (as indicated by even longer  $\lambda_{\max}$  in very polar solvents). Consistent with our model, EFISH measurements of **1**, performed in a variety of solvents<sup>7</sup> ranging in polarity from cyclohexane to *N*-methyl-pyrrolidin-2-one (NMP), exhibited peaked behaviour. Compared to **1** (in chloroform solution), **2** (in chloroform solution) absorbs at higher energy and is substantially less nonlinear. At first glance, considering the structural similarity between the two compounds, this result is somewhat surprising. However, given the solvatochromic behaviour observed for **1**, we considered the possibility that the decreased  $\lambda_{\max}$  and  $\beta$  observed for **2** could be attributed to a bound solvent effect. In particular, the nonpolar *tert*-butyl groups could hinder solvent stabilization of charge on the quinone oxygen atom, thereby

destabilizing the charge-transfer state. Accordingly, we measured the optical spectrum of **1** in the relatively nonpolar solvent cyclooctene (95% *cis*, 5% *trans*). We found  $\lambda_{\max}$  to be  $559 \pm 2$  nm, (within experimental error the same value observed for **2** in chloroform) but the measured nonlinearity ( $\beta$ ) of **1** in this solvent,  $20 \times 10^{-30}$  esu, is substantially lower than that for **2** in chloroform ( $78 \times 10^{-30}$  esu). Thus, although the lower nonlinearity of **2** is consistent with bound solvent of low polarity (the *tert*-butyl groups) affecting the relative energies of the ground and excited states, the relatively poor absolute agreement between these numbers suggests that other factors may be coming into play as well.

In conclusion, we have prepared and characterized a class of compounds related to dimethylindaoaniline, whose  $\beta$  measured by EFISH were found to increase with the electron-donating strength as expected. The lower  $\beta$  and higher-energy absorption of **2** compared to **1** can be rationalized as resulting from the destabilization of the CT form of **2** owing to the non-polar environment experienced by the quinone oxygen arising from the proximity of the two *tert*-butyl groups. A study of non-*tert*-butylated dyes of the same class is in progress.

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