Hyperpolarizability of 6-Vertex Carboranes
Quantum Chemical Study

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Abstract: Structure and molecular first hyperpolarizability (β) of nitro-amino-substituted 6-vertex 1,6-carboranes are investigated by means of DFT calculations. The results obtained have revealed that the relative orientation of substituents with respect to the carborane cage influences bond lengths distribution in the cage, which leads to significant changes in the values of hyperpolarizabilities. Calculations with different basis sets have demonstrated that the value of β is not significantly affected by the choice of basis set. The calculated data shows that hyperpolarizability of carborane molecules substituted for carbon atoms is lower than when substituted for boron atoms. For latter molecule, the value of β is of the same order as that of para-nitroaniline molecule.

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1 Introduction

The design of molecular compounds with nonlinear optical (NLO) properties is still of significant importance, due to their potential use in optoelectronic and photonic devices [1], [2], [3]. The main requirements that must be fulfilled for such compounds are high molecular first hyperpolarizability (β) and thermal stability. Hyperpolarizability is usually associated with an extended π-conjugated system, capped with donor and acceptor substituents. The efficiency of the π-bridge as a pathway for charge transfer between donor and acceptor groups has been the subject of extensive theoretical and experimen-

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tal studies [4], [5], [6], [7], [8], [9]. A variety of π-conjugated moieties, namely polyene and polyyne chains, aromatic cycles such as benzene, pyridine, thiophene and other heterocycles, as well as their combinations, have been investigated. A high value of $\beta$ can be reached by manipulating substituents and π-electronic bridges, while the fabrication of thermally stable materials is still an open question as far as organic compounds are concerned. The family of closo-carboranes ($\text{C}_2\text{B}_n\text{H}_{n+2}$, $n=4$-$10$) is characterized by high thermal stability [10], [11], [12] and these systems have been regarded as three-dimensional aromatic analogues of benzene [13]. However, very little attention has been paid to the study of carboranes as potential NLO-materials ([14], [15], [16], [17])† and the hyperpolarizability of donor/acceptor-substituted 6-vertex carboranes has not been investigated. Earlier studies on 10- and 12-vertex boranes and carboranes [17] have suggested that these molecules may be promising candidates in the design of NLO-effective compounds. In particular, a high value of $\beta$ was achieved for boranes and carboranes with charged aromatic donor and acceptor substituents: namely, tropylium and cyclopentadienyl moieties [17].

In this study, the structures and hyperpolarizabilities of the nitro/amino-substituted 6-vertex 1,6-carboranes are investigated by means of $ab$ initio calculations.

2 Calculation

Calculations have been carried out using the Gaussian 94 program package [18]. We chose B3LYP method for our calculations, for two reasons. First, B3LYP was successfully used for the prediction of linear and nonlinear optical properties of boron clusters ($\text{B}_n$, $n=3$-$8$, 10) [19]. Secondly, DFT is the “cheapest” method which accounts for electron correlation, as is necessary for NLO calculations. First hyperpolarizability was estimated at a static limit in terms of the CPHF approach (see, for instance, ref. [5]) as implemented in the Gaussian 94 program at the B3LYP/6-31+G* level. According to CPHF model, hyperpolarizability is expressed by the third derivative of energy with respect to applied electric field

$$\beta_{ijk} = \frac{\partial^3 W(E)}{\partial E_i \partial E_j \partial E_k}$$

Before hyperpolarizability was calculated, all molecular structures were optimized at the same level of theory. Keyword “Tight” was used throughout the calculation to decrease convergence criteria, in order to improve the precision of the results.

3 Results and Discussion

The molecules investigated in this study are sketched in the scheme below, with standard numbering presented in brackets.

The orientation of substituents in the carbon atoms with respect to the square base of bipyramid ($\text{B}(2)$-$\text{B}(3)$-$\text{B}(4)$-$\text{B}(5)$ plane) and in the boron atoms ($\text{B}(3)$-$\text{C}(1)$-$\text{B}(5)$-$\text{C}(6)$

† These few references cover about 90% of all investigated carboranes
plane) may differ. In order to examine this situation in detail, we carried out optimization and calculation of frequencies for conformers, using all possible relative orientations of substituents (see figure 1 and scheme for notations) assuming $C_S$ symmetry ($C_{2v}$ symmetry is broken by pyramidalization of the NH$_2$ group).

According to $C_S$ symmetry, the nitro-group can be located so that the oxygens are projected on the boron or carbon atoms (eclipsed conformation) or onto the centers of the B-B bonds (staggered conformation) of the square base of the bipyramid, while the amino-group can be approximately parallel or perpendicular to the nitro-group (see fig. 1). For conformer 2c the optimized structure appeared to have $C_{2v}$ symmetry, despite the fact that the initial $C_S$ symmetry geometry was taken into account. Calculations without symmetry restraints for both molecules were carried out as well, with unsymmetrical initial geometries. These unconstrained minimizations lead exactly to the 1a and 2a conformers (which have $C_S$ symmetry), respectively. For CCCARB, the 1a structure is the only conformer with no imaginary frequencies, while for BBCARB, the 2a and 2b structures correspond to minima on the potential energy surface (PES) with the 2a being more stable (see fig.1). All other conformers in the study correspond to transition states or saddle points.

In CCCARB’s ground state (1a), the nitro-group is in an eclipsed conformation with respect to the B(2)-B(3)-B(4)-B(5) fragment, while the lone pair (LP) of the amino-group appears in trans-orientation to the C(1)-B(4) bond (approximately parallel to the NO$_2$-group). This orientation leads to an elongation of the C(1)-B(3), C(1)-B(5), C(6)-B(2), C(6)-B(4) bonds and a shortening of the C(1)-B(2), C(1)-B(4), C(6)-B(3), C(6)-B(5) bonds, which is probably the consequence of the backdonation of the electron density of the N-O $\pi$-bonds and the LP of the amino-group, to the corresponding antibond MOs of carborane cage. Bond lengths in the B(2)-B(3)-B(4)-B(5) fragment are less affected by substituents, and are slightly elongated. This is due to slight increase of B-C-B bond angles and distortion of C-B-B triangles, which are isosceles in an unsubstituted molecule. The bond lengths for the unsubstituted carboranes (calculated using the same method/basis) and substituted conformers are presented in Table 1. In support
Fig. 1 Structures of calculated conformers of CCCARB (a) and BBCARB (b) molecules. Projections on B(2)-B(3)-B(4)-B(5) plane (a) and on B(3)-C(1)-B(5)-C(6) plane (b) is shown. The presence of imaginary frequencies is presented.
of the above-mentioned influence of NH$_2$ and NO$_2$ substituents, it is interesting to compare the bond length redistribution for other conformers, in which the orientation of the substituents does not favor effective backdonation. It is clear from Table 1 that the C-B bonds in 1c and 1d are nearly the same as in unsubstituted carboranes. At the same time, a significant difference is found between the B(2)-B(3) and B(4)-B(5) pair and the B(3)-B(4) and B(2)-B(5) pair. NBO analysis can probably explain this fact, and we plan to study this in our future work.

|       | 1a   | 1b   | 1c   | 1d   |
|-------|------|------|------|------|
| C(1)-B(2) | 1.593 | 1.632 | 1.620 | 1.617 |
| C(1)-B(3) | 1.646 | 1.603 | 1.617 | se   |
| C(1)-B(4) | 1.591 | se   | se   | 1.620 |
| C(1)-B(5) | se   | 1.606 | se   | se   |
| C(6)-B(2) | 1.668 | 1.610 | 1.629 | 1.634 |
| C(6)-B(3) | 1.601 | 1.656 | 1.634 | se   |
| C(6)-B(4) | 1.673 | se   | se   | 1.629 |
| C(6)-B(5) | se   | 1.652 | se   | se   |
| B(2)-B(3) | 1.727 | 1.726 | 1.732 | 1.702 |
| B(3)-B(4) | 1.728 | se   | 1.717 | 1.748 |
| B(4)-B(5) | se   | se   | se   | 1.704 |
| B(2)-B(5) | se   | 1.725 | 1.719 | se   |
| Total Energy | -439.0946 | -439.0918 | -439.0930 | -439.0920 |
| Relative Energy | 0.0 | 1.8 | 1.0 | 1.6 |
| $\beta$ | 681 | 127 | 693 | 141 |

Table 1 (First half) Main bond lengths (Å), total energies (au), relative energies (kcal/mol) and molecular hyperpolarizabilities (au) of conformers 1a-d and 2a-d.
(For unsubstituted 1-6-C$_2$B$_4$H$_6$, bond lengths are 1.625 Å for B-C and 1.713 Å for B-B bonds). Relative energies are calculated assuming energy for 1a for CCCARB and for 2a for BBCARB to be zero.

Nearly the same trends are found in the case of BBCARB, while the details are somewhat different. In 2a, which corresponds to the global minimum, oxygens are projected on carbons and the relative orientation of the NH$_2$-group is the same as in 1a. Conformer 2c, in which oxygens are projected onto boron atoms, does not correspond to the minimum as can be expected. However, 2b (perpendicular orientation of substituents) corresponds to a local minimum, which is not the case for CCCARB (1b).

In molecules with a parallel orientation of substituents (2a, 2c), deviations of the bond lengths from corresponding values in unsubstituted carborane are more pronounced than
Table 1 (Second half) Main bond lengths (Å), total energies (au), relative energies (kcal/mol) and molecular hyperpolarizabilities (au) of conformers 1a-d and 2a-d.
(For unsubstituted 1-6-C$_2$B$_4$H$_6$, bond lengths are 1.625 Å for B-C and 1.713 Å for B-B bonds).
Relative energies are calculated assuming energy for 1a for CCCARB and for 2a for BBCARB to be zero.
Molecular hyperpolarizabilities are calculated with the following formula:
\[ \beta = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}, \]
where \( \beta_i = \beta_{ixx} + \beta_{iyy} + \beta_{izz} \)

| Bond          | 1a   | 1b   | 2c   | 2d   |
|---------------|------|------|------|------|
| B(2)-C(1)     | 1.653| 1.601| 1.584| 1.636|
| B(2)-B(3)     | 1.654| 1.698| 1.719| 1.664|
| B(2)-C(6)     | se   | 1.600| se   | se   |
| B(2)-B(5)     | 1.656| se   | se   | 1.670|
| B(4)-C(1)     | 1.603| 1.659| 1.676| 1.613|
| B(4)-B(3)     | 1.781| 1.721| 1.704| 1.761|
| B(4)-C(6)     | se   | 1.652| se   | se   |
| B(4)-B(5)     | 1.782| se   | se   | 1.763|
| C(1)-B(3)     | 1.639| 1.631| 1.633| 1.638|
| B(3)-C(6)     | se   | 1.632| se   | se   |
| C(6)-B(5)     | se   | se   | se   | se   |
| C(1)-B(5)     | 1.638| se   | se   | 1.633|
| Total Energy  | -439.1643| -439.1632| -439.1592| -439.1539|
| Relative Energy | 0.0  | 0.7  | 3.2  | 6.5  |
| \( \beta \)   | 1154 | 458  | 565  | 127  |

Those in 2b and 2d, the substituents of which are oriented perpendicularly. This is also the case for CCCARB (1a and 1b).

Some other details which are common for all the structures under study should be noted. The optimal nitro-group orientation is an eclipsed conformation with respect to the B(2)-B(3)-B(4)-B(5) or B(3)-C(1)-B(5)-C(6) fragment. This is supported by the available experimental data for NO$_2$-substituted 6-vertex boranes [20], [21], [22]. From this experimental data, it follows that the B-B bond lengths in the acceptor part of the molecule are shorter than those in the unsubstituted part (see scheme) [20], [21], [22]. This is in agreement with our calculated results. The same trends are observed for \( \pi \)-acceptor- and \( \pi \)-donor-substituted benzene molecules [23], which might be considered as an additional characteristic that relates 2-dimensional and 3-dimensional electronic delocalization.

For 1a, different basis sets were applied so that their influence on hyperpolarizability and bond lengths distribution could be investigated (Table 2).
The latter are not significantly affected by an extension of the basis set and are not shown in Table 2; largest differences were found to be less than 0.005 Å. Hyperpolarizability is more sensitive to choice of basis set; however, it does not vary significantly when basis set is augmented with diffuse and polarization functions for hydrogens, as well as $f$-functions and the corresponding value changes by only 10% when going from a double- to triple-split-valence basis. Taking these results into account, all other calculations were carried out with the 6-31+G* basis set to save computational time.

The calculated hyperpolarizabilities for all the structures under consideration are listed in Table 1. As can be seen from Table 1, the values of $\beta$ are presented, but not only for the stable conformers which correspond to minima. This is done to investigate the influence of molecular geometry on the values of $\beta$. It is interesting to compare our results with those obtained for well-known conjugated organic molecules, which are characterized by 2-dimensional instead of 3-dimensional electronic delocalization. Assuming that the planar geometry for donor/acceptor-substituted heterocyclic is analogous to stilbene, conformers with different cis/trans molecular moieties orientations were considered, and it has been shown that both energy and the hyperpolarizability do not change significantly [9]. The situation with regard to 6-vertex carboranes is more complicated. First of all, it is not evident a priori as to which conformer of $C_s$ symmetry is the most stable. In the case of BBCARB, 2a and 2b conformers belong to minima on PES and differ by only 0.7 kcal/mol, while the difference in their hyperpolarizabilities is 2.5 times that. Conformer 2c, which can be expected to belong to the minimum on PES (see above discussion), corresponds to the transition state. Its hyperpolarizability is comparable to that of 2b and is two times lower than $\beta$ of 2a. Different trends are found for CCCARB. Values of $\beta$ for 1a and 1c are comparable, while 1b appears to be 5.5 times lower than that of 1a.

From the analysis of the calculated geometries of the conformers of BBCARB and CCCARB it follows that in the conformers with the lowest energies, interaction between the substituents and the carborane cage is more pronounced, providing a more efficient charge transfer. This is despite the fact that the energies of the conformers do not differ significantly. This fact has a significant influence on the molecular hyperpolarizability of the carboranes under consideration.

Donor-acceptor substitution at the carbon atoms yields a lower $\beta$ value than substitution at the borons. In the latter case (2a), hyperpolarizability (Table 1) is of the same order as for para-nitroaniline molecule (1745 au), which we have calculated using the same method/basis for correct comparison. Taking into account the unusual stability of the carboranes [12], these compounds might be considered to be promised candidates for design of effective new NLO materials.

|          | 6-31+G* | 6-31++G** | 6-311++G** | 6-311++G(df,p) |
|----------|---------|-----------|------------|----------------|
| $\beta$, au | 682.6   | 670.9     | 597.1      | 597.1          |

Table 2 Dependence of hyperpolarizabilities of 1a on basis set.
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