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A New Class of Carborane Compounds for Second-Order Nonlinear Optics: Ab Initio Molecular Orbital Study of Hyperpolarizabilities for 1-(1′,*X*′-Dicarba-*closo*-dodecaborane-1′-yl)-*closo*-dodecaborate Dianion ($X = 2, 7, 12$)

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Up to now, almost all of the organic molecules investigated for the second-order NLO materials contain electron-donating and withdrawing groups linked through an intervening π backbone. Though it is well established that the extension of the π conjugation path between the electron-donating and withdrawing groups strongly increases electronic molecular hyperpolarizability, β, the extension of the π-conjugation path also causes a bathochromic shift of the intramolecular charge-transfer absorption band, and thus the requirement of high transparency to visible light is missing. Indeed, the relationship between log β and log $\lambda_{\max}$ has been shown to be approximately linear.[1] This means that materials with large second-order NLO properties would absorb in the visible range light. From the theoretical aspect, it is surely inevitable to induce a bathochromic shift of the $\pi \rightarrow \pi^*$ absorption band with π conjugation length. In our previous papers, we proposed novel highly transparent NLO materials based on the concept of spiroconjugation of polyene.[2−5] We present here one possibility to break through this dilemma by using the concept of a through-space interaction. We have investigated inorganic boron cluster compounds 1-(1′,*X*′-dicarba-*closo*-dodecaborane-1′-yl)-*closo*-dodecaborate dianion ($X = 2$, 7, 12), $[B_{12}H_{11}\text{-}C_2B_{10}H_{11}]^{2-}$, which consist of an electron-rich polyborane dianion, *closo*-$B_{12}H_{12}{}^{2-}$, and an electron-deficient neutral dicarbaborane, *closo*-$C_2B_{10}H_{12}$, with expectation of the possibility for charge transfer from the electron-rich cluster to the electron-deficient cluster by through-space interaction between the adjacent boron clusters.

The extraordinary thermal stability of the *closo*-dicarbaboranes $C_2B_nH_{n+2}$ ($n = 3-10$) is one of the most exciting properties of this large class of deltahedral heteroboranes.[6] The most stable *closo*-dicarbaboranes are the three members of the icosahedral isomers, 1,2-, 1,7-, and 1,12-dicarba-*closo*-$C_2B_{10}H_{12}$, which are known as *o*-, *m*-, *p*-carborane, respectively. These carboranes have the icosahedral geometry, in which the carbon and boron atoms are hexacoordinate. This feature of the molecular structure gives rise to the unusual properties of such molecules and their carbon and boron derivatives. Moreover, carboranes have been suggested to be characterized as "pseudoaromatic" or "superaromatic" systems,[6c,7] and the remarkable thermal stability of the carboranes are interesting in the field of advanced materials.[6f,g] More remarkable is the transparency to UV light down to about 200 nm of the *closo*-polyheteroboranes along with the chemical and optical stability of these compounds.[7] The present theoretical study was motivated by these structural characteristics of carboranes which make these compounds attractive for second-order NLO materials.[8]

The geometry optimization for $[B_{12}H_{11}\text{-}p\text{-}C_2B_{10}H_{11}]^{2-}$ was performed in C_{5v} symmetry using the 6-31G** basis set,[9] and those for $[B_{12}H_{11}\text{-}o\text{-}C_2B_{10}H_{11}]^{2-}$ and $[B_{12}H_{11}\text{-}m\text{-}C_2B_{10}H_{11}]^{2-}$ were performed in C_s symmetry. On the basis of these geometries, the static $\beta(0)$ values, in the limit of a static field, were calculated using the coupled-perturbed Hartree−Fock formalism based on ab initio SCF wave functions with the 6-31G** basis sets.[10,11] Moreover, we calculated the three crucial two-level properties (the difference between the *x*-components of the dipole moments in the excited and the ground states $\Delta\mu_x$, the oscillator strength *f*, transition energies $h\omega_{ge}$) of the lowest lying optical transition by employing the ab initio CIS/6-31G** method,[12] in which all electronic states were included which are generated by singly exciting all electrons in the twenty highest occupied MOs to the twenty lowest unoccupied MOs with respect to the ground state. All of the calculations were carried out using the Gaussian94 program.[13]

The calculated values of $\beta(0)$, the *x* components of the dipole moments in the ground state $(\mu_x)_g$, those in the first excited state $(\mu_x)_e$, $\Delta\mu_x$, *f*, $h\omega_{ge}$, and $\lambda_{\max}$ are listed in Table 1, along with those for widely adopted standard compounds 4-nitroaniline (*p*-NA). One can find that the $\beta(0)$ values of polyborane-linked carboranes are sufficiently large comparable to that of *p*-NA. By taking into account the short transition wavelengths, these results are worthy of remarks. From the ab initio CIS/6-31G** calculation, the wave

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Table 1. Ab Initio 6-31G** Electronic Properties for Polyborane-Linked Carborane Dianions

	$\beta(0)^a$	$(\mu_x)_g{}^b$	$(\mu_x)_e$	$\Delta\mu_x{}^c$	f	$h\omega_{ge}{}^d$	$\lambda_{max}{}^e$
$[B_{12}H_{11}$-*o*-$C_2B_{10}H_{11}]^{2-}$	3.4	12.10	4.90	−7.20	0.112	8.184	271
$[B_{12}H_{11}$-*m*-$C_2B_{10}H_{11}]^{2-}$	3.6	15.25	3.79	−11.46	0.108	8.356	265
$[B_{12}H_{11}$-*p*-$C_2B_{10}H_{11}]^{2-}$	3.6	16.98	3.05	−13.93	0.283	8.519	260
p-NA	6.2	7.47	11.43	3.96	0.504	5.923	374

[a] All β are in units of 10^{-30} cm^5 esu^{-1} and calculated using the following equation:

$$\beta = (\beta_x{}^2 + \beta_y{}^2 + \beta_z{}^2)^{1/2},\ \beta_i = ({}^1/_3)\Sigma_k(\beta_{ikk} + \beta_{kik} + \beta_{kki}),\ k = x, y, z$$

[b] Debye. [c] $\Delta\mu_x = (\mu_x)_e - (\mu_x)_g$. [d] eV. [e] Transition wavelengths in units of nm scaled by a factor of 0.56, which was set to reproduce the transition wavelength for *p*-NA.

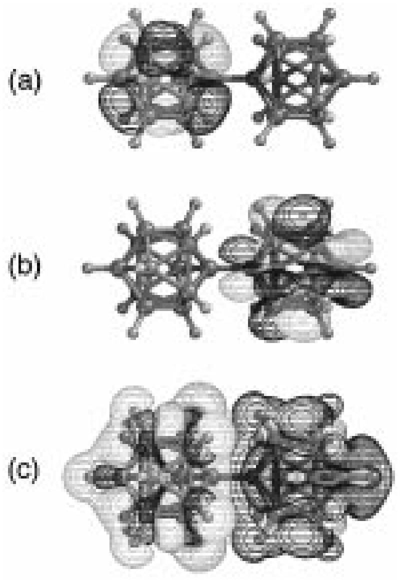

Figure 1. (a) HOMO and (b) LUMO of $[B_{12}H_{11}$-*o*-$C_2B_{10}H_{11}]^{2-}$ calculated using the ab initio SCF/6-31G** method and (c) difference electron density between the ground and first excited states calculated by the ab initio CIS/6-31G** method. The dark-colored contours correspond to regions of increased electron density in the excited state, while the light-colored regions correspond to depleted regions from the ground state.

function of the first excited state, $|\Phi_e\rangle$, for $[B_{12}H_{11}$-*o*-$C_2B_{10}H_{11}]^{2-}$ was found to be given as

$$|\Phi_e\rangle = 0.47|\Psi_{HOMO\rightarrow LUMO}\rangle + 0.38|\Psi_{HOMO-1\rightarrow LUMO}\rangle$$

where $|\Psi\rangle$ is the Slater determinant obtained for the ground electronic state, $|\Psi_{HOMO\rightarrow LUMO}\rangle$ is the monoexcited configuration state function, in which an electron is excited from the HOMO to the LUMO. Figures 1a and 1b show the HOMO and LUMO, respectively. The charge density around *closo*-dodecaborane cage is enhanced in the HOMO, and the LUMO exhibits enhanced charge density around the dicarba-*closo*-dodecaborane cage. Moreover, we calculated the difference electron density between the ground and the first vertical excited states as shown in Figure 1c.[14] Both from the MOs and the charge density difference plot, it has become apparent that the dicarba-*closo*-dodecaborane cage act as an electron-withdrawing group and the *closo*-dodecaborane cage act as an electron-donating group and that the first excited state is characterized by a charge transfer state, where an electron transition occurs from the electron-rich cluster to the electron-deficient cluster by a through-space interaction. This nature of the first excited state is considered to give a large negative value of $\Delta\mu$ and thus contribute to the large hyperpolarizability. First electronic hyperpolarizabilities are often described within the dipolar approximation on the basis of the so-called two-state model.[15,16] Within the framework of the two-state model, the static β value, $\beta(0)$, is expressed as

$$\beta(0) = ({}^3/_2)\{(M_{ge})^2\Delta\mu\}/(h\omega_{ge})^2$$

where M_{ge} is the transition dipole moment between the ground and excited states. The two-state model implies that $\beta(0)$ increases as both $\Delta\mu$ and M_{ge} increase. Hence, compounds with large $\Delta\mu$ will have large hyperpolarizabilities as were found in pyridinium betaines developed by our research group.[17] In addition to large negative values of $\Delta\mu$, the "pseudoaromatic" nature of the boron cluster cages would play an important role in the charge distribution.

In conclusion, the possibility for construction of novel inorganic second-order NLO materials consist of an electron-rich boron cluster and electron-deficient carborane cluster was presented through the theoretical investigations. These new carborane compounds are considered to have an unusual electronic structure compared to the conventional second-order NLO materials in a point that neither polarizable conjugated π nor σ electrons are included. This finding is significant for development a new class of second-order NLO materials with both thermal stability and high optical transparency to visible light. To the best of our knowledge, this is the first example to demonstrate a novel inorganic boron cluster compound exhibiting large β value without utilizing both π- and σ-conjugated molecular systems.

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