Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis of iodobenzoborirene, a boraaromatic cycloproparene derivative

Holger F. Bettinger

Lehrstuhl für Organische Chemie 2

Ruhr-Universität Bochum, Universitätsstr. 150, 44780 Bochum, Germany

Experimental and Computational Details

Diiodophenylborane was synthesized from iodobenzene and borontriiodide according to Siebert et al.[1] and stored under vacuum in a glass flask at −80 °C. Matrix experiments were carried out according to standard techniques[2] with APD CSW-20 displex closed-cycle helium cryostats. Diiodophenylborane, held at +5 − +10 °C, was sublimed onto a cold CsI window (30 K) with a large excess of argon (Messer Griesheim, 99.9999%), which was dosed to 2.0 sccm by a mass flow controller (MKS Mass Flo Type 247 four-channel read out). Irradiations were performed at 10 K at 308 nm (XeCl, 1 Hz, ~150 mJ/pulse, Lambda Physics) or with a low-pressure mercury lamp (254 nm, Gräntzel).

Geometries of stationary points were optimized and harmonic vibrational frequencies were obtained using the B3LYP hybrid functional in conjunction with triple-ζ basis sets. For C, H, and B the 6-311+G** or the correlation consistent cc-pVTZ[3] basis sets were used, while for iodine the all-electron 6-311G* basis set of Glukhovtsev et al.[4] or a relativistic effective core pseudopotential cc-pVTZ-PP of Peterson et al.[5] was employed. Single energy calculations were performed at the coupled-cluster level of theory including single, double and a perturbative estimate of triple excitations, CCSD(T), using the B3LYP/cc-pVTZ-(PP) optimized structures and the cc-pVTZ-(PP) basis set. All B3LYP computations were performed with Gaussian 03,[6] while coupled-cluster computations employed Molpro[7] and the frozen-core approximation.

Table S1. Vibrational frequencies (in cm^{-1}) and infrared intensities of C_6H_4BI (^{11}B and ^{10}B isotopomers) from experiment and theory (B3LYP/6-311+G**(C,H,B);6-311G**(I), unscaled; intensities in km mol^{-1} given in parentheses).

Number	Symmetry	ν_{exp}/cm^{-1}	rel. Int.	ω_{theor}/cm^{-1} (I/km mol^{-1})
30	A1			3184.5 (27.7)
29	B2			3175.3 (29.4)
28	A1			3165.4 (0.3)
27	B2			3158.1 (1.0)
26	A1			1688.4 (217.7) [a]
26	A1	1630.5	0.20	1672.6 (166.7)
25	B2			1630.8 (2.9) [a]
25	B2			1629.9 (2.8)
24	B2			1503.1 (21.6) [a]
24	B2	1473.2	0.09	1501.5 (21.4)
23	A1			1466.7 (131.0) [a]
23	A1	1438.7	0.29	1460.9 (113.9)
22	A1			1418.2 (52.4) [a]
22	A1			1417.2 (57.5)
21	B2			1327.0 (0.0) [a]
21	B2			1325.1 (0.0)
20	A1			1192.8 (0.9) [a]
20	A1			1192.6 (0.3)
19	B2			1168.1 (0.6) [a]
19	B2			1167.6 (0.6)
18	A1	1102.8 1096.4 1086.2 1080.0	1.0	1123.2 (326.9) [a] 1103.6 (317.4)
17	B2			1027.5 (0.4) [a]
17	B2			1026.1 (0.5)
16	A2			1023.2 (0.0)

15	A1	990.0	0.07	1012.2 (22.1)
14	B1			983.5 (0.0)
13	A1			969.6 (13.4) [a]
13	A1	942.7	0.04	961.5 (26.6)
12	A2			900.2 (0.0)
11	B1	751.7	0.13	769.3 (54.2)
10	A2			728.3 (0.0)
9	B2			732.7 (1.4)
9	B2			720.9 (1.0)
8	A1			625.9 (17.8) [a]
8	A1	609.4	0.05	623.4 (19.6)
7	B2			559.8 (10.2) [a]
7	B2	543.3	0.03	552.5 (10.4)
6	B1			464.9 (15.8) [a]
6	B1			455.2 (15.4)
5	A2			428.4 (0.0)
4	B1			346.6 (0.3) [a]
4	B1			341.9 (0.2)
3	A1			245.8 (2.5) [a]
3	A1			245.5 (2.6)
2	B2			134.9 (1.1) [a]
2	B2			133.5 (1.0)
1	B1			81.1 (0.9) [a]
1	B1			80.4 (0.9)

[a] ^{10}B Isotopomer, natural abundance 19.2 %.

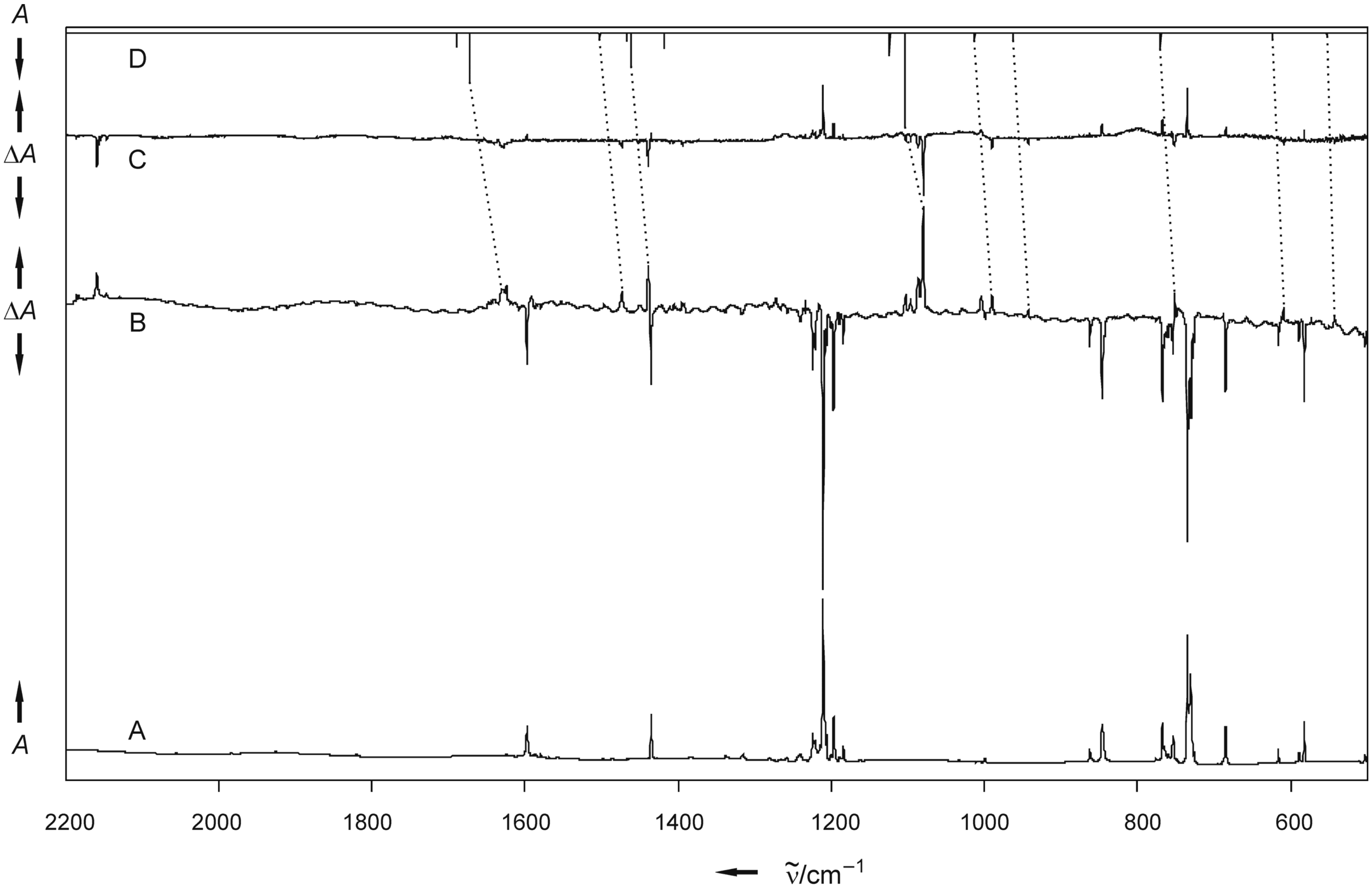
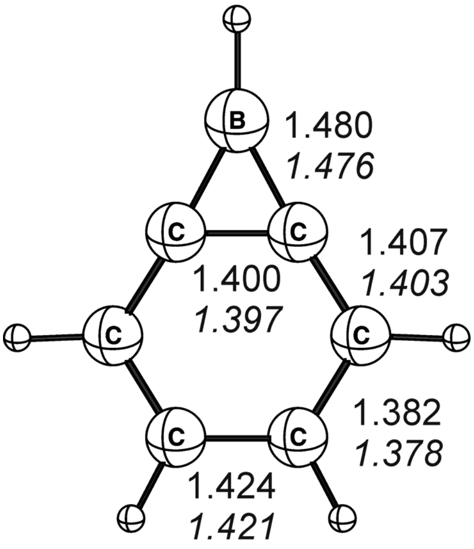
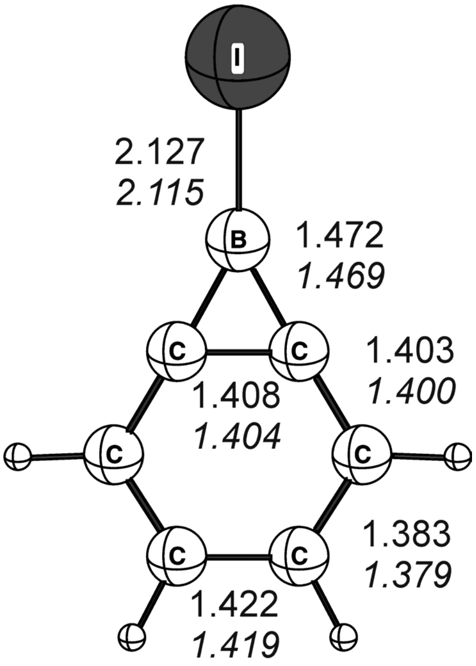


Figure 1 (as in the manuscript) enlarged



2a



2b

Figure 2. Geometries computed for **2a** and **2b** at the B3LYP level of theory using either 6-311+G** (C, B, H) and 6-311G* (I) basis sets (normal type) or cc-pVTZ (C, H, O) and cc-pVTZ-PP (I) basis sets. All bond lengths are given in Å.

References

[1] Siebert, W.; Rittig, F. R.; Schmidt, M. *J. Organomet. Chem.* **1970**, *25*, 305.

[2] Dunkin, I. R. *Matrix-Isolation Techniques*; Oxford University Press: Oxford, 1998.

[3] Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

[4] Glukhovtsev, M. N.; Pross, A.; McGrath and, M. P.; Radom, L. *J. Chem. Phys*. **1995**, *103*, 1878.

[5] Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. *J. Chem. Phys*. **2003**, *119*, 11113.

[6] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; J. A. Montgomery, J.; 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.; Li, X.; 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, Revision B.4, Pittsburgh PA, 2003.

[7] MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles with contributions from R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, H. Stoll, A. J. Stone, R. Tarroni, and T. Thorsteinsson. Version 2000.1.