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B$_4$(CO)$_2$: A New, Observable σ–π Diradical

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Diradicals, unusual species containing two unpaired electrons,[1] are known as intermediates or transition states in reactions such as ring opening and closure of strained cycloalkanes,[2] Cope rearrangements,[3] and bicyclobutane inversion.[4] They also might serve as building blocks to construct molecular materials with ferromagnetic or conductive properties.[5] Singlet diradicals usually are short-lived because of the unpaired electrons. A few singlet diradicals have been generated photochemically, but their longest lifetimes are on the order of microseconds.[6] Recently, Bertrand et al. claimed a persistent diradical with an alternating phosphorus-boron four-membered ring.[7] We now report the preparation, the infrared spectral analysis, and theoretical investigation of an observable B$_4$-(CO)$_2$ diradical. We present theoretical evidence that it may possess an aromatic open-shell singlet ground state with three π electrons.

B$_4$(CO)$_2$, prepared by co-deposition of laser evaporated boron cluster fragments and atoms with CO in excess argon at 8 K, was investigated using Fourier transformed infrared spectroscopy.[8] Augmented by the isotopic substitution technique, infrared absorption spectroscopy is a very powerful method for the structural characterization of novel species generated by laser ablation and isolated in matrixes.[9]

Experiments were carried out using low CO concentrations (0.05–0.1% in argon) and a relatively high laser energy to optimize the formation of boron cluster species. The BCO and BBCO molecules were the primary reaction products observed after sample deposition.[10] Absorptions due to OCBBCO and B$_4$(CO)$_2$ were produced on sample annealing, which allows the primary products to join together. Spectra in the 1380–1290 cm^{-1} region of particular interest are shown in Figure 1. Two vibrational modes (C–O and B–B stretching modes with approximately 4:1 relative intensities) were observed for B$_4$(CO)$_2$. Nine absorptions due to B–B stretching vibrations of different B$_4$(CO)$_2$ isotopomers, at 1365.8, 1358.0, 1349.6, 1343.9, 1337.4, 1329.7, 1324.9, 1317.4, and 1309.6 cm^{-1}, were observed in ^{10}B-enriched or natural abundance boron experiments (Table 1 of Supporting Information). These absorptions group into a triplet of triplets (as shown in Figure 1c). Each triplet exhibits approximately 1:8:16 relative intensities. This indicates that the vibration involves two equivalent boron atoms and is strongly coupled to the other two equivalent boron atoms.[11] The "larger" triplet pattern originates from isotopomers with ^{10}B^{10}B, ^{10}B^{11}B, and ^{11}B^{11}B at the CO-bearing positions, while the "smaller" triplet pattern originates from isotopomers with ^{10}B^{10}B, ^{10}B^{11}B, and ^{11}B^{11}B at the transannular positions. The antisymmetric C–O stretching mode (b$_{1u}$) of ^{10}B$_4$(CO)$_2$ was observed at 1993.3 cm^{-1} (Figure 1 of Supporting Information). Each absorption splits into triplets with

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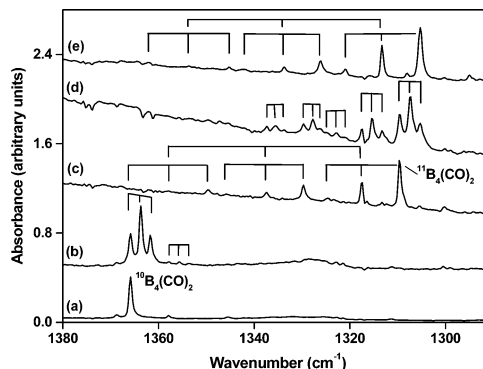§ University of Georgia.

Figure 1. Infrared spectra in the 1380–1290 cm^{-1} region from co-deposition of laser evaporated boron with CO in excess argon. (a) ^{10}B-enriched target, 0.075% ^{12}C^{16}O, (b) ^{10}B-enriched target, 0.075% ^{12}C^{16}O + 0.075% ^{12}C^{18}O, (c)–(e) natural abundance boron, (c) 0.075% ^{12}C^{16}O, (d) 0.075% ^{12}C^{16}O + 0.075% ^{12}C^{18}O, and (e) 0.075% ^{12}C^{18}O.
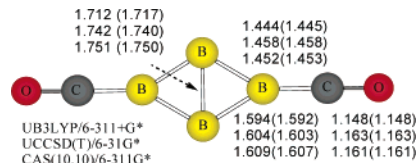

Figure 2. Optimized structures (in Å) of open-shell singlet (^{1}B$_{2g}$) and triplet (^{3}B$_{2g}$) (in parentheses) B$_4$(CO)$_2$ at various levels.

the mixed ^{12}C^{16}O + ^{12}C^{18}O sample (Figure 1b and d), indicating that two equivalent COs are involved. These data point to a B$_4$-(CO)$_2$ structure having D_{2h} symmetry.

Theoretical computations support this conclusion and provide insight into the electronic structure of B$_4$(CO)$_2$.[12] The extremely small HOMO–LUMO gap (less than 12 kcal/mol), calculated at (R)B3LYP/6-311+G* on an assumed D_{2h} closed-shell singlet (^{1}A$_g$), points to a diradical ground state (i.e., open-shell singlet or triplet) for this species. While multireference-based approaches are best to characterize such diradicals, DFT, using symmetry-broken unrestricted wave functions, can describe singlet diradicals, like para-benzyne, well (despite spin contamination).[13] Our scan of the B$_4$(CO)$_2$ potential energy surfaces at (U)B3LYP/6-311+G* shows that the D_{2h} open-shell singlet (^{1}B$_{2g}$) and triplet (^{3}B$_{2g}$) states are very close, both in energy (Table 2 of Supporting Information) and in geometry (Figure 2). These are more stable than other alternatives. The open-shell singlet is 1.4 kcal/mol lower in energy than the triplet adiabatically at (U)B3LYP/6-311+G* and 1.1 kcal/mol at (U)CCSD(T)/6-31G*.

The singly occupied π 2b$_{2g}$ and σ 9a$_g$ molecular orbitals (SOMOs; see Figure 3) indicate that B$_4$(CO)$_2$ is a σ–π diradical regardless of whether the ground state is an open-shell singlet or a
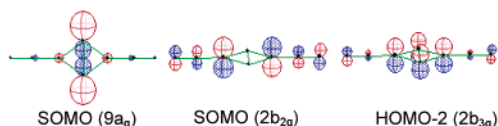
Figure 3. Molecular orbital depictions of cyclic $B_4(CO)_2$ showing the highest occupied $9a_g$, $2b_{2g}$, and $2b_{3g}$ valence molecular orbitals.

triplet. The $9a_g$ SOMO contributes to the diagonal B−B interaction, and its $2b_{2g}$ counterpart is involved with the B−C bonding. The closed-shell singlet (^1A_g) with a doubly occupied $2b_{2g}$ orbital (the lower SOMO) is 25.9 kcal/mol higher in energy than the open-shell singlet ($^1B_{2g}$) at B3LYP/6-311+G*.

The multireference complete active space self-consistent field (CASSCF) method was used to avoid spin contamination. The open-shell singlet is 3.3 kcal/mol more stable than the triplet adiabatically at CAS(10,10)/6-311G*. The singlet preference is 2.4 kcal/mol after inclusion of dynamic correlation at CASPT2(10,10)/6311G*-//CASSCF(10,10)/6-311G*. CASSCF calculations with various numbers of active orbitals and electrons gave very similar values (Supporting Information, Table 2). At CASPT2(10,10)/6-311G*//CASSCF(10,10)/6-311G*, the closed-shell (^1A_g) singlet is 24.3 kcal/mol higher in energy than the open-shell singlet.

At (U)B3LYP/6-311+G*, the antisymmetric B−B (b_{1u}) and C−O (b_{1u}) stretching vibrations of open-shell singlet $^{10}B_4(CO)_2$ were predicted to be 1438 and 2101 cm^{-1}, respectively (1376 and 2100 cm^{-1}, respectively, for $^{11}B_4(CO)_2$). These two modes are the most intense IR active absorptions (300 and 4644 km/mol), whereas all other modes have intensities less than 20 km/mol. The vibrational frequencies and isotopic frequency shifts of the triplet $B_4(CO)_2$ are about the same as those of the singlet (Table 3 of Supporting Information). For comparison, we also computed a number of related species with different structures and electron occupancies, including the D_{4h} symmetry isomer, the radical anion, the radical cation, the dianion, and the dication of $B_4(CO)_2$. None of these were computed to have infrared spectral features that match the observed frequencies.

Figure 3 also shows the doubly occupied $2b_{3g}$ MO, which mainly involves the B_4 unit. Thus, both singlet and triplet $B_4(CO)_2$ possess three π electrons. The aromaticities of these species were characterized by the simple and widely used nucleus independent chemical shift (NICS) method[14] at the gauge-including atomic orbital (GIAO)[15] UB3LYP/6-311+G**//UB3LYP/6-311+G** level. The NICS at ring centers and 1 Å above are nearly the same, −16.7 and −9.8 for the singlet versus −16.9 and −9.2 for the triplet, respectively. The corresponding benzene values are −8.0 and −10.2. In annulenes, the aromaticity or antiaromaticity of triplets and of singlets with a given electron count are exactly opposite.[16] Yet both of the $B_4(CO)_2$ diradicals, singlet and triplet, are aromatic because the SOMOs have dual σ and π character. The geometries, energies, and vibrational frequencies also are nearly the same.

The disjoint pattern of two singly occupied π nonbonding orbitals and dynamic spin polarization are responsible for the violation of Hund's rule in non-Kekulé hydrocarbons.[1,17] Similar considerations may apply to $B_4(CO)_2$, which has nearly degenerate σ and π SOMOs. While both have some bonding character, they are disjoint (see Figure 3). Hence, we favor an open-shell singlet assignment to the ground state of this species but concede the limitations of the theoretical levels employed. Unfortunately, the IR spectra do not differentiate between the singlet and triplet. ESR and magnetic circular dichroism experiments to help confirm the assignment are planned.

Supporting Information Available: Tables 1−3 mentioned in the text and infrared spectra in the 2040−1980 cm^{-1} (Figure 1) and 1550−1290 cm^{-1} (Figure 2) regions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Statistically, a vibrational mode which involves two equivalent boron atoms will split into three absorptions with approximately 1:8:16 relative intensities using natural abundance boron (^{10}B: 19.8%, ^{11}B: 80.2%). The 1329.7 and 1317.4 cm^{-1} bands ($^{11}B_3{}^{10}B$ isotopomers) exhibit equivalent integrated intensity, indicating that there is not a substantial $^{10}B/^{11}B$ equilibrium isotopic effect.

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