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A photoelectron spectroscopic and computational study of the *o*-dicarbadodecaborane parent anion

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We report a combined photoelectron spectroscopic and computational study of the *o*-dicarbadodecaborane (*o*-carborane) parent anion, $(C_2B_{10}H_{12})^-$. Previous studies that focused on the electrophilic nature of *o*-carborane led to tantalizing yet mixed results. In our study, we confirmed that *o*-carborane does in fact form a parent anion and that it has considerable stability. This anion is an isomer ("Anion iso 2") where unlike in neutral *o*-carborane, the two carbon atoms are not bound. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4953773]

INTRODUCTION

Ortho-dicarbadodecaborane (o-$C_2B_{10}H_{12}$), or simply *o*-carborane, was first synthesized in 1963. The *o*-carborane molecule exhibits a slightly distorted icosahedral structure, and it is quite stable. Carboranes are known to exist in three (*o*-, *m*-, *p*-) isomeric forms.[1–9]

Information on the electrophilic properties of carboranes is sparse. Nevertheless, since the hydrogen atoms bonded to *o*-carborane's two carbon atoms are acidic, the doubly deprotonated di-anion, $(C_2B_{10}H_{10})^{2-}$ has been produced by reacting *o*-carborane with n-butyl-lithium in tetrahydrofuran.[10–12] Moreover, the $C_2B_{10}H_{12}$ cage itself can accommodate two additional electrons. The $(C_2B_{10}H_{12})^{2-}$ di-anion has been prepared by reacting *o*-carborane with the Na/K alloy in tetrahydrofuran,[13] and based on calculations, it is thought to have a *nido*-structure.[14,15] Even though the $(C_2B_{10}H_{12})^{2-}$ di-anion is well documented, relatively less is known about the mono-anion of *o*-carborane. The anionic moieties of the salts, $[(15\text{-crown-5})_3Na_2]^{2+}[(C_2B_{10}H_{11})_2]^{2-}$ and $[(P(C_6H_5)_3CH_3]_2^{2+}[(C_2B_{10}H_{11})_2]^{2-}$ are thought to be connected double cages with a single negative charge on each cage.[16,17] Also, $(C_2B_{10}H_{12})^-$ has been observed to be in equilibrium with $(C_2B_{10}H_{10}RR')^-$ in mixtures of $(C_2B_{10}H_{12})^{2-}$ and $C_2B_{10}H_{10}RR'$ in solution.[13] There have also been a few anionic-related studies of *o*-carborane in isolation, i.e., *in vacuo*. An early mass spectrometric study reported observing the parent, mono-anion of *o*-carborane, $(C_2B_{10}H_{12})^-$.[18] Calculations at a low level of theory found the adiabatic electron affinity (EA) of *o*-carborane to be −2.2 eV, implying that its anion is unstable.[19] Electron transmission spectroscopic studies of *o*-carborane observed several temporary anion states at low electron energies, including near "zero" energy.[20] That suggested the formation of $(C_2B_{10}H_{12})^-$ parent, mono-anions, although no mass analysis was available to follow-up on the implication. Here, in the present work, we report the observation of the parent (intact) mono-anion of *o*-carborane, i.e., $(C_2B_{10}H_{12})^-$ in the gas phase, confirming earlier evidences for its existence.[18]

We have characterized it by recording its mass spectrum, by measuring its anion photoelectron spectrum, and by conducting density functional theory calculations, the latter both validating and assisting in interpreting the experimental results.

EXPERIMENTAL AND THEORETICAL METHODS

Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. It is governed by the energy-conserving relationship, $h\nu = EBE + EKE$, where $h\nu$ is the photon energy, EBE is the electron binding (transition) energy, and EKE is the electron kinetic energy. Our anion photoelectron spectrometer, which has been described previously,[21] consists of a laser vaporization anion source, a linear time-of-flight mass analyzer/selector, a pulsed Nd:YAG photodetachment laser, and a magnetic bottle electron energy analyzer. Photoelectron spectra were calibrated against the well-known photoelectron spectrum of Cu^-.[22] Parent anions of *o*-carborane were generated in a laser vaporization source. Briefly, a silver rod was coated with a thin layer of *o*-carborane powder (Alfa Aesar, 98%) and then interrogated by a pulsed Nd:YAG laser beam operating at a wavelength of 532 nm. It is thought that the underlying silver rod provided photoelectrons during the laser vaporization process. The resulting plasma was cooled by supersonically expanding a plume of helium gas from a pulsed gas valve (backing pressure of ∼100 psi). Negatively charged anions were then extracted into the spectrometer prior to mass selection and photodetachment.

Density functional theory calculations were conducted by applying Becke's three-parameter hybrid functional (B3LYP)[23–25] using the Gaussian09 software package[26] to determine the geometries of both neutral and anionic *o*-carborane, the adiabatic electron affinity (EA) and vertical detachment energy (VDE) values, the potential energy surface, and the charge distribution. All geometries, including that of the anion and its corresponding neutral molecule, were fully optimized without any geometrical constraints using the 6-311++G (d, p) basis set. The EA value is the energy

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difference between the ground state of the neutral and the ground state of the anion with zero point energy corrections applied. The VDE value is the energy difference between the ground state of the anion and its neutral counterpart, where the latter has the same structure as the anion. The potential energy surface was scanned along the C–C coordinate with a step width of 0.05 Å by sequentially relaxing the rest of the molecule to its ground state. Natural population analysis (NPA), as implemented in the Gaussian09 code, was also carried out to determine the charge distribution in the anion. The NPA method has been found to be satisfactory in calculating the charge distribution within a cluster.[27–33]

RESULTS

Experimental

The mass spectrum in the neighborhood of $(C_2B_{10}H_{12})^-$ is presented in Figure 1(a). Mass peaks are observed ranging from 135 to 146 amu. Figure 1(b) is the simulated isotopic distribution pattern for $(C_2B_{10}H_{12})^-$. Comparison of the two figures shows that the $(C_2B_{10}H_{12})^-$ parent anion is indeed the major component of the ion signal, but that weaker intensities of $(C_2B_{10}H_n)^-$, n < 12, fragment ions were also present. Thus, in order to avoid contamination from those fragment ions, we measured the photoelectron spectrum at mass, 146 amu. The resulting photoelectron spectrum, recorded with 3.49 eV photons, is presented in Figure 2. Two vibronic bands are in evidence. The lowest EBE band begins from EBE ~1.5 eV and reaches a maximum at a fitted value of 2.33 eV. The higher EBE band, which accesses an excited electronic state of the anion's neutral counterpart, can be estimated to begin at EBE ~ 2.6 eV and extends beyond our experimental EBE range without reaching a maximum. The VDE is the EBE value at which the maximum Franck-Condon overlap is achieved between the anion and its neutral counterpart at the anion's geometry. This occurs at the peak maximum of the lowest EBE band, and thus the experimentally determined VDE value is 2.33 eV.
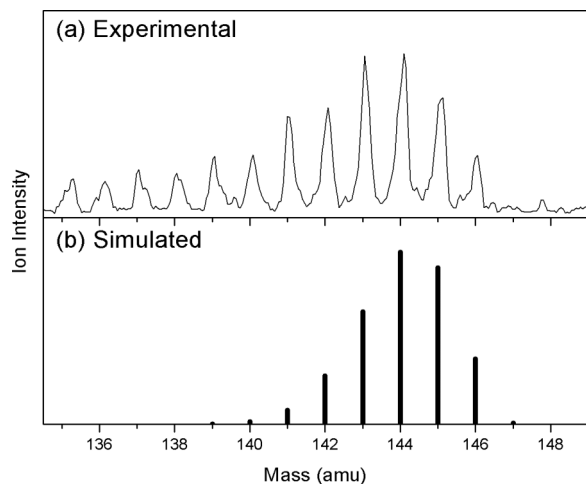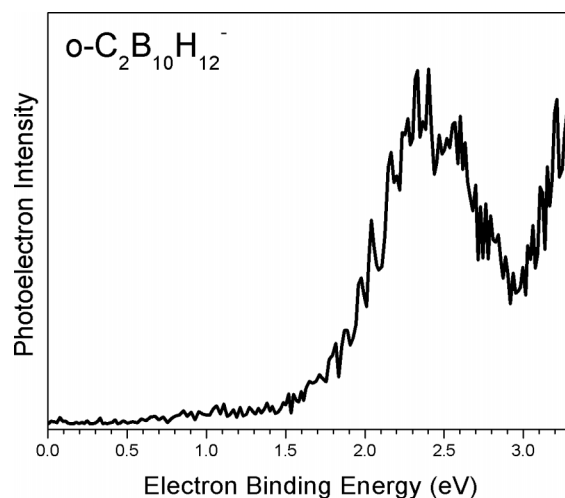
FIG. 2. The anion photoelectron spectrum of $C_2B_{10}H_{12}^-$ recorded with 3.49 eV photons.

Computational

The optimized structures of $C_2B_{10}H_{12}^{0/-}$ are embedded in Figure 3. Carbon atoms are shown in grey, hydrogen atoms in white, and boron atoms in pink. The neutral o-$C_2B_{10}H_{12}$ molecule exhibits a C_{2v}, slightly distorted icosahedral structure, as we know from the literature that it should. Two isomers of the $(C_2B_{10}H_{12})^-$ anion were found. "Anion iso 1" in Figure 3 has a very similar structure to that of neutral, $C_2B_{10}H_{12}$. "Anion iso 2" has a structure that differs from that of "Anion iso 1" primarily in that it has no chemical bond between its two carbon atoms, although it maintains C_{2v} symmetry. See supplementary material for the coordinates of both the neutral and anionic isomers.[34] The energy of "Anion iso 1" is 1.07 eV higher than that of "Anion iso 2" and 0.06 eV higher than that of the neutral $C_2B_{10}H_{12}$. The EA value was obtained by taking the difference between the zero point energy-corrected energies of neutral $C_2B_{10}H_{12}$ and "Anion iso 2." The calculated EA value was thus found to be 1.19 eV. The VDE value was calculated as the energy difference between fully relaxed "Anion iso 2" and its neutral counterpart with exactly the same structure. The calculated VDE value was thus found to be 2.26 eV.

Our natural population analysis showed that the charge on each of the two carbon atoms in "Anion iso 2" is −0.75 e, indicating that the excess electron is primarily attached to the carbon atoms. This is likely due to the higher electronegativity of carbon relative to those of boron and hydrogen. The high degree of excess negative charge on the carbon atoms makes the C–C coordinate pivotal in following the electron detachment process computationally. This realization underpinned our decision to map the potential energy curves of both the anion and the neutral along the C–C coordinate as shown in Figure 3. There, the neutral curve is shown in red, while the anion is shown in black.

For neutral $C_2B_{10}H_{12}$, only one potential well is observed and its equilibrium C–C bond distance is 1.624 Å, whereas the reported C–C bond length in o-carborane is 1.622 Å.[11] For the anion potential curve, two wells are observed, i.e., at 1.614 Å and 2.389 Å, these corresponding to the equilibrium

FIG. 1. (a) Experimental and (b) stimulated mass spectra of $C_2B_{10}H_{12}^-$, the latter showing its expected isotopic distribution.
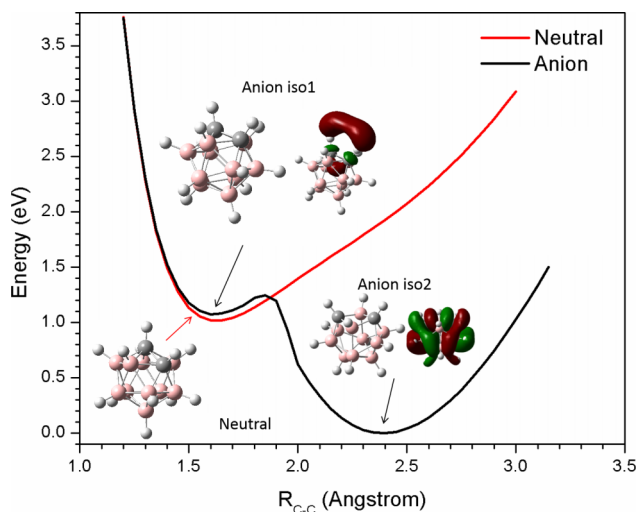
FIG. 3. Potential energy surfaces of neutral (red) and anionic (black) *o*-carborane along the C–C coordinate. Their structures and HOMO's are embedded in the figure.

C–C bond distances of "Anion iso 1" and "Anion iso 2," respectively. Between the two wells, there is a barrier of 0.17 eV in going from "Anion iso 1" to "Anion iso 2."

In Figure 3, next to the structures for "Anion iso 1" and "Anion iso 2," we present their highest occupied molecular orbitals (HOMO), where their excess electrons dwell. For "Anion iso 1," the electron cloud is diffused and located beside the two C–H groups, while in "Anion iso 2," it is delocalized over the entire molecule.

DISCUSSION

Our experimental results can be best understood in terms of our computational results. Consider the potential curves shown in Figure 3. The fact that the energy of "Anion iso 1" is higher than that of neutral *o*-carborane (albeit only slightly) implies that "Anion iso 1" could not have been present in the anion beam.

The anion that was actually made in our experiment was "Anion iso 2." Figure 3 shows that there was far too little Franck-Condon overlap between "Anion iso 2" and the ground state of the neutral *o*-carborane for photodetachment to have captured the origin transition in the anion photoelectron spectrum. The C–C bond displacement between "Anion iso 2" and neutral *o*-carborane is as large as 0.77 Å. The adiabatic electron affinity (EA) is best determined through computation, and it is 1.19 eV.

The VDE value, on the other hand, comes directly from the anion photoelectron spectrum as described above, and it is 2.33 eV. The calculated VDE value (2.26 eV) is in very good agreement with the experimental value. The reason why the calculated VDE value does not appear to agree with the energy difference between "Anion iso 2" and the potential energy curve of neutral *o*-carborane directly above it in Figure 3 is because there, only the C–C distance is shown. That figure represents these anions and the neutral in their fully relaxed states along the C–C bond. The calculated VDE value is the energy difference between the fully relaxed anion

("Anion iso 2") and its corresponding neutral at that same structure.

Our calculations indicate that "Anion iso 1" is unstable (albeit slightly so) relative to neutral *o*-carborane, whereas "Anion iso 2" is quite stable. The HOMOs for these two anionic isomers depicted in Figure 3 offer an explanation. The HOMO for "Anion iso 1" looks diffuse, indicating that "Anion iso 1" might be a dipole bound anion. However, the theoretical methods in the current study are not adequate to describe such a fragile dipole bound anion. Moreover, our experimental results do not support the existence of a dipole bound anion. The HOMO for "Anion iso 2" is delocalized over the entire molecular anion. "Anion iso 2" is simply better able to accommodate the excess electron. Thus, while *o*-carborane is not electrophilic in the usual sense, where the corresponding anion retains its bond connectivity, although not necessarily its bond lengths and angles, *o*-carborane is electrophilic in that it attaches an excess electron to form "Anion iso 2," where its C–C bond connectivity has been compromised.

ACKNOWLEDGMENTS

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