

The Effect of varying Ground-state Aromaticity on the First Molecular Electronic Hyperpolarizabilities of Organic Donor–Acceptor Molecules

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A series of compounds of the form 4-dimethylaminophenyl–polyene–acceptor, where the polyene ranges from nothing to all-*trans*-1,3,5-hexatriene and the acceptor is 2-nitrovinyl, formyl, or 2,2-dicyanovinyl has been prepared and their β values measured by solution electric-field-induced second-harmonic generation; these molecules, which lose only one aromatic resonance upon charge-transfer excitation, show enhanced β compared to bi-aromatic molecules with the same substitution and total conjugation length, such as 4-dimethylamino-4'-nitrostilbene (DANS), a well-known benchmark for high β organic molecules.

Using a two-state model,^{1,2} it was recently shown that there is an optimal combination of donor and acceptor strengths for a given bridge that maximizes the first molecular electronic hyperpolarizability (β).³ More recently, we have shown that the peaked dependence of β upon donor and acceptor strengths can be correlated with an optimal degree of bond length alternation in a polyene-like bridge that links the donor and acceptor.⁴ To better understand this correlation, it is illustrative to discuss the geometric and electronic structure of the ground state in terms of a linear combination of the two limiting charge-transfer (CT) resonance structures, one of which is neutral and the other is charge separated. For polyenes with weak donors and acceptors, the neutral resonance form will dominate the ground-state wavefunction and the molecule will exhibit a high degree of bond-length alternation.⁵ As the donor and acceptor strength increases, so will the contribution of the charge-separated resonance form to the ground-state structure [Fig. 1(a)]. When the two resonance structures contribute equally, the molecule will exhibit essentially no bond alternation, behaving much like a cyanine, and will have vanishing β .³ Molecules in which the neutral resonance form contains aromatic rings will have a diminished contribution of the charge-separated form to the ground-state wavefunction due to the energetic price associated with the loss of aromaticity in that form. As a result, molecules with aromatic ground states will tend to be more bond alternated for a given, moderate strength donor and

acceptor pair than a polyene of comparable length [Fig. 1(b) and (c)].⁴ We believe that, to date, aromatic molecules with sufficiently strong donors and acceptors have not been synthesized to maximize β .[†] Indeed, the search for aromatic molecules with higher β has become a search for ever stronger donors and acceptors.^{6–8} Based on the above argument, we have suggested that only moderately strong donors and acceptors can give high β molecules when placed on linkers with lessened aromaticity in the ground state.^{1,3} This report corroborates our hypothesis.

A series of molecules has been prepared using the dimethylaminophenyl group as the donor, the nitrovinyl, formyl or dicyanovinyl group as the acceptors, and polyene linkers of different lengths. Since these molecules have only one ring that loses aromatic stabilization upon CT excitation, we expect them to have more nearly the correct degree of bond-length alternation and, therefore, to exhibit a larger β with moderate electron acceptors than similarly substituted stilbenes or other bi-aromatic compounds of equal conjugation length. Experimental measurements of β by solution

[†] If the donor and acceptor strengths are increased beyond the optimal point, the change in dipole moment between the CT excited state and the ground state will lower β . Experimental β values of aromatic compounds have been found to increase with increasing donor and acceptor strength.^{6,7}

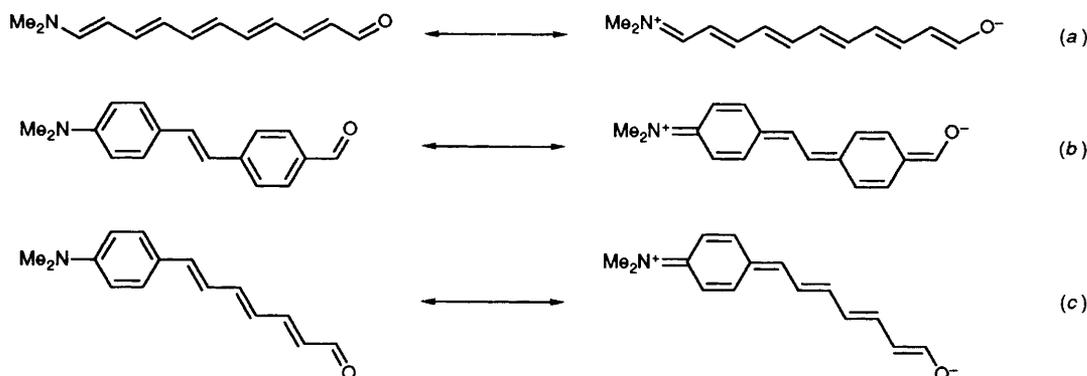


Fig. 1 Neutral and charge-transfer resonance forms for molecules of comparable conjugation lengths: α -dimethylamino- ω -formyl substituted π -systems; (a) polyene (b) stilbenyl, (c) phenylhexatrienyl

electric-field-induced second-harmonic generation (EFISH) measurements⁹⁻¹¹ support this hypothesis. Details of the EFISH experiment have been reported elsewhere.⁶ The measured β values (using fundamental wavelength $\lambda_0 = 1907$ nm) were corrected for dispersive enhancement using the two-state model¹ to yield the zero-frequency hyperpolarizability $\beta(0)$. We find that β of these model compounds are indeed higher than in analogous bi-aromatic systems. Table 1 presents the optical data for this series of compounds, including previously reported values inserted for comparison.[‡] The deleterious effect that phenyl rings has on β is clear: **6** and **7** have the same conjugation length and acceptor substitution, but $\beta(0)$ for the biphenyl is lower by a factor of 2.5. Likewise, in comparing **10** with **12** and **14** with **15**, $\beta(0)$ values for the bi-aromatic compounds are lower than their mono-aromatic homologues by factors of 3.0 and 2.4. Similarly, the aldehyde **8** exhibits a $\beta(0)$ value nearly 3.5 times greater than its bi-aromatic homologue **11**. Indeed, even the much shorter **1** shows a higher $\beta(0)$ than **11**, with which it differs structurally only by the absence of the second phenyl ring. Thus, inserting a *para*-phenyl ring into **1** adjacent to the formyl group increases λ_{\max} incrementally but reduces $\beta(0)$. Similarly, in comparing **6** with **15** and **10** with **16**, a decrease in $\beta(0)$ results from the introduction of the second phenyl ring, although here λ_{\max} is longer in the more nonlinear nitrovinyls.

To realize high β molecules in aromatic systems, strong donors and acceptors are required. In this context it has been suggested that the dicyanovinyl group is superior to the nitro group as an electron acceptor.⁸ If instead the dicyanovinyl and the nitrovinyl groups (which have identical numbers of conjugated atoms in the longest run) are compared, the nitro compounds except for the longest pair, **13** vs. **14** are found to give higher nonlinearities, and for all but the shortest **3**, improved transparency as well. Thus, comparing **2** with **3**, **5** with **6**, and **9** with **10** shows that $\beta(0)$ (nitrovinyl)/ $\beta(0)$ (dicyanovinyl) to be 1.5, 1.8, and 1.6 even though λ_{\max} of the nitrovinyls becomes increasingly less than for the dicyanovinyls as the conjugation length increases. However, for **13** vs. **14**, this ratio is 0.71.

To understand the results for the shorter compounds, it is important to realize that the EFISH determined β is a vectorial projection of the β tensor along the molecular dipole direction, *i.e.* it samples the dominant tensor components only if the dipole direction is coincident with the molecular charge-transfer axis. For both the dicyanovinyl and the nitrovinyl substituted molecules, the group dipole moment of the acceptor is not coincident with the charge transfer axis of the molecule. Since the dicyanovinyl moiety may have a larger group dipole than the nitrovinyl moiety and thus its contribu-

Table 1 Summary of linear and nonlinear optical data for compounds of the form $\text{Me}_2\text{NC}_6\text{H}_4-(E-\text{CH}=\text{CH})_n-\text{R}$. All phenyl groups are 1,4-disubstituted. Conjugation length (column 4) counts the longest chain of atoms with multiple bonds or lone pairs. λ_{\max} , μ and β are as measured in chloroform solution, and the dispersion-corrected $\beta(0)$ values (last column) were calculated using a two-state model.¹

Com- pound	<i>n</i>	R	Length/ atoms	λ_{\max} / nm	μ / 10^{18} esu	β / 10^{30} esu	$\beta(0)$ / 10^{30} esu
1 ⁷	1	-CHO	9	384	5.6	30	24
2 ⁷	0	-CH=C(CN) ₂	9	420	7.8	32	25
3 ⁷	1	-NO ₂	9	438	6.5	50	37
4 ⁷	2	-CHO	11	412	6.0	52	40
5 ⁷	1	-CH=C(CN) ₂	11	486	8.4	82	57
6 ⁷	2	-NO ₂	11	466	6.5	140	100
7 ⁷	0	-C ₆ H ₄ -NO ₂	11	390	5.5	50	40
8 ⁷	3	-CHO	13	434	6.3	88	66
9 ⁷	2	-CH=C(CN) ₂	13	520	9.0	163	106
10 ⁷	3	-NO ₂	13	487	6.6	240	166
11 ⁷	1	-C ₆ H ₄ -CHO	13	406	3.5	24	19
12 ⁷	1	-C ₆ H ₄ -NO ₂	13	430	6.6	73	55
13 ⁷	3	-CH=C(CN) ₂	15	546	8.9	432	267
14 ⁷	4	-NO ₂	15	502	7.6	280	188
15 ⁷	2	-C ₆ H ₄ -NO ₂	15	442	7.6	107	79
16 ⁷	3	-C ₆ H ₄ -NO ₂	17	458	8.2	131	95

tion to the overall dipole moment direction may be larger, then the EFISH experiment may sample a smaller component of the β tensor for the dicyanovinyl molecules. Another possible explanation is that the dicyanovinyl is in fact a stronger acceptor than the nitrovinyl, however the localization of electron density in the C-N triple bonds prevents effective delocalization onto the nitrogen atoms of the acceptor. This, in effect, makes the dicyanovinyl compounds shorter molecules with stronger acceptors than the corresponding nitrovinyls. In comparisons of molecules of different length and different acceptor strength, it has been previously observed that the longer molecule has an improved transparency nonlinearity trade-off. This may be attributed to an increase in the transition dipole moment between the ground and charge-transfer states. At present, it is not clear why this trend is reversed for **13** vs. **14**.

In conclusion, we have prepared a series of reduced ground-state aromaticity, conjugated donor-acceptor molecules and measured their second-order optical nonlinearities by the solution EFISH method. Without exception, the observed nonlinearities are substantially greater than in bi-aromatic systems of otherwise equal length and substitution indicating the benefit of avoiding phenyl ring-based conjugated linkers when designing high β chromophores for nonlinear optics.

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‡ All new compounds in Table 1 gave satisfactory characterization data.

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