Inorg. Chem. **2001,** *40,* 3373−3380

Polyhedral-Based Nonlinear Optical Materials. 2.[1] Theoretical Investigation of Some New High Nonlinear Optical Response Compounds Involving Polyhedral Bridges with Charged Aromatic Donors and Acceptors

Damian G. Allis and James T. Spencer*

Department of Chemistry and W. M. Keck Center for Molecular Electronics, Center for Science and Technology, Syracuse University, Syracuse, New York 13244

Received July 17, 2000

A theoretical study of several new classes of polyhedral-based molecules has shown that these species display large calculated nonlinear optical responses. These new classes of molecules are based on charged aromatic subunits connected through polyhedral cluster bridges, such as *closo*-[1-(C_7H_6)-12-(C_5Me_4)$C_2B_{10}H_{10}$]. These compounds show calculated first hyperpolarizabilities (β) ranging from 6.5 to 8413.9 × 10^{-30} cm^5 esu^{-1}. A basis for understanding the origin of these large responses is proposed based on the two-state model and consideration of the orbital and electronic features of the molecules. In general, the highest occupied molecular orbitals for these species are localized on the aromatic donor rings, such as the cyclopentadienyl system, while the lowest unoccupied molecular orbitals are largely on the aromatic acceptor rings, such as the tropylium system. The electronic properties of these polyhedral-based systems appear to be significantly different from the analogous organic [5.6.7]quinarene system (tropyliumcyclopentadienylbenzene). The organic quinarene appears to behave as a completely electron-delocalized system over all three rings while the polyhedral-based compounds can best be described as consisting of two relatively independent, highly polarized regions.

Introduction

The critical aspect of nonlinear optical (NLO) design is the response of materials to applied electromagnetic fields, specifically relating to how the materials generate new electromagnetic fields with altered properties, such as frequency and phase, after irradiation with an external electromagnetic field. Materials efficient at nonlinear photonic signal manipulation are of interest for a large number of technological applications, including optical communications and computation, optical switching and limiting, data storage and retrieval, and dynamic image processing, among numerous others.[2] One of the primary limitations encountered, however, is the availability of suitable materials with large nonlinear optical responses. If the relationship between molecular architecture and nonlinear optical response were fully understood, it would then be possible to rationally tune the observed nonlinear response by selectively manipulating the chemical structure of the chromophore. Major research initiatives have therefore been synergystically directed both toward gaining a detailed understanding of fundamental structural−optical property relationships and the experimental syntheses and nonlinear optical response measurements of designed optical modulators. A great deal of computational and experimental work, primarily with organic systems, has now begun to effectively address these important relationships.[2]

Molecular NLO materials, in contrast with more traditional NLO solid-state materials, have many attractive properties, including ultrafast response times, lower dielectric constants, significantly improved processability, facile three-dimensional design capabilities, and greatly enhanced NLO responses.[3] Most molecular nonlinear optical materials employ electron-donating (donors) and electron-withdrawing groups (acceptors) connected through an organic π-delocalized framework,[3] although several metalloorganic systems have also been explored.[4] Recently, theoretical work with twisted molecular π-chromophores has suggested new approaches in the design of enhanced NLO molecular materials.[5]

The rational design and optimization of new NLO materials has primarily involved addressing what chemical factors affect the molecular first hyperpolarizabilities (β) of the material. The most commonly employed model for understanding the fundamental relationships between β and molecular structure is the two-state model.[6] When the electric field component of a moderate strength electromagnetic wave interacts with a molecule, a linear electronic polarization occurs within the molecule due to photon−electron interactions.[2] The incident oscillating electric field causes an oscillating dipole to be generated in the chromophore proportional to the applied field strength. At high incident field strength, however, the induced electronic polarization becomes nonlinear, ultimately leading to second harmonic generation. A power series expansion can be used to describe the nonlinear behavior of the induced polarization. In rigorously centrosymmetric chromophores, the second-order response (β) is zero. Molecular parameters that enhance a noncentrosymmetric electronic polarization in a molecule, therefore, enhance

---

(1) Part I: Allis, D. G.; Spencer, J. T. *J. Organomet. Chem.* **2000**, *614*, 309.

(2) (a) Prasad, P. R.; Williams, D. J. *Introduction to Non-linear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (b) Chemla, D. S.; Zyss, J. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic: Orlando, FL, 1987. (c) Hann, R. A.; Bloor, D. *Organic Materials for Nonlinear Optics*; Royal Society of Chemistry: London, 1989. (d) Zernike, F.; Midwinter, J. E. *Applied Nonlinear Optics*; Wiley: New York, 1973; p 41.

(3) Blau, W. *Phys. Technol.* **1987**, *18*, 250.

(4) Cummings, S. D.; Cheng, L.-T.; Eisenberg, R. *Chem. Mater.* **1997**, *9*, 440.

(5) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 11174.

(6) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.

10.1021/ic0007761 CCC: $20.00

its second-order response. For organic NLO materials involving electron-donating and electron-withdrawing groups (often referred to as "push−pull" systems), the value of β is primarily dictated by the intramolecular charge polarization, the oscillator strength, and the excited state of the compound. The donor and acceptor groups employed in most molecular NLO materials have primarily functioned to achieve an asymmetric electronic distribution through simple inductive or resonance effects, such as alkyl and amino groups for the electron donors and nitro and SO_2CH_3 groups for the electron acceptors. The two-state model assumes that second-order responses (β) are thus due primarily to an intramolecular charge-transfer interaction between the acceptor and donor portions of the chromophore. The overall value of β is given by the sum of an additive portion (β_{add}) and a charge-transfer portion (β_{ct}). The additive portion (β_{add}) accounts for the interactions between the individual substitutents and the bridge framework. The dominant intramolecular electronic redistribution, or charge-transfer contribution (β_{ct}), is given by

$$\beta_{ct} = \frac{3e^2}{2\hbar^3} \frac{\omega_{ge} f_{ge} \Delta\mu_{ge}}{[\omega_{ge}^2 - \omega^2][\omega_{ge}^2 - 4\omega^2]}$$

(where ω_{ge} is the optical transition energy to the lowest excited state, f_{ge} is the associated oscillator strength, $\Delta\mu_{ge}$ is the difference between the ground- and excited-state dipole moments, and ω is the excitation energy of the light field).[4] The two-state model is an approximate description but has been shown to be particularly useful in understanding the nonlinear optical properties of many molecular systems.[2] Thus, in push−pull organic compounds, increasing the length of the π-conjugated pathway between the donating and the withdrawing groups and increasing the donor−acceptor group strengths typically leads to an increase in the observed hyperpolarizabilities.[7] Increasing the length of the π-framework, however, also usually leads to a bathochromic shift of the intramolecular charge-transfer absorption, typically into the visible region, which often limits the usefulness of the these materials. The calculated second-order responses for twisted π-chromophores, however, have been recently shown to be relatively unresponsive toward these typical strategies for increasing β. This is primarily because the second-order responses for these twisted compounds are mostly dependent on factors that effectively bring about and ultimately stabilize intramolecular charge separation.[5]

Quantum mechanical calculations have greatly enhanced the study of the relationships between nonlinear optical responses and molecular architectures. The application of these theoretical methods in NLO work has been recently very well-reviewed.[8] Three methods have been extensively and effectively employed in these calculations: *semiempirical* (MOPAC and ZINDO principally) methods, density-functional theory methods, and ab initio methods.[8] Significant advantages in calculational speed have been particularly realized by employing *semiempirical* methods, which apparently retain much of the NLO calculational accuracy obtained with higher order ab initio basis sets.[5,8] Thus, the work described in this paper employs *semiempirical* methods. Where experimental data exist, remarkably good agreement is generally obtained between *semiempirical* calculated values and experimental values of β.[8]

Many classes of molecular NLO compounds have been thus far investigated, especially organic- and organometallic-based systems.[2,3] These studies have yielded a steady progress in new molecules with enhanced second-order responses. A number of organic compounds, for example, have achieved relatively large second-order responses through the use of extended π-conjugated organic bridges with strong electron-donor and electron-acceptor groups.[7] Thus far, however, relatively little exploration has been directed toward the use of either molecular polyhedral-based systems or compounds with charged aromatic donor−acceptor moieties.[9−12] Polyhedral clusters appear to provide an entry into a new class of potentially very high second-order response molecular systems with particularly desirable chemical and physical properties.[9] Previous work has reported the synthesis and second-order responses of a series of icosahedral carboranes.[10] The first hyperpolarizabilities (second-order responses, β) for these substituted 1,2-dicarba-*closo*-dodecaborane compounds were reported to be between 2.7 and 13.2 × 10^{-30} cm^5 esu^{-1} at 1.17 eV. A second study has reported the calculated hyperpolarizabilities for the $[B_{12}H_{11}$-(*o*,*m*,*p*)-$C_2B_{10}H_{12}]^{2-}$ linked bis-cluster compounds range between 3.4 and 3.6 × 10^{-30} cm^5 esu^{-1} (β_0).[11a] These values compare favorably with the experimental value of 6.2 × 10^{-30} cm^5 esu^{-1} reported for the standard *p*-nitroaniline benchmark typically used for evaluating new NLO compounds. The NLO properties of a platinum organometallic derivative of *closo*-1,2-$[C_2B_{10}H_{12}]$ have also been reported with $\mu^*\beta_0$ values ranging between 118 and −166 × 10^{-48} esu, depending on the solvent employed for the measurement.[11b] Finally, one very recent paper has appeared that reports the synthesis and NLO response of a tropylium-substituted 1-carba-*closo*-dodecaborate anion that displays an experimental β of 7.2 × 10^{-30} cm^5 esu^{-1} at 1.17 eV (calcd β at 0.5 eV = 34.6 × 10^{-30} cm^5 esu^{-1}).[12]

As described by the two-state model, the first hyperpolarizabilities for molecular NLO materials are primarily determined by their intramolecular polarizations, oscillator strengths, and excited states. Chemical approaches designed to appropriately alter these parameters by modifying the molecular architecture of the chromophore should therefore directly result in increases in the observed nonlinear optical response. Several reasonably successful approaches have been developed for new organic and organometallic systems that have yielded observed increases in β by nearly 2 orders of magnitude. When approaches that increase intramolecular polarization, such as in the twisted π-organic species,[5] are coupled with appropriate bridge moieties, new materials with enhanced nonlinear optical responses should be formed. We have, therefore, investigated the use of charged aromatic organic groups, particularly the tropylium ($C_7H_7^+$) and cyclopentadienyl ($C_5H_5^-$) ring systems, bridged by polyhedral boron-based cluster and π-electron delocalized units.[9] This paper deals primarily with the theoretical calculation of the molecular

---

(7) Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631.

(8) (a) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195. (b) Kurtz, H. A.; Dudis, D. S. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: New York, 1998; pp 241−298. (c) Li, D.; Ratner, M. A.; Marks, T. J. *J. Phys. Chem.* **1992**, *96*, 4325.

(9) Littger, R.; Taylor, J.; Rudd, G.; Newlon, A.; Allis, D. G.; Kotiah, S.; Spencer, J. T. In *Contemporary Boron Chemistry*; Davidson, M. G., Hughes, A. K., Marder, T. B., Wade, K., Eds.; Royal Society of Chemistry: Cambridge, U.K., 2000; Vol. 253, p 67 and references therein.

(10) (a) Murphy, D. M.; Mingos, D. M. P.; Forward, J. M. *J. Mater. Chem.* **1993**, *3*, 67. (b) Murphy, D. M.; Mingos, D. M. P.; Haggitt, J. L.; Powell, H. R.; Westcott, S. A.; Marder, T. B.; Taylor, N. J.; Kanis, D. R. *J. Mater. Chem.* **1993**, *3*, 139.

(11) (a) Abe, J.; Nemoto, N.; Nagase, Y.; Shirai, Y.; Iyoda, T. *Inorg. Chem.* **1998**, *37*, 172. (b) Base, K.; Tierney, M. T.; Fort, A.; Muller, J.; Grinstaff, M. W. *Inorg. Chem.* **1999**, *38*, 287.

(12) Grüner, B.; Janousek, Z.; King, B. T.; Woodford, J. N.; Wang, C. H.; Vsetecka, V.; Michl, J. *J. Am. Chem. Soc.* **2000**, *122*, 11274.

structures, electronic structures, and nonlinear optical responses of new cluster-based molecules with both charged aromatic donor and acceptor moieties. Subsequent papers describe the synthesis, characterization, and properties of prototype examples of these new polyhedral-based molecular systems.

Computational Methodology

Semiempirical geometry optimization and time-dependent Hartree−Fock (TDHF) first hyperpolarizability calculations were performed using both GAMESS−US (geometry optimizations and field-dependent NLO responses from 0.0 to 1.17 eV) and MOPAC (geometry optimizations and field-dependent NLO responses at 0.5 eV).[13] All structures were fully optimized with the AM1 Hamiltonian without symmetry restrictions using methods we have previously published.[13] The choice of employing the AM1 Hamiltonian over modified intermediate neglect of differential overlap (MINDO) parametrization was determined primarily by the literature reports, which indicate that (i) AM1 provides superior structural and electronic results for π-organic systems, (ii) AM1 is significantly better at accurately predicting dipole moments, and (iii) AM1 provides better structural information, including improved BH and BB bond distances for the classes of boron compounds investigated here.[13c−f] AM1 calculations have been reported for an extensive set of boron-containing compounds and provide consistently better results than those given by MINDO.[13f] Nonresonant TDHF first hyperpolarizabilities were calculated using methods established in the literature[10] and were well-reviewed elsewhere.[8] Absorption spectra and oscillator strengths were calculated using the maximum number allowed of single (26) and double (18) excitations with the INDO/S Hamiltonian in ZINDO.

Results and Discussion

To assess the potential of charged aromatic donor−acceptor moieties coupled with molecular polyhedral-based systems for NLO applications, we have employed *semiempirical* calculational methods to investigate the structures, bonding, and nonlinear optical responses of a series of compounds that incorporate these features. We have focused on well-known main group clusters and substitution patterns that are well-established in the literature.[14,15] The structures of the polyhedra investigated include both boranes and carboranes and display a diversity of three-dimensional structures including *closo* frameworks, such as $C_2B_{10}H_{12}$, $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$, and $B_6H_6^{2-}$; *nido* structures, such as $B_{10}H_{14}$, $C_2B_4H_6$, and B_5H_9; and the complex *conjuncto* framework structures, such as $B_{18}H_{22}$.[14−16]

The structures and calculated nonresonant β values for the compounds investigated in this work are given in Tables 1 (carboranes) and 2 (boranes). Each structure was fully self-consistent field optimized at the AM1 level of theory (without symmetry restrictions)[13], and nonresonant β values were calculated using the methods previously reported in detail.[8b] The *semiempirical* methods employed here have been shown, by extensive previous work, to accurately reproduce experimental NLO responses, especially second-order responses, over a range of at least 3 orders of magnitude.[19]

The molecular structures for several of the boron-based polyhedral compounds studied in this work are shown in Figure 1. The overall calculated geometries, bond lengths, and bond angles within the borane and carborane cages were found to be very consistent with known structures that incorporate similar cage units.[2,14−16] Additionally, all the cyclopropenylium, cyclopentadienyl, and tropylium rings in the structures were found to be planar, as anticipated based on the proposed π-aromaticity of the rings. Substitution of various organic groups, such as methyl, phenyl, cyano, nitro, and indenyl moieties, onto these rings did not affect their planarity. The observed distances and angles within these ring systems were also found to be fully consistent with known structures containing these ring systems.[20,21]

Molecular NLO materials have primarily achieved asymmetric electronic distributions through simple inductive or resonance effects. Terminally bound, charged aromatic donor−acceptor moieties, such as the tropylium (*cyclo*-$C_7H_7^+$, Tp), cyclopropenylium (*cyclo*-$C_3H_3^+$, CPr), and cyclopentadienyl (*cyclo*-$C_5H_5^-$, Cp) moieties, however, may act both through charge-based inductive and Hückel $4n + 2$ aromatic π-stabilization effects to achieve a significantly polarized electronic arrangement.[17] It should, therefore, be possible to employ aromatic π-stabilization as a driving force to achieve very significant charge separations. The coupling of mutually reinforcing NLO molecular architectural features such as the π-aromatic stabilization of charged donors and acceptors with the unique properties of polyhedral bridges for maximizing intramolecular polarization and, therefore, potentially increasing the observed nonlinear optical responses has not been previously investigated.

From inspection of the results in Table 1, it is clear that these polyhedral-based compounds display exceptionally large calculated first hyperpolarizabilities (β). These values appear to be among the largest reported for molecular compounds to date. For example, the calculated β values for $[1\text{-}(C_7H_6)\text{-}12\text{-}(C_5Me_4)\text{-}B_{12}H_{10}]^{2-}$ ($\beta_{\mathrm{calcd(0.5eV)}} = 1209 \times 10^{-30}$ cm^5 esu^{-1}) and $[(C_7H_6)\text{-}B_{18}H_{20}(C_5Me_4)]$ ($\beta_{\mathrm{calcd(0.5eV)}} = 4146 \times 10^{-30}$ cm^5 esu^{-1}), given in Table 2, are more than 225 and 780 times larger than the commonly used *p*-nitroaniline NLO benchmark at 0.5 eV. It is important to note that the calculated values of β in Tables 1 and 2 are at an excitation energy of 0.5 eV, while many of the

---

(13) (a) Glass, J. A., Jr.; Whelan, T. A.; Spencer, J. T. *Organometallics* **1991**, *10*, 1148. The calculations employed here utilized MOPAC and ZINDO within the 4.0.1 CAChe Worksystem (Oxford Molecular) software package. Oscillator strengths were calculated using the INDO/S Hamiltonian in ZINDO. (b) GAMESS: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347. (c) MOPAC: Stewart, J. J. P. *J. Comput.-Aided Mol. Des.* **1990**, *4*, 1. (d) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221. (e) ZINDO: Zerner, M. C. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1991; pp 313−365. (f) Dewar, M. J. S.; Jie, C.; Zoebisch, E. G. *Organometallics* **1988**, *7*, 513.

(14) Grimes, R. N. *Carboranes*; Academic: New York, 1970.

(15) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1985.

(16) (a) Onak, T. Polyhedral Organoboranes. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, 1982; Vol. 1, Chapter 5.4, p 411. (b) Grimes, R. N. Metallacarboranes and Metallaboranes. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, 1982; Vol. 1, Chapter 5.5, p 485. (c) Spencer, J. T. In *The Encyclopedia of Inorganic Chemistry*; King, R. B., Burdett, J. K., Wells, R., Crabtree, R., Sleight, A., Scott, R., Lukehart, C., Eds.; Wiley: New York, 1994; pp 538−557.

(17) Lloyd, D. *Chemistry of Conjugated Cyclic Compounds: To Be or Not to Be Like Benzene*; Wiley: New York, 1989.

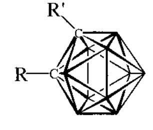
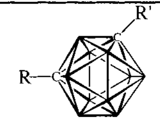
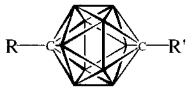
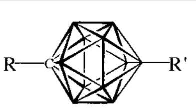
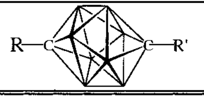
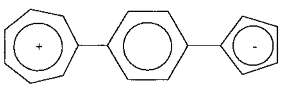
(18) (a) Harmon, K. M.; Harmon, A. B.; Thompson, B. C.; Spix, C. L.; Coburn, T. T.; Ryan, D. P.; Susskind, T. Y. *Inorg. Chem.* **1974**, *13*, 862. (b) Harmon, K. M.; Nelson, T. E.; Stachowski, B. M. *J. Mol. Struct.* **1995**, *350*, 135. (c) Harmon, K. M.; Harmon, A. B.; Thompson, B. C. *J. Am. Chem. Soc.* **1967**, *89*, 5309.

(19) Barnett-Thamattoor; Zheng, G.; Ho, D. M.; Jones, M., Jr. *Inorg. Chem.* **1996**, *35*, 7311.

(20) (a) Harmon, A. B.; Harmon, K. M. *J. Am. Chem. Soc.* **1966**, *88*, 4093. (b) Harmon, K. M.; Harmon, A. B.; MacDonald, A. A. *J. Am. Chem. Soc.* **1969**, *91*, 323.

(21) Harmon, K. M. In *Carbonium Ions*; Olah, G. A., Ed.; Interscience Publishers: New York, 1973; Vol. 4, p 1579.

Table 1. Selected Calculated Average Second-Order Responses ($\mu\beta$ and β) at 0.5 eV for Carborane Compounds[a,b]

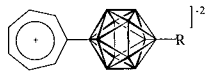
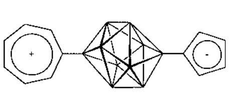
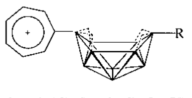
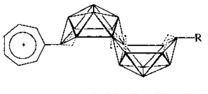
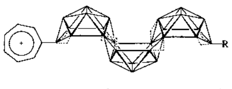
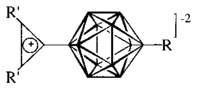
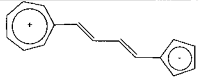
$[(R)C_2B_{10}H_{10}(R')]$	R	$\mu\beta$[a]	β[a]
 *1,2-(ortho)-isomer*	$R = C_7H_6$, $R' = C_5H_4$, charge = 0	688.8	55.1
	$R = C_7H_6$, $R' = CH_3$, charge = +1[c]	209.7	18.4[d]
	$R = B_{12}H_{11}$, $R' = H$, charge = -2[c]	131.6	8.6[e]
 *1,7-(meta)-isomer*	$R = C_7H_6$, $R' = C_5H_4$, charge = 0	1330.3	110.1
	$R = B_{12}H_{11}$, $R' = H$, charge = -2[c]	133.5[e]	9.3[e]
 *1,12-(para)-isomer*	$R = C_7H_6$, $R' = C_5H_4$, charge = 0	11686.7	681.9
	$R = C_7H_6$, $R' = C_5Me_4$, charge = 0	15767.1	998.0
	$R = C_7H_6$, $R' = C_5Et_4$, charge = 0	17903.0	1063.5
	$R = C_7H_6$, $R' = C_5(CN)_2Me_2$, charge = 0	36716.7	1353.5
	$R = C_7H_6$, $R' = C_5(CN)_2Ph_2$, charge = 0	54126.4	1783.1
	$R = B_{12}H_{11}$, $R' = H$, charge = -2[c]	159.2	10.4[e]
	$R = 12\text{-}(C_7H_6B_{12}H_{10})$, $R' = C_5H_4$, charge = -2[c]	4393.8	158.3
	$R = 12\text{-}(C_5H_4B_{12}H_{10})$, $R' = C_7H_6$, charge = -2[c]	15512.5	1226.0
$[(R)CB_{11}H_{10}(R')]$		$\mu\beta$[a]	β[a]
	$R = C_7H_6$, $R' = C_5H_4$, charge = -1[c]	1369.0	118.2
	$R = C_5H_4$, $R' = C_7H_6$, charge = -1[c]	21704.0	1064.6
	$R = H$, $R' = C_7H_6$, charge = 0[f]	455.1	36.6[f]
	$R = C_7H_6$, $R' = H$, charge = 0	550.3	34.4
$[(R)C_2B_8H_8(R')]$		$\mu\beta$[a]	β[a]
	$R = C_7H_6$, $R' = C_5H_4$, charge = 0	7785.7	503.6
	$R = C_7H_6$, $R' = C_5Me_4$, charge = 0	9393.6	664.8
		$\mu\beta$[a]	β[a]
H_2N—(Bridge)—NO_2	bridge = 1,4-C_6H_4, charge = 0	43.5	5.3 6.2[e] 16.2[g]
	bridge = 1,12-$B_{12}H_{10}$, charge = -2[c]	13.2	2.1
$[1,4\text{-}(C_7H_6)C_6H_4(R)]$		$\mu\beta$[a]	β[a]
 [5.6.7]quinarene system	*all co-planar*	222.7	52.1
	perpendicular[h]	7924.3	383.1

[a] Second-order responses (β) were calculated using *semiempirical* methods with AM1 parametrization at 0.5 eV using the E4 method, unless otherwise noted. The values of β are reported in units of 10^{-30} cm^5 esu^{-1}, and the values of $\mu\beta$ are given in units of 10^{-48} esu. [b] Shown for representative molecules is a schematic line drawing. The terminal cage, tropylium, and cyclopentadienyl hydrogens are omitted from the drawings, and cage borons are shown as unlabeled vertexes. [c] Dipole moments of ions were calculated by setting the origin at the center of gravity. This is performed as the default in the MOPAC program and used for the calculations reported here. [d] Known cationic compound (ref 18c), although an experimental hyperpolarizability was not measured. [e] Literature β_0 values (ref 11) have been reported using ab initio calculations at 6-31G** for these compounds as 1,12-$[(B_{12}H_{11})(C_2B_{10}H_{11})]^{2-} = 3.4$, 1,7-$[(B_{12}H_{11})(C_2B_{10}H_{11})]^{2-} = 3.6$, and 1,2-$[(B_{12}H_{11})(C_2B_{10}H_{11})]^{2-} = 3.6 \times 10^{-30}$ cm^5 esu^{-1}. For comparison, *p*-nitroaniline had a β value of 6.2×10^{-30} cm^5 esu^{-1} using similar calculations (ref 11). [f] Known cationic compound (ref 12) with an experimental hyperpolarizability of $236 \pm 50 \times 10^{-30}$ cm^5 esu^{-1} at 1.17 eV. [g] Calculated with the Pariser−Parr−Pople model (PPP) at 1.17 eV (ref 8). [h] The tropylium and cyclopentadienyl rings are perpendicular to the central phenylene ring.

values reported in the literature are at 1.17 eV. The magnitude of β is very sensitive to excitation energy and increases significantly with increases in energy.[8] Thus, while the NLO responses given in Tables 1 and 2 for the new compounds are very large, they are even more remarkable when compared to other known compounds at similar excitation energies. This is seen most clearly in Figure 2, which compares the responses of the new compounds with *p*-nitroaniline as a function of excitation energy. Most of our calculations, however, were performed primarily at an excitation energy of 0.5 eV both to completely ensure that nonresonant hyperpolarizabilities were calculated and for calculational facility. High molecular hyperpolarizabilities must, however, be coupled with an appropriate three-dimensional assembly in a noncentrosymmetric solid-state structure in order to achieve desired properties for application as new NLO materials.

Also given in Table 1 are the structural and NLO data for the organic (phenylene) bridged [5.6.7]quinarene species, tropyliumcyclopentadienylbenzene,[22,23] along with *p*-nitroaniline for an NLO response benchmark. The organic [5.6.7]quinarene

Table 2. Selected Calculated Average Second-Order Responses ($\mu\beta$ and β) at 0.5 eV for Borane Compounds[a,b]

Compound	R	$\mu\beta^a$	β^a
 *closo*-[1-(C_7H_6)-12-$B_{12}H_{10}$(R)]$^{-2}$	R = C_5H_4	12579.2	777.3
	R = C_5Me_4	9726.3	1208.7
	R = C_5Et_4	1724.5	1072.9
	R = $C_5(C_6H_5)_4$	1696.3	365.9
	R = indenyl	13957.7	685.6
 *closo*-[(C_7H_6)$B_{10}H_8$(R)]$^{-2}$ (1,10-isomer shown)	R = C_5H_4		
	1,2 isomer	162.0	20.8
	1,6 isomer	91.0	6.5
	1,10 isomer	3379.0	260.4
	2,3 isomer	423.9	43.7
	2,4 isomer	252.8	32.2
	2,6 isomer	1083.8	71.0
	R = C_5Me_4		
	1,10 isomer	606.5	296.1
 *nido*-[6-(C_7H_6)-9-(R)$B_{10}H_{12}$]	R = C_5H_4	22463.7	1029.8
	R = C_5Me_4	29155.6	1371.7
 *conjuncto*-[(C_7H_6)$B_{18}H_{20}$(R)]	R = C_5H_4	92138.3	2914.7
	R = C_5Me_4	129963.9	4145.7
 *conjuncto*-[(C_7H_6)$B_{27}H_{28}$(R)]	R = C_5H_4	244761.5	5937.8
	R = C_5Me_4	345786.0	8413.9
 *closo*-[1-($C_3R'_2$)-12-(R)$B_{12}H_{10}$]$^{-2}$	R = C_5H_4, R' = H	2567.1	150.8
	R = C_5Me_4, R' = H	984.0	127.6
 [1-(C_7H_6)C_4H_4-4-(C_5H_4)]		131.6	48.8

[a] Second-order responses (β) were calculated using *semiempirical* methods with AM1 parametrization at 0.5 eV using the E4 method. The values of β are reported in units of 10^{-30} cm^5 esu^{-1}, and the values of $\mu\beta$ are given in units of 10^{-48} esu. [b] Shown for each molecule is a schematic line drawing. The terminal cage and tropylium hydrogens have been omitted from the line drawings, and cage borons are shown as unlabeled vertexes. Dipole moments of ions were calculated by setting the origin at the center of gravity. This is performed as the default in the MOPAC program and used for the calculations reported here.

system provides a particularly interesting comparison for the *closo*-icosahedral borane-bridged system as shown in Figure 3. The [5.6.7]quinarene compound (**1**) and the *closo*-icosahedral borane-bridged analogue (**3**) differ structurally only by the identity of the central bridging moiety. The *closo*-icosahedral borane and carborane clusters have often been considered, with significant theoretical[24] and experimental support in the literature,[14,19,25,26] to be a main group, three-dimensional, aromatic analogue of two-dimensional organic π-aromatic species, such as benzene. The recognition of *closo*-carboranes, in general, as three-dimensional aromatic compounds comes primarily from their very high stability, nonclassical bonding, benzenelike reactivity, structural properties (bond length equalization, bond

---

[22] (a) Niem, T.; Rausch, M. D. *J. Org. Chem.* **1977**, *42*, 275. (b) Takahashi, K.; Ookawa, I.; Takase, K. *Chem. Lett.* **1974**, 1215. (c) Takahashi, K.; Takase, K. *Terahedron. Lett.* **1975**, 245.

[23] Nakamura, H.; Aoyagi, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1167.

[24] (a) Schleyer, P. v. R.; Najafian, K. *Inorg. Chem.* **1998**, *37*, 3454. (b) Schleyer, P. v. R.; Najafian, K.; Mebel, A. M. *Inorg. Chem.* **1998**, *37*, 6765.

[25] (a) Jotham, R. W. In *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*; Longman Press: London, 1974; p 450. (b) Williams, R. E. *Prog. Boron Chem.* **1970**, *2*, 37.

[26] (a) Schleyer, P. v. R.; Subramanian, G.; Dransfeld, A. *J. Am. Chem. Soc.* **1996**, *118*, 9988. (b) Schleyer, P. v. R.; Subramanian, G.; Jiao, H.; Najafian, K.; Hofmann, M. In *Advances in Boron Chemistry*; Siebert, W., Ed.; The Royal Society of Chemistry: Cambridge, U.K., 1997. (c) Schleyer, P. v. R.; Najafian, K. In *The Borane, Carborane, Carbocation Continuum*; Casanova, J., Ed.; Wiley: New York, 1998. (d) Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209. (e) Plesek, J. *Chem. Rev.* **1992**, *92*, 269. (f) Andrews, J. S.; Zyas, J.; Jones, M., Jr. *Inorg. Chem.* **1985**, *24*, 3715. (g) Albagli, D.; Zheng, G.; Jones, M., Jr. *Inorg. Chem.* **1986**, *25*, 129. (h) Ditter, J. F.; Klausmann, E. B.; Williams, R. E.; Onak, T. *Inorg. Chem.* **1976**, *15*, 1063. (i) Siwapinyoyos, G.; Onak, T. *Inorg. Chem.* **1982**, *21*, 156. (j) Olsen, R. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1970**, *92*, 5072. (k) Warren, R.; Paquin, D.; Onak, T.; Dunks, G.; Spielman, J. R. *Inorg. Chem.* **1970**, *9*, 2285. (l) Beltram, G.; Fehlner, T. *J. Am. Chem. Soc.* **1979**, *101*, 6237. (m) Takimoto, C.; Siwapinyoyos, G.; Fuller, K.; Fung, A. P.; Liauw, L.; Jarvis, W.; Millhauser, G.; Onak, T. *Inorg. Chem.* **1980**, *19*, 107. (n) Ng, B.; Onak, T.; Banuelos, T.; Gomez, F.; DiStefano, E. W. *Inorg. Chem.* **1985**, *24*, 4091. (o) Abdou, Z. J.; Soltis, M.; Oh, B.; Siwapinyoyos, G.; Banuelos, T.; Nam, W.; Onak, T. *Inorg. Chem.* **1985**, *24*, 2363. (p) Nam, W.; Onak, T. *Inorg. Chem.* **1987**, *26*, 1581.

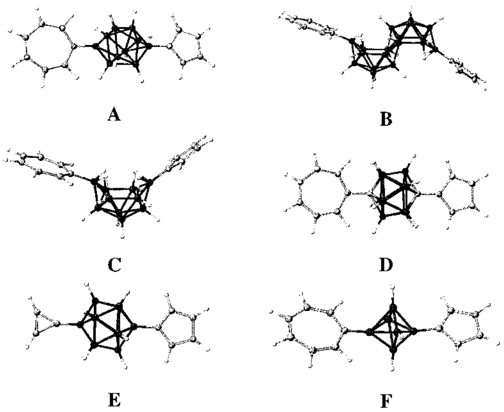


Figure 1. Selected geometry-optimized structures (AM1) for new NLO polyhedral compounds with both charged aromatic donor−acceptor moieties. (A) *closo*-[1-(C_7H_6)-10-(C_5H_4)$B_{10}H_8$]$^{2-}$, (B) *conjuncto*-[9-(C_7H_6)-9′-(C_5H_4)$B_{18}H_{20}$], (C) *nido*-[6-(C_7H_6)-9-(C_5H_4)$B_{10}H_{12}$], (D) *closo*-[1-(C_7H_6)-12-(C_5H_4)$C_2B_{10}H_{10}$], (E) *closo*-[1-(C_3H_2)-10-(C_5H_4)$B_{12}H_{10}$]$^{2-}$, and (F) *closo*-[1-(C_7H_6)-6-(C_5H_4)B_6H_4]$^{2-}$.

order indices, etc.), energetic properties (calculated resonance and aromatic stabilization energies), and magnetic considerations (chemical shifts, magnetic susceptibility anisotropies, etc.).[24,26] The clusters and the π-organic species differ, however, in their distribution of conformal minima and in details of their electronic structures. One particularly interesting difference between the two analogues is that, in the [5.6.7]quinarene compound, the bridging benzene unit is known to provide essentially complete electronic π-communication between tropylium and cyclopentadienyl units, leading to a fully delocalized system as illustrated in **2**. In contrast, the boron-based polyhedral bridge significantly reduces the electronic communication between the two charged pendant aromatic substituents, leading to a highly charge-polarized species. This reduction of electronic communication between the cage and the pendant groups has been previously observed experimentally for 12-vertex species.[27] This feature directly impacts the calculated first hyperpolarizabilities (β) for the two structurally analogous systems. The first hyperpolarizability for the [5.6.7]quinarene (**1**) ring system shows a marked dependence on the relative orientation of the rings with a minimum β value at the point where all three rings are coplanar ($\beta_{0.5\text{eV}} = 52.1 \times 10^{-30}$ cm^5 esu^{-1}) and a maximum β value when the central benzene unit is twisted nearly perpendicular to the plane of the cyclopentadienyl and tropylium groups ($\beta_{0.5\text{eV}} = 383.1 \times 10^{-30}$ cm^5 esu^{-1}). This is similar to what was observed for the twisted π-chromophores where the second-order responses were most dependent on stabilizing the intramolecular charge separation.[5] The charge separation is maximized by forcing the rings to rotate to an almost orthogonal configuration through the substitution of bulky pendant groups, thereby minimizing the contribution of the fully electron-delocalized resonance structure to the overall description.[5] In contrast, however, the three-dimensional cluster bridged system, [1-(C_7H_6)-12-(C_5H_2-3,4-$(CH_3)_2$)-$C_2B_{10}H_{10}$] **3**, showed a much larger first hyperpolarizability ($\beta_{0.5\text{eV}} = 998.0 \times 10^{-30}$ cm^5 esu^{-1}) than the [5.6.7]quinarene with relatively little dependence on the relative orientation of the cyclopentadienyl and tropylium groups. Interestingly, this restriction of electronic communication between the cage and the pendant groups in the 12-vertex boranes (**3**) is not fully carried over to the 10-vertex species (**4**) in which significant electronic delocalization among the constituents is known to occur.[27] As anticipated, therefore, the first hyperpolarizabilities of the 10-vertex systems are significantly smaller ($\beta_{0.5\text{eV}} = 296.1 \times 10^{-30}$ cm^5 esu^{-1} for *closo*-[1-(C_7H_6)-10-(C_5Me_4)$B_{10}H_8$]$^{2-}$) than the 12-vertex analogue ($\beta_{0.5\text{eV}} = 1208.7 \times 10^{-30}$ cm^5 esu^{-1} for *closo*-[1-(C_7H_6)-12-(C_5Me_4)-$B_{12}H_{10}$]$^{2-}$). Similar results are also observed in the corresponding carborane species ($\beta_{0.5\text{eV}} = 664.8 \times 10^{-30}$ cm^5 esu^{-1} for

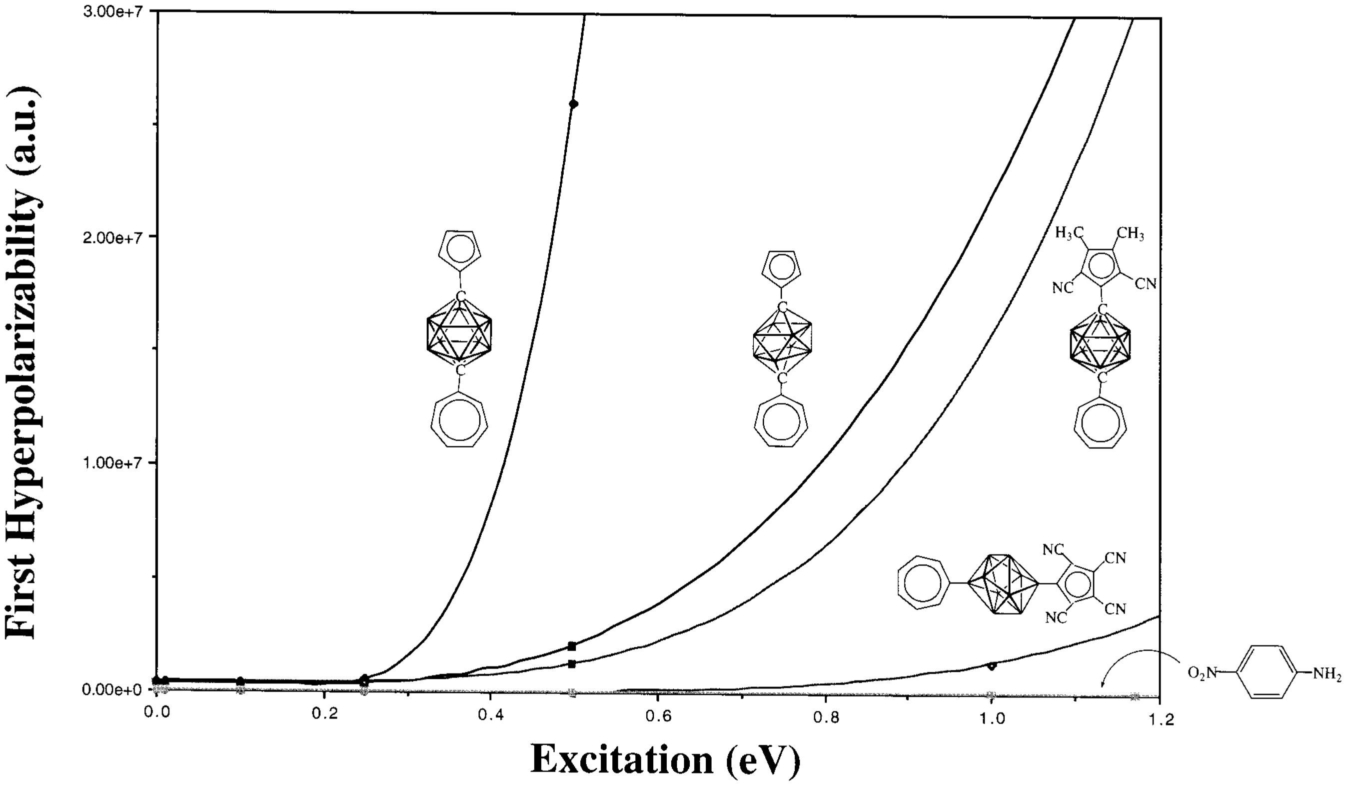


Figure 2. Comparison of the calculated β values for several polyhedral-based and reference literature NLO compounds as a function of excitation energy (AM1).

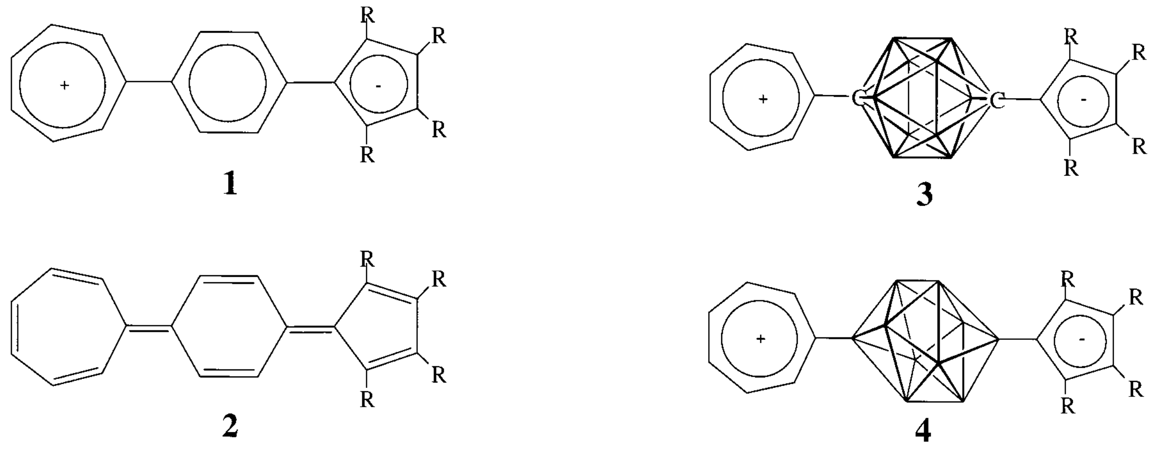
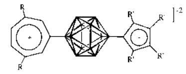


Figure 3. Comparison between the resonance structures of the organic [5.6.7]quinarene system (**1** and **2**) and examples of polyhedral borane and carborane clusters bridging charged aromatic donor−acceptor units (**3** and **4**).

closo-[1-(C_7H_6)-10-(C_5Me_4)$C_2B_8H_8$] and $\beta_{0.5eV} = 998.0 \times 10^{-30}$ cm^5 esu^{-1} for *closo*-[1-(C_7H_6)-12-(C_5Me_4)$C_2B_{10}H_{10}$]). The enhancement of the molecular nonlinear optical properties provided by the polyhedral bridge can also clearly be seen when *closo*-[1-(C_7H_6)-12-(C_5H_4)$C_2B_{10}H_{10}$] is compared with the simple π-conjugated, butadiene-bridged compound [1-(C_7H_6)-4-(C_5H_4)C_4H_4] (Table 2). The first hyperpolarizability for the polyhedral compound is 681.9×10^{-30} cm^5 esu^{-1} while the first hyperpolarizability for the butadiene-bridged compound is 48.8×10^{-30} cm^5 esu^{-1}, more than an order of magnitude smaller. Additionally, the combined effect of the cage with the charged aromatic rings can clearly be seen when *closo*-[1-(NH_2)-12-(NO_2)$B_{12}H_{10}$]$^{2-}$ ($\beta_{0.5eV} = 2.1 \times 10^{-30}$ cm^5 esu^{-1}) is compared with *closo*-[1-(C_7H_6)-12-(C_5H_4)$B_{12}H_{10}$]$^{2-}$ ($\beta_{0.5eV} = 777.3 \times 10^{-30}$ cm^5 esu^{-1}), which differs by more than 2 orders of magnitude.

A significant dependence was observed between the calculated first hyperpolarizabilities for the cluster-based species and the nature and position of substitutions on the organic π-aromatic ring pendants on the cluster bridges. NLO responses for a number of compounds with various ring substituents on both cyclopentadienyl and tropylium rings are given in Table 3, while data showing the effect of the number and position of the substitution on the cyclopentadienyl ring are given in Table 4. Overall, more than a 4-fold increase in the first hyperpolarizability was observed by these substitutions relative to the unsubstituted system, and even larger increases were found by combining these simple substitution effects. The greatest effects were found when the substituents were located on the ring carbon atoms farthest from the point of attachment to the cluster bridge. The effect of the substitution on the carbons farthest from the cluster attachment point is to move the center of the charge on the rings further away from the bridge, leading to a greater charge polarization and larger molecular dipole moment. Thus, the 4,5-biscyano-substituted tropylium ring shows a much greater effect relative to the 2,7-substituted case. The net result of this substitution pattern is to increase the dipole moment of the 4,5-substituted species ($\mu = 21.2$ D) over the 2,7-substituted species ($\mu = 9.9$ D). As anticipated, the addition of electron-releasing substituents on the cyclopentadienyl group and of electron-withdrawing groups on the tropylium ring generally led to greater β values, similar to the effects observed for previously known NLO chromophores.[8]

Table 3. Calculated Average β Values at 0.5 eV as a Function of Substituent for *closo*-[1-($C_7H_4R_2$)-12-($C_5R'_4$)$B_{12}H_{10}$]$^{2-}$ [a]



R↓\R′ →	H	CH_3	NH_2	$N(CH_3)_2$	OCH_3
H	777.3	1208.7	1366.3	1017.2	571.3
F	334.2	779.8	681.6	772.2	977.2
Cl	60.0	577.9	79.3	1453.1	1095.3
CF_3	1080.2	1457.6	1513.4	1623.2	448.5
NO_2	504.1	551.0	550.8[b]	780.9	758.3
COH	1414.9	1862.1	2211.4	1217.5	1615.9
CN	1339.0	1805.8	1875.8	2180.8	677.5
SO_2CH_3	382.0[b]	446.1	469.2	473.3	487.8
SO_2F	224.3[b]	248.0	245.8	211.0	257.9

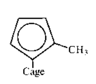
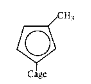
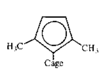
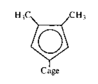
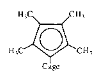
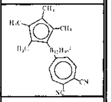
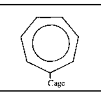
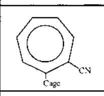
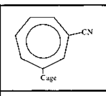
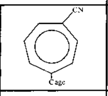
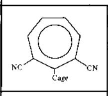
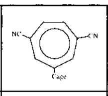
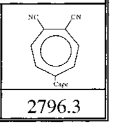
[a] Second-order responses (β) were calculated using *semiempirical* methods with AM1 parametrization at 0.5 eV field strength using the E4 method. The values of β are reported in units of 10^{-30} cm^5 esu^{-1}. The $B_{12}H_{10}$ cage unit in this comparative study was chosen both as a representative cluster and for calculational facility. Similar trends are expected for other cage geometries, structures, and overall charge. [b] The tropylium ring is slightly distorted from the planar configuration in the geometry-optimized calculated structure.

A partial understanding for the exceptionally large calculated responses for the charged aromatic and polyhedral systems may be gained by examining selected molecular orbitals for the NLO chromophores. The HOMO and LUMO are shown for a typical new compound, *closo*-[1-(C_7H_6)-12-(C_5Me_4)$B_{12}H_{10}$]$^{2-}$, in Figure 4. It appears that, similar to the twisted π-organic chromophores, the ground state for these polyhedral-based systems may best be described as two relatively independent, highly polarized regions.[5] The HOMO, for example, is primarily localized on the cyclopentadienyl ring, while the LUMO is primarily located on the tropylium ring. Unlike the twisted π-organic molecules, however, the transfer moment remains relatively large because of the electronic properties and three-dimensional configuration of the polyhedron with a calculated oscillator strength of nearly 1.0. Increasing the charge separation between the organic rings and the polyhedron leads to substantial π-aromatic stabilization of both tropylium and cyclopentadienyl subunits without introducing significant strain energy. Such an extremely large polarization, coupled with a large oscillator strength, would be expected to lead to the very large response properties observed. Distribution of the charge throughout the entire molecular system, in contrast, would lead to a diminution of the aromatic stabilization and would provide greater conjugation between the

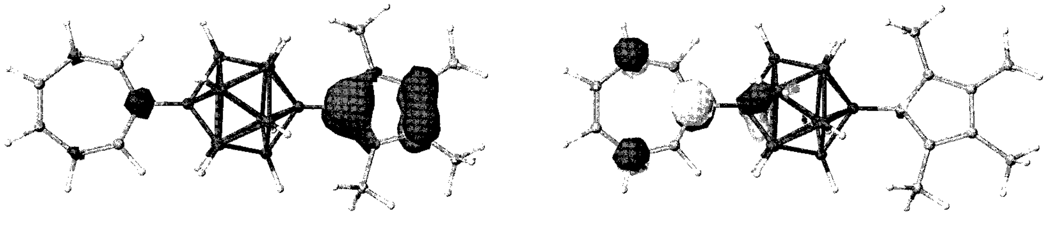
---

(27) Pakhomov, S.; Kaszynski, P.; Young, V. G., Jr. *Inorg. Chem.* **2000**, *39*, 2243.

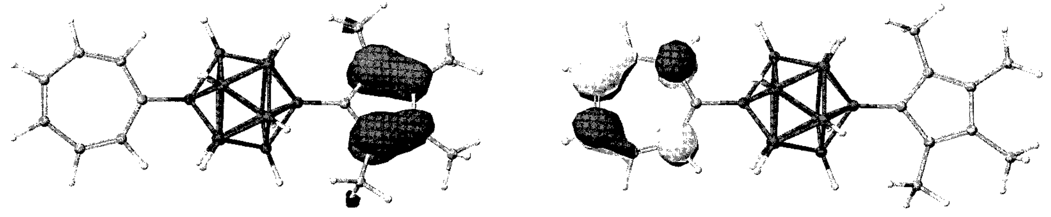
Table 4. Calculated Average β Values at 0.5 eV as a Function of Substitution Pattern of the Tropylium (Tp) and Cyclopentadienyl (Cp) Units in *closo*-[1-(Tp)-12-(Cp)$B_{12}H_{10}$]$^{-2}$ Compounds[a]

		Monosubstituted		Disubstituted		Tetrasub.	Combined
Compound[a]							
β	777.3	860.7	948.3	948.9	1086.6	1208.7	3368.1
		Monosubstituted			Disubstituted		
Compound[a]							
β	777.3	634.0	67.6	1379.2	142.5	1339.0	2796.3

[a] Second-order responses (β) were calculated using *semiempirical* methods with AM1 parametrization at 0.5 eV field strength using the E4 method. The values of β are reported in units of 10^{-30} cm^5 esu^{-1}. The $B_{12}H_{10}$ cage unit in this comparative study was chosen both as a representative cluster and for calculational facility. Similar trends are expected for other cage geometries, structures, and overall charge. For the calculations varying the substitution pattern of the cyclopentadienyl ring, the unsubstituted tropylium ring system (C_7H_6) was used. Similarly, for the calculations varying the substitution on the tropylium ring, the unsubstituted cyclopentadienyl ring system (C_5H_4) was employed. The methyl substitutents for the cyclopentadienyl ring and the cyano groups for the tropylium ring were chosen as representatives of ring substitution pattern effects. Similar trends are expected for other substitutents.



HOMO LUMO



HOMO − 1 LUMO + 1

Figure 4. Frontier molecular orbitals calculated at the AM1 level of theory for *closo*-[1-(C_7H_6)-12-(C_5Me_4)$B_{12}H_{10}$]$^{2-}$.

polyhedron and the organic ring systems, resulting in smaller β values. Mulliken electron population analyses on the polyhedral-based systems show that the negative charge is essentially localized on the cyclopentadienyl ring, while the positive charge is localized on the tropylium ring system, providing further support for the zwitterionic description of these molecules.

Many of the parent boranes and carboranes are known to display permanent dipole moments that contribute to the observed molecular electronic asymmetry of the substituted species. The calculations clearly show that the addition of tropylium and cyclopentadienyl groups to the parent clusters significantly increases the molecular dipole moments of the substituted species, strongly contributing to the very large observed β values. For example, *closo*-[1-(C_7H_6)-7-(C_5H_4)-$C_2B_{10}H_{10}$] and *closo*-[1-(C_7H_6)-12-(C_5Et_4)$C_2B_{10}H_{10}$] have calculated dipole moments of 12.0 and 16.1 D, respectively, in comparison with the known dipole moment of 4.45 D for *closo*-[1,2-$C_2B_{10}H_{12}$].[10] This observation again reinforces the view that the ground state in these molecules is best viewed as zwitterionic. The greatest increase in dipole moment typically occurs with axial substitutions on the cluster.

The absorption spectra of aromatic substituted polyhedral compounds are of significant interest relative to the potential applications of the material. The calculated UV−visible and infrared spectra for these types of compounds typically display very large infrared absorptions without visible absorptions. This is consistent with the known UV−visible spectrum for the 12-$C_7H_6^+$-$CB_{11}H_{11}^-$ compound, which is transparent in the visible region.[12] The ZINDO calculations agree very well with the observed spectral features in the previously reported organic-substituted *closo*-[$B_{10}H_{10}$] and *closo*-[$C_2B_{10}H_{10}$] clusters.[18,27] The calculated absorption spectrum of *closo*-[1-(C_7H_6)-12-(C_5Me_4)-$C_2B_{10}H_{10}$] shows that the absorption maximum shifts to the near-infrared region (λ_{max} = 810 nm) with a strong UV absorption also at 195 nm. The long wavelength transitions arise from HOMO to LUMO charge-transfer transitions involving the pendant ring systems.

Acknowledgment. We are grateful to Profs. Bruce S. Hudson, Thomas H. Walnut, and Michael B. Sponsler for their invaluable assistance. Finally, we thank the National Science Foundation and the Donors of the Petroleum Research Fund for their generous support of this work (PRF35284-AC3).

IC0007761