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Note

Polyhedral-based nonlinear optical materials. Part 1. Theoretical investigation of some new high nonlinear optical response compounds involving carboranes and charged aromatic donors and acceptors

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Dedicated to Professor Sheldon Shore on the occasion of his 70th birthday.

Abstract

A calculational investigation using *semiempirical* methods of the molecular and electronic structures, along with the nonlinear optical responses, of a series of compounds in which icosahedral carborane polyhedra bridge charged aromatic donor and acceptor moieties, specifically tropyl ($C_7H_7^+$) and cyclopentadienyl ($C_5H_5^-$) groups, found that these molecules show exceptionally large calculated second-order responses. These compounds were found to give calculated first hyperpolarizabilities (β) ranging from 8.6 to 1226.0 × 10^{-30} cm^5 esu^{-1} at 0.5 eV excitation energy. These nonlinear optical responses are understood within the framework of the two-state model using molecular orbital and electronic structure considerations. © 2000 Elsevier Science B.V. All rights reserved.

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Nonlinear optical materials have recently been employed in a variety of technological applications, such as optical communications and computation, optical switching and limiting, data storage and retrieval, and dynamic image processing, due to their ability to uniquely alter the properties of applied electromagnetic fields, especially in frequency and phase [1–6]. Most molecular nonlinear optical materials, however, are relatively inefficient photonic modulators. Thus, much of the current research in this area involves the discovery of new materials efficient at nonlinear photonic signal manipulation along with the determination of the important relationships between molecular architecture and nonlinear responses.

Numerous classes of molecular nonlinear optical compounds have been thus far investigated, especially for the organic and organometallic-based systems [1–6]. 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 acceptor groups. Thus far, however, relatively little exploration has been directed toward either the application of molecular polyhedral-based systems or compounds with charged aromatic donor and acceptor moieties. The synthesis and NLO responses of a series of substituted 1,2-dicarba-*closo*-dodecaborane compounds have been previously reported [7,8]. The first hyperpolarizabilities (second-order responses, β) for these compounds were

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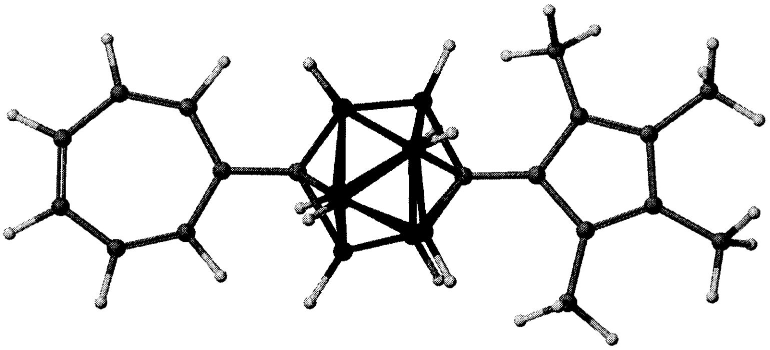

Fig. 1. Geometry optimized structure (AM1) of a typical new NLO polyhedral compound with both charged aromatic donor and acceptor moieties, *closo*-1,12-[$(C_7H_6)C_2B_{10}H_{10}(C_5Me_4)$].

reported to be between 2.7 and 13.0 × 10^{-30} cm^5 esu^{-1} at 1.17 eV. A second study has reported the calculated static hyperpolarizabilities ($\beta_{(0)}$) for the [$B_{12}H_{11}$-(*o*,*m*,*p*)-$C_2B_{10}H_{12}$]$^{-2}$ linked cluster compounds to range between 3.4 and 3.6 × 10^{-30} cm^5 esu^{-1} [9]. These values compare favorably with the value of 6.2 × 10^{-30} cm^5 esu^{-1} for the standard *p*-nitroaniline benchmark often used for evaluating new NLO compounds. Finally, a recent paper has reported the synthesis and NLO response of a tropyl-substituted 1-carba-*closo*-dodecaborate anion which displays an experimental β of 236 (± 50) × 10^{-30} cm^5 esu^{-1} at 1.17 eV [10]. In our work reported here, we describe the initial results of a theoretical study of the nonlinear responses of several main group polyhedral compounds with both charged aromatic donor and acceptor moieties, specifically tropyl and cyclopentadienyl substituted carboranes, which show exceptionally large calculated second-order responses with β values ranging from 8.6 to 1226.0 × 10^{-30} cm^5 esu^{-1} at 0.5 eV.

Quantum mechanical calculations have been extensively and effectively employed in evaluating the nonlinear optical properties of new materials[1,2] [11]. In order to understand the potential of charged aromatic donor and acceptor moieties, specifically tropyl ($C_7H_6^+$, Tp) and cyclopentadienyl ($C_5H_4^-$, Cp) ligands, coupled with molecular polyhedral-based systems for second harmonic generation, we have calculated the molecular and electronic structures, along with their second-order responses, for a series of model compounds incorporating these structural features using *semiempirical* methods (MOPAC) [12–14]. Examples of the species investigated and their calculated non-resonant β and $\mu\beta$ values are given in Table 1. Also given in the table are the structural and nonlinear optical data for the organic (phenyl) bridged analogous [5.6.7]quinarene species, tropylcyclopentadienylbenzene [15–17], along with *p*-nitroaniline for comparison. Each structure was fully SCF optimized at the AM1 level (without symmetry restrictions) and non-resonant β values were calculated using the methods previously reported in detail [12–14]. The *semiempirical* methods employed here have been shown previously to accurately reproduce experimental second-order responses over a range of at least three orders of magnitude [12–14,18].

The structures of the carborane polyhedra investigated here are based upon *closo*-icosahedral frameworks, such as $C_2B_{10}H_{12}$ and $CB_{11}H_{12}^{-1}$. A typical structure is shown is Fig. 1. From the results in Table 1, it is clear that these new species have very large calculated β values. For example, the calculated β value for [$(C_7H_6)C_2B_{10}H_{10}$–$B_{12}H_{10}(C_5H_4)$]$^{-2}$ ($\beta_{calc(0.5\ eV)}$ = 1226 × 10^{-30} cm^5 esu^{-1}) is more than 58 times larger than that for the known large extended π-conjugated 'push–pull' organic compound 1,4-[$(NO_2CH{=}CHCH{=}CH)(C_6H_4)(NH_2)$] ($\beta_{calc(0.5\ eV)}$ = 21 × 10^{-30} cm^5 esu^{-1}) and 198 times greater than the benchmark *p*-nitroaniline at 0.5 eV. As a comparison, the calculated response for the linked [$(C_7H_6)C_2B_{10}H_{10}$–$B_{12}H_{10}(C_5H_4)$]$^{-2}$ aromatic substituted compound is more than two orders of magnitude larger than the parent [$(H)C_2B_{10}H_{10}$–$B_{12}H_{10}(H)$]$^{-2}$ compound. It is important to note that the calculated non-resonant values of β in Table 1 are at an excitation energy of 0.5 eV while most of the values reported in the literature are at an excitation energy of 1.17 eV. The choice of 0.5 eV in this work was both to ensure that non-resonant β values were calculated and for calculational facility. The magnitude of β is, however, very sensitive to excitation energy and increases significantly with increases in excitation energy [11]. Thus, while the NLO responses given for the new compounds are large, they are even more remarkable when compared with other known compounds at similar excitation energies. For example, the reported β value for 12-[$(C_7H_6)CB_{11}H_{11}$] is 236 (± 50) × 10^{-30} cm^5 esu^{-1} at

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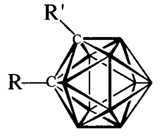
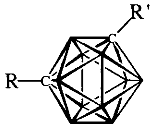
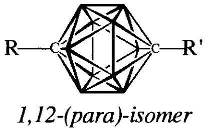
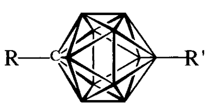
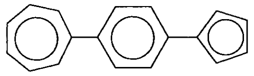
[1] This method has been used extensively in the literature for the calculation of molecular hyperpolarizabilities [12].

[2] The calculations employed here utilized MOPAC and ZINDO within the 4.0.1 CAChe Worksystem (Oxford Molecular) software package. For MNDO-AM1 method and parameterization, see [14]. Oscillator strengths were calculated using the INDO/S Hamiltonian in ZINDO.

Table 1
Calculated average second-order responses ($\mu\beta$ and β) at 0.5 eV for selected NLO 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 $R = C_7H_6$, $R' = CH_3$, charge = +1[g] $R = B_{12}H_{11}$, $R' = H$, charge = -2[g]	688.8 209.7 131.6	55.1 18.4[c] 8.6[d]
 *1,7-(meta)-isomer*	$R = C_7H_6$, $R' = C_5H_4$, charge = 0 $R = B_{12}H_{11}$, $R' = H$, charge = -2[g]	1330.3 133.5[d]	110.1 9.3[d]
 *1,12-(para)-isomer*	$R = C_7H_6$, $R' = C_5H_4$, charge = 0 $R = C_7H_6$, $R' = C_5Me_4$, charge = 0 $R = C_7H_6$, $R' = C_5Et_4$, charge = 0 $R = B_{12}H_{11}$, $R' = H$, charge = -2[g] $R = 12\text{-}(C_7H_6B_{12}H_{10})$, $R' = C_5H_4$, charge= -2[g] $R = 12\text{-}(C_5H_4B_{12}H_{10})$, $R' = C_7H_6$, charge= -2[g]	11686.7 15767.1 17903.0 159.2 4393.8 15512.5	681.9 998.0 1063.5 10.4[d] 158.3 1226.0
$[(R)CB_{11}H_{10}(R')]$		$\mu\beta^a$	β^a
	$R = C_7H_6$, $R' = C_5H_4$, charge = -1[g] $R = C_5H_4$, $R' = C_7H_6$, charge = -1[g] $R = H$, $R' = C_7H_6$, charge = 0[e] $R = C_7H_6$, $R' = H$, charge = 0	1369.0 21704.0 455.1 550.3	118.2 1064.6 36.6[e] 34.4
		$\mu\beta^a$	β^a
H_2N—(Bridge)—NO_2	bridge = 1,4-C_6H_4, charge = 0	43.5	6.2[d] 5.3 16.2[f]
	bridge = 1,12-$B_{12}H_{10}$, charge = -2[g]	13.2	2.1
$[1,4\text{-}(C_7H_6)C_6H_4(R)]$		$\mu\beta^a$	β^a
	*all co-planar*	222.7	52.1

[a] Second-order responses (β) were calculated using *semiempirical* methods with AM1 parameterization 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 $\mu\beta$ are given in units of 10^{-48} esu.

[b] Shown for representative molecules is a schematic line drawing. The terminal cage, tropyl, and cyclopentadienyl hydrogens are omitted from the line drawings and cage borons are shown as unlabeled vertices.

[c] Known cationic compound [22], although an experimental hyperpolarizability was not measured.

[d] Literature $\beta_{(0)}$ values [9] 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 [9].

[e] Known cationic compound [10] with an experimental hyperpolarizability of $236 \pm 50 \times 10^{-30}$ cm^5 esu^{-1} at 1.17 eV.

[f] Calculated with the Pariser–Parr–Pople model (PPP) at 1.17 eV [19,20].

[g] 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.

1.17 eV while our calculated value for the same molecule at 0.5 eV is 34.0×10^{-30} cm^5 esu^{-1} [10].

A power series expansion is often used to describe the nonlinear behavior of the total induced polarization when the electric field component of a strong incident electromagnetic wave interacts with a molecule. The most widely employed model for understanding the relationships between β and molecular structure is the two-state model [11,21]. In this model, β is given by:

$$\beta \propto \frac{(\mu_{ee} - \mu_{gg})}{\Delta e_{eg}^2} \mu_{eg}^2$$

where μ_{ee} is the dipole moment of the excited state, μ_{gg} is the dipole moment of the ground state, and μ_{eg} is the transition dipole moment between the ground and the charge-transfer excited state. Molecular parameters which enhance a noncentrosymmetric electronic polarization in a molecule enhance its second-order response.

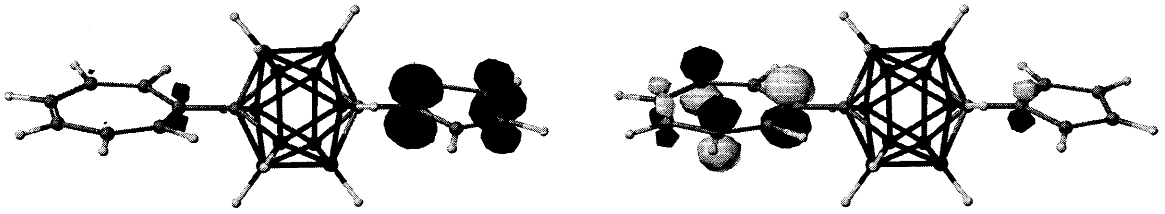


Fig. 2. Calculated HOMO (left) and LUMO (right) frontier orbitals for *closo*-1,12-[$(C_7H_6)C_2B_{12}H_{10}(C_5H_4)$].

The large second-order responses (β) of asymmetric molecules with both electron donating and withdrawing substituents are dictated by the intramolecular charge polarization, the transition dipole moment, and the excited state of the compounds. Polyhedral carboranes often combine a permanent dipole moment with a highly delocalized environment containing a large, accessible pool of polarizable electrons. When this delocalized bridge environment is coupled with charged aromatic donor and acceptor species, the resulting noncentrosymmetric electronic polarization can be greatly enhanced as observed in the data in Table 1. The enhancement provided by the polyhedral bridge can be clearly seen when 1,12-[$(C_7H_6)C_2B_{10}H_{10}(C_5H_4)$] is compared with the π-conjugated, butadiene-bridged compound 1,4-[$(C_7H_6)C_4H_4(C_5H_4)$]. 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 different. Additionally, the combined effect of the cage with the charged aromatic rings can clearly be seen when 1,12-[$(NH_2)B_{12}H_{10}(NO_2)$]$^{2-}$ ($\beta_{(0.5\ \mathrm{eV})} = 2.1 \times 10^{-30}$ cm^5 esu^{-1}) is compared with 1,12-[$(C_7H_6)B_{12}H_{10}(C_5H_4)$]$^{2-}$ ($\beta_{(0.5\ \mathrm{eV})} = 777.3 \times 10^{-30}$ cm^5 esu^{-1}), which differ by more than two orders of magnitude.

In order to understand the origins of the large calculated responses for these polyhedral-based systems, we have examined the molecular orbitals for the NLO chromophores. The HOMO and LUMO are shown in Fig. 2 for a typical compound studied, 1,12-[$(C_7H_6)C_2B_{10}H_{10}(C_5H_4)$]. The best description for the ground state for these polyhedral-based systems is as two relatively independent, highly polarized regions [12–14]. The HOMO is localized mainly on the cyclopentadienyl ring while the LUMO is centered on the tropyl ring. The transition dipole moment remains relatively large for these systems due to the electronic properties and three dimensional configuration of the polyhedron with a calculated oscillator strength of nearly 1.0 [12–14]. Mulliken electron population analyses also show a significant negative charge localized on the cyclopentadienyl ring of the molecule and a positive charge localized on the tropyl ring system, providing further support for the zwitterionic description.

As mentioned above, many of the parent carboranes display permanent dipole moments which contribute to the molecular electronic asymmetry. The calculations clearly show that the addition of tropyl and cyclopentadienyl groups significantly increases these dipole moments, strongly contributing to the very large β values. For example, *closo*-1,7-[$(C_7H_6)C_2B_{10}H_{10}(C_5H_4)$] and *closo*-1,12-[$(C_7H_6)C_2B_{10}H_{10}(C_5Et_4)$] have calculated dipole moments of 12.0 and 16.1 D, respectively, in comparison with the known dipole moment of 4.45 D for the parent *closo*-1,2-[$C_2B_{10}H_{12}$] [8]. This observation reinforces the view that the ground state in these molecules is best viewed as zwitterionic. Finally, the calculated absorption spectrum of 1,12-[$(C_7H_6)C_2B_{10}H_{10}(C_5Me_4)$] shows that the absorption maximum shifts to the near infrared region ($\lambda_{\max} = 810$ nm) with a strong absorption also at 195 nm.

Work is currently in progress on the synthesis of these and similar polyhedral-based NLO compounds with charged aromatic donor and acceptor groups to experimentally study their molecular structures and nonlinear responses.

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