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

Bruce G. Tiemann, a,b Lap-Tak Cheng*c and Seth R. Marder*a,b

a Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA
b Molecular Materials Resource Center, The Beckman Institute, 139-74, California Institute of Technology, Pasadena, CA 91125, USA
c Central Research and Development Department, E. I. DuPont de Nemours and Company, Inc., Wilmington, DE 19880-0356, USA

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-nitroviny1, 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.1 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
electric-field-induced second-harmonic generation (EFISH) measurements\textsuperscript{6-11} support this hypothesis. Details of the EFISH experiment have been reported elsewhere.\textsuperscript{6} The measured $\beta$ values (using fundamental wavelength $\lambda_0 = 1907$ nm) were corrected for dispersive enhancement using the two-state model\textsuperscript{1} to yield the zero-frequency hyperpolarizability $\beta(0)$. We find that $\beta$ of these model compounds is 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.\textsuperscript{6} The deleterious effect that phenyl rings have on $\beta$ 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 $\lambda_{\text{max}}$, 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 $\lambda_{\text{max}}$ is longer in the more nonlinear nitrovinyls.

To realize high $\beta$ 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.\textsuperscript{5} 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 $\lambda_{\text{max}}$ of the nitrovinys 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 $\beta$ is a vectorial projection of the $\beta$ tensor along the molecular dipole direction, \textit{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-

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|l|l|l|l|}
\hline
Compound $n$ & $R$ & Length/\text{max} & $\lambda_{\text{max}}/\text{nm}$ & $p'/\text{10}^8\text{esu}$ & $\beta/\text{10}^{20}\text{esu}$ & $\beta(0)/\text{10}^{20}\text{esu}$ \\
\hline
1 & -CHO & 9 & 384 & 5.6 & 30 & 24 \\
2 & -CH-(CN)$_2$ & 9 & 420 & 7.8 & 32 & 25 \\
3 & -NO$_2$ & 9 & 438 & 6.5 & 50 & 37 \\
4 & -CHO & 11 & 412 & 6.0 & 52 & 40 \\
5 & -CH-(CN)$_2$ & 11 & 486 & 8.4 & 82 & 57 \\
6 & -NO$_2$ & 11 & 466 & 6.5 & 140 & 100 \\
7 & -CH$_2$-NO$_2$ & 11 & 390 & 5.3 & 50 & 40 \\
8 & -CHO & 13 & 454 & 6.3 & 88 & 66 \\
9 & -CH-(CN)$_2$ & 13 & 520 & 9.0 & 163 & 106 \\
10 & -NO$_2$ & 13 & 487 & 6.6 & 240 & 166 \\
11 & -CH$_2$-CHO & 13 & 406 & 3.5 & 24 & 19 \\
12 & -CH$_2$-NO$_2$ & 13 & 430 & 6.6 & 73 & 55 \\
13 & -CH-(CN)$_2$ & 15 & 546 & 8.9 & 432 & 267 \\
14 & -NO$_2$ & 15 & 502 & 7.6 & 280 & 188 \\
15 & -CH$_2$-NO$_2$ & 15 & 442 & 7.6 & 107 & 79 \\
16 & -CH$_2$-NO$_2$ & 17 & 458 & 8.2 & 131 & 95 \\
\hline
\end{tabular}
\caption{Summary of linear and nonlinear optical data for compounds of the form $\text{Me}_2\text{NC}_{\text{N}4}\text{H}_4\text{-(E-CH-CH)}_n\text{R}$. All phenyl groups are 1,4-disubstituted. Conjugation length (column 4) counts the longest chain of atoms with multiple bonds or lone pairs. $\lambda_{\text{max}}$, $p'$, and $\beta$ are measured in chloroform solution, and the dispersion-corrected $\beta(0)$ values (last column) were calculated using a two-state model.\textsuperscript{1}}
\end{table}

\textsuperscript{†} All new compounds in Table 1 gave satisfactory characterization data.

\textsuperscript{1} The work in this paper was performed, in part, by the Center for Space Microelectronics Technology, Jet Propulsion...
Laboratory (JPL), California Institute of Technology and was sponsored by the Strategic Defense Initiative Organization, Innovative Science and Technology Office and The Defense Advanced Research Projects Agency through grant No. 91-NC-146 administered by the Air Force Office of Scientific Research through agreements with the National Aeronautics and Space Administration. Support from the National Science Foundation (Grant CHE-9106689) is also gratefully acknowledged.

Received, 27th October 1992; Com. 2105739E

References