

Supporting Information

Investigating the Weak to Evaluate the Strong: An Experimental Determination of the Electron Binding Energy of Carborane Anions and Acidity of Carborane

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H(CHB₁₁Cl₁₁)

Energy = -5375.674669 (B3LYP/aug-cc-pVDZ); -5375.890250 (B3LYP/aug-cc-pVTZ// B3LYP/aug-cc-pVDZ); ZPE = 0.090697 (unscaled); Thermal correction to 298 K = 0.111518; -5375.772808 (B3LYP/6-311+G(d,p); ZPE = 0.091433 (unscaled); Thermal correction to 298K = 0.112226; G3(MP2) = -5369.930917 (0 K), -5369.909345 (298 K).

B	0.54754400	0.42532700	1.48617400
Cl	1.22836500	1.14293300	2.97933200
Cl	2.01973500	-2.36809400	1.79666900
B	0.99978300	-1.20902300	0.91172400
B	-0.69083600	-0.85162300	1.46565700
Cl	-1.34266900	-1.67728800	2.90018900
Cl	3.24529100	0.93887300	0.00000000
B	1.56768000	0.20380100	0.00000000
B	0.25857800	1.37853800	0.00000000
Cl	0.95678700	3.13934200	0.00000000
H	2.23897000	2.53646000	0.00000000
Cl	-2.21836100	1.88632800	1.85324300
B	-1.14207700	0.80642500	0.91915600
B	-1.72872500	-0.61802100	0.00000000
C	-0.37637200	-1.70557500	0.00000000
H	-0.60617100	-2.76937800	0.00000000
B	0.99978300	-1.20902300	-0.91172400
Cl	2.01973500	-2.36809400	-1.79666900
B	0.54754400	0.42532700	-1.48617400
B	-1.14207700	0.80642500	-0.91915600
B	-0.69083600	-0.85162300	-1.46565700
Cl	-1.34266900	-1.67728800	-2.90018900
Cl	-3.40012400	-1.22634200	0.00000000
Cl	1.22836500	1.14293300	-2.97933200
Cl	-2.21836100	1.88632800	-1.85324300

CHB₁₁Cl₁₁⁻

Energy = -5375.289591 (B3LYP/aug-cc-pVDZ); -5375.501993 (B3LYP/aug-cc-pVTZ// B3LYP/aug-cc-pVDZ)
 ZPE = 0.083528 (unscaled); Thermal correction to 298K = 0.104086; -5375.388559 (B3LYP/6-311+G(d,p); ZPE =
 0.083831 (unscaled); Thermal correction to 298 K = 0.104330; G3(MP2) = -5369.552856 (0 K), -5369.531915 (298 K).

B	0.00004700	1.54206000	0.59445700
Cl	0.00007600	3.16548300	1.37162400
Cl	-1.79134700	2.46557700	-1.87961400
B	-0.89935300	1.23786200	-0.92322000
B	0.89936100	1.23785600	-0.92322000
Cl	1.79134700	2.46557700	-1.87961400
Cl	-3.01053000	0.97826000	1.37162400
B	-1.46657200	0.47656700	0.59445700
B	0.00000000	0.00000000	1.53787900
Cl	0.00000000	0.00000000	3.33843300
Cl	3.01057700	0.97811600	1.37162400
B	1.46660100	0.47647900	0.59445700
B	1.45518900	-0.47282400	-0.92322000
C	0.00000000	0.00000000	-1.70821700
H	0.00000000	0.00000000	-2.79520900
B	-1.45519200	-0.47281600	-0.92322000
Cl	-2.89846000	-0.94176700	-1.87961400
B	-0.90643800	-1.24752600	0.59445700
B	0.90636300	-1.24758000	0.59445700
B	-0.00000500	-1.53007800	-0.92322000
Cl	0.00000000	-3.04762100	-1.87961400
Cl	2.89846000	-0.94176700	-1.87961400
Cl	-1.86068500	-2.56088500	1.37162400
Cl	1.86056300	-2.56097400	1.371624000

CHB₁₁Cl₁₁[•]

Energy = -5375.065941 (B3LYP/aug-cc-pVDZ); -5375.279907 (B3LYP/aug-cc-pVTZ// B3LYP/aug-cc-pVDZ)
 ZPE = 0.080125 (unscaled); Thermal correction to 298K = 0.101447; -5375.165025 (B3LYP/6-311+G(d,p); ZPE =
 0.080348 (unscaled); Thermal correction to 298 K = 0.101625; G3(MP2) = -5369.320093 (0 K), -5369.298264 (298 K).

B	-0.93034300	1.21805300	0.64050300
Cl	-1.86895400	2.48775000	1.43665100
Cl	-2.89435600	1.01152700	-1.84416100
B	-1.45478600	0.52804000	-0.93152600
B	-0.00077200	1.56112100	-0.91492600
Cl	-0.00291200	3.10917300	-1.78092500
Cl	-2.99738700	-1.04769400	1.32626300
B	-1.46530300	-0.53052100	0.58878900
B	-0.00270400	-0.04720200	1.55322800
Cl	-0.00483200	-0.08299600	3.33904200
Cl	1.84775200	2.49769800	1.44415200
B	0.91836900	1.22414400	0.64469400
B	1.45542700	0.53351200	-0.92837200
C	0.00302300	0.05164200	-1.72509700
H	0.00438600	0.07310600	-2.81309900
B	-0.91679300	-1.20676200	-0.97243000
Cl	-1.78173200	-2.39790200	-1.94551100
B	0.00090000	-1.56598900	0.57008000
B	1.46577500	-0.52395700	0.59306900
B	0.92987600	-1.20033100	-0.96889500
Cl	1.80370600	-2.38882700	-1.93834100
Cl	2.89667800	1.02679000	-1.83403000
Cl	0.00404500	-3.20281700	1.27117500
Cl	2.99677100	-1.03231800	1.33701400

Note – B3LYP/aug-cc-pVDZ geometries are provided above; the exact energy of H (-0.5 H) was used in computing DFT BDES.

Experimental Section

General: (1-C₄F₉SO₂)₂NH was purchased from Wako chemical and used as obtained. Cs(CHB₁₁Cl₁₁), Cs(CHB₁₁Br₆H₅), Cs(CHB₁₁Cl₆H₅), Cs(CHB₁₁I₆H₅), Cs(CHB₁₁Br₆Me₅), and H(CHB₁₁Cl₁₁) were prepared as previously described in the literature.¹⁰

Gas-phase experiments: A dual cell model 2001 Finnigan Fourier transform mass spectrometry was used with a 3 T superconducting magnet and IonSpec (now Varian) electronics including the Omega 8.0 data system. Bis(nonafluorobutane-1-sulfonyl)imide was directly introduced into the analyzer cell of the mass spectrometer and electron ionization (7.5 eV) afforded C₄F₉SO₂)₂N⁻ (*m/z* 580). This ion was cooled with a pulse of argon and transferred to the source cell where it was allowed to react with H(CHB₁₁Cl₁₁). The carborane acid is very sensitive to moisture, so it was placed in a sealed glass capillary which was ruptured against a gate valve in the solid probe at ~0.05 Torr and then was immediately introduced into the main vacuum chamber at ~10⁻⁹ Torr; the solid probe was also heated to 150° C. In addition, experiments were carried out with an IonSpec ESI FTMS also equipped with a 3 T magnet. Aqueous methanol solutions (30 mM, 3:1 (v/v) CH₃OH/H₂O) of the cesium salts of carborane anions were sprayed into the instrument, and the resulting carborane anions were isolated, cooled with a pulse of argon, and allowed to react with static pressures (~10⁻⁹ – 10⁻⁷ Torr) of the desired reagents.

Photoelectron Spectroscopy: A 1 mM solution of Cs(CHB₁₁Cl₁₁) in 3:1 (v/v) CH₃OH/H₂O was sprayed to generate the CHB₁₁Cl₁₁⁻ anion. The resulting ions were guided by a series of rf-only quadrupole devices and then bent 90° into a temperature-controlled Paul trap where they were accumulated and cooled to 70 K before being pulsed into the extraction zone of a time-of-flight mass spectrometer.¹⁵ The desired species were mass-selected and decelerated before being detached by a 157 nm (7.866 eV) F₂ excimer laser in the interaction zone of a magnetic-bottle photoelectron analyzer operated at a 20 Hz

repetition rate with the ion beam on and off on alternating laser shots for background subtraction. Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 5.2 m long electron flight tube. Time-of-flight photoelectron spectra were collected and converted to kinetic energy spectra calibrated with the known spectra of I^- and ClO_2^- . The electron binding energy spectrum reported herein was obtained by subtracting the kinetic energy spectrum from the detachment photon energy. The energy resolution ($\Delta E/E$) of the magnetic-bottle electron analyzer was 2% (i.e., 20 meV for 1 eV electrons).

Computations: All structures were fully optimized with the B3LYP density functional¹² and the 6-311+G(d,p) and aug-cc-pVDZ basis sets. In the latter case, single point energy calculations also were carried out with the aug-cc-pVTZ basis set. Vibrational frequencies were computed for each structure too to confirm that they are energy minima on the potential energy surface and to enable temperature corrections to 298 K. Unscaled frequencies were used for this purpose, and small vibrational modes which contribute more than $1/2(RT)$ to the thermal energy were replaced by $0.30 \text{ kcal mol}^{-1}$. G3(MP2) energies also were computed as described in the literature.¹³ All of the resulting energetics are reported as enthalpies at 298 K in this work. The calculations were carried out using Gaussian 03^a on workstations at the Minnesota Supercomputer Institute for Advanced Computational Research.

References

(a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; X., L.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Gaussian, Inc., Pittsburgh, PA, 2003., 2003.