Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information (ESI)

Molecular Wheel to Monocyclic Ring Transition in Boron-Carbon Mixed Clusters $C_2B_6^-$ and $C_3B_5^-$

Timur R. Galeev,[a] Alexander S. Ivanov,[b] Constantin Romanescu,[c] Wei-Li Li,[c] Konstantin V. Bozhenko*[b], Lai-Sheng Wang*[c] and Alexander I. Boldyrev*[a]

[a] *Department of Chemistry and Biochemistry, Utah State University, Old Main Hill 0300, Logan, UT 84322-0300, USA. Fax: +1 435-797-3390, Tel: +1 435 7971630; E-mail: a.i.boldyrev@usu.edu*
[b] *Department of Physical and Colloid Chemistry, Peoples' Friendship University of Russia, 6 Miklukho-Maklaya St., Moscow 117198, Russian Federation. E-mail: kbogenko@mail.ru*
[c] *Department of Chemistry, Brown University, 324 Brook Street, Providence, Rhode Island 02912, USA. Tel: +1 401-863-3389; E-mail: Lai-Sheng_Wang@brown.edu*

Complete references 26 and 27:

26 Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford, CT, 2004.

27 MOLPRO, version 2006.1, H.-J. Werner, P. J. Knowles, F. R. Manby, M. Schütz, P. Celani, G. Knizia, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, A. Wolf .

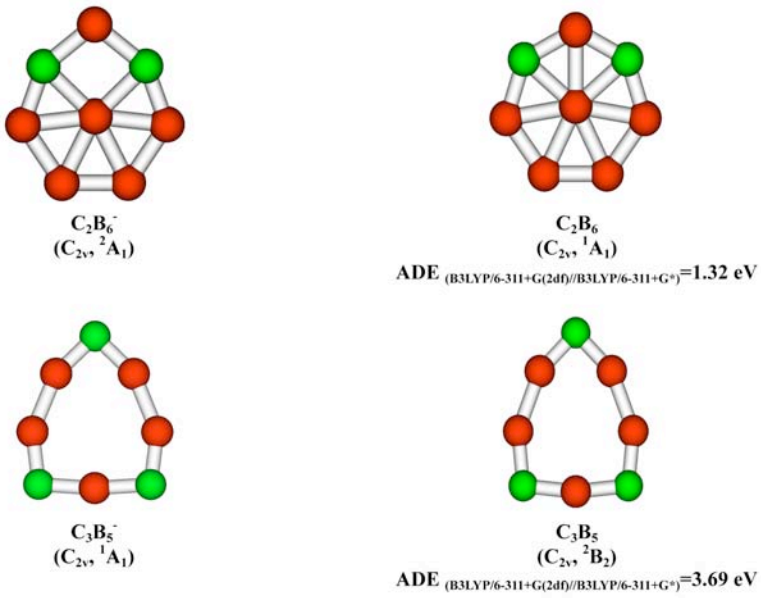

Fig. 1S Adiabatic Detachment Energies (ADE) of the $C_2B_6^-$ and $C_3B_5^-$ clusters

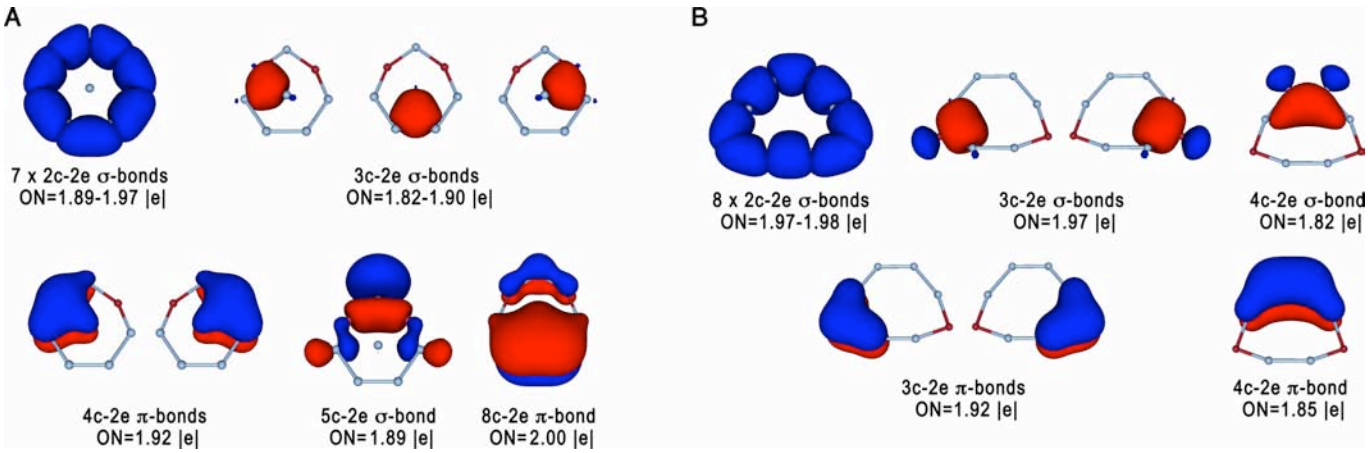

Fig. 2S The chemical bonding patterns revealed by the AdNDP analysis for the $C_2B_6^{2-}$ cluster at the optimized geometries of the global minimum wheel-type structure I.1 (**A**) and lowest ring isomer I.6 (**B**) of the $C_2B_6^-$ cluster. The extra electron was added in order to avoid complications of the chemical bonding picture caused by spin polarization in the open-shell $C_2B_6^-$ cluster. The 2c-2e C-B and B-B bonds of both isomers are superimposed on a single molecular framework.

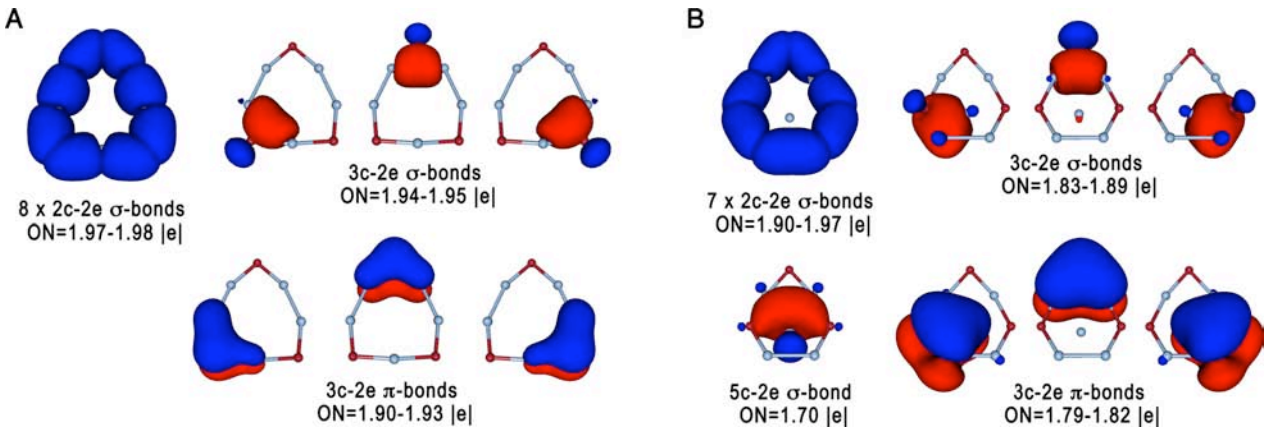

Fig. 3S The chemical bonding patterns revealed by the AdNDP analysis for the global minimum ring isomer II.1 (**A**) and the lowest wheel-type isomer II.5 (**B**) of the $C_3B_5^-$ cluster. The 2c-2e C-B and B-B bonds of both isomers are superimposed on a single molecular framework.

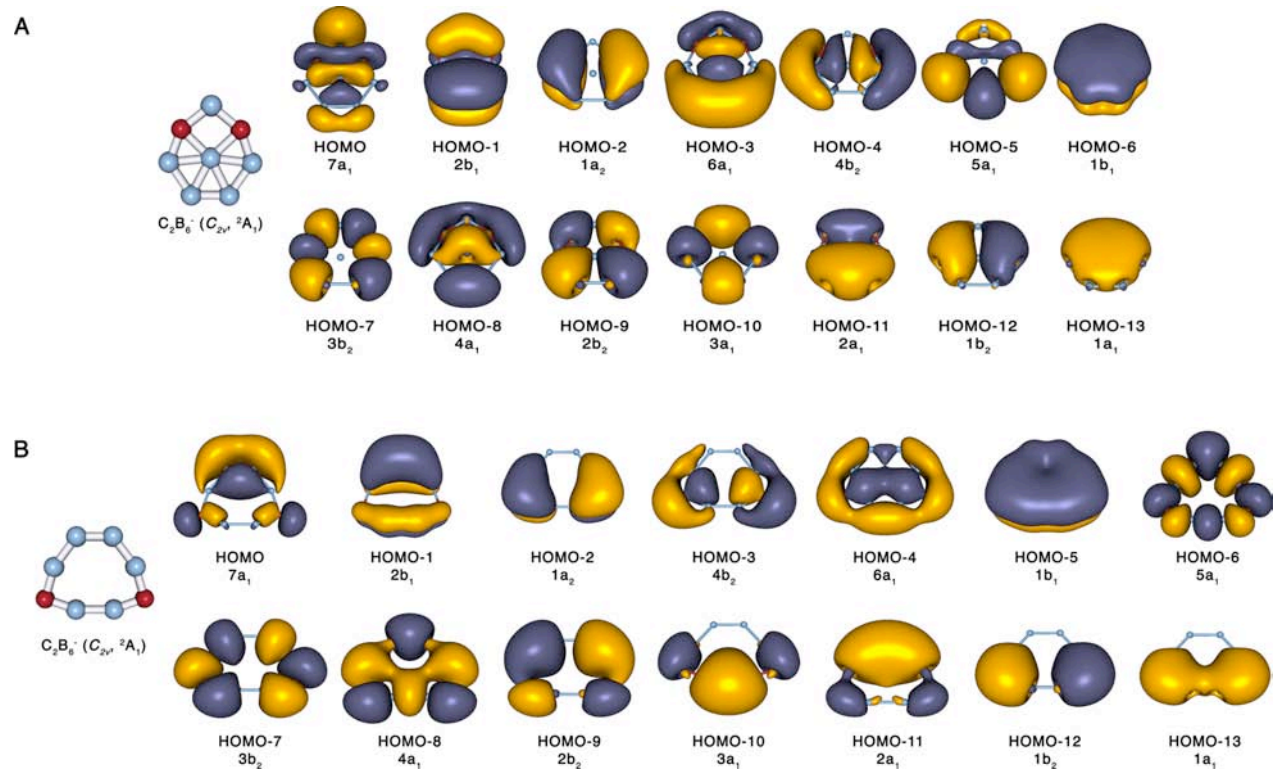

Fig. 4S Valence canonical molecular orbitals (B3LYP/6-311+G*) of the global minimum wheel-type structure I.1 (**A**) and the lowest-lying ring isomer I.6 (**B**) of the $C_2B_6^-$ cluster.

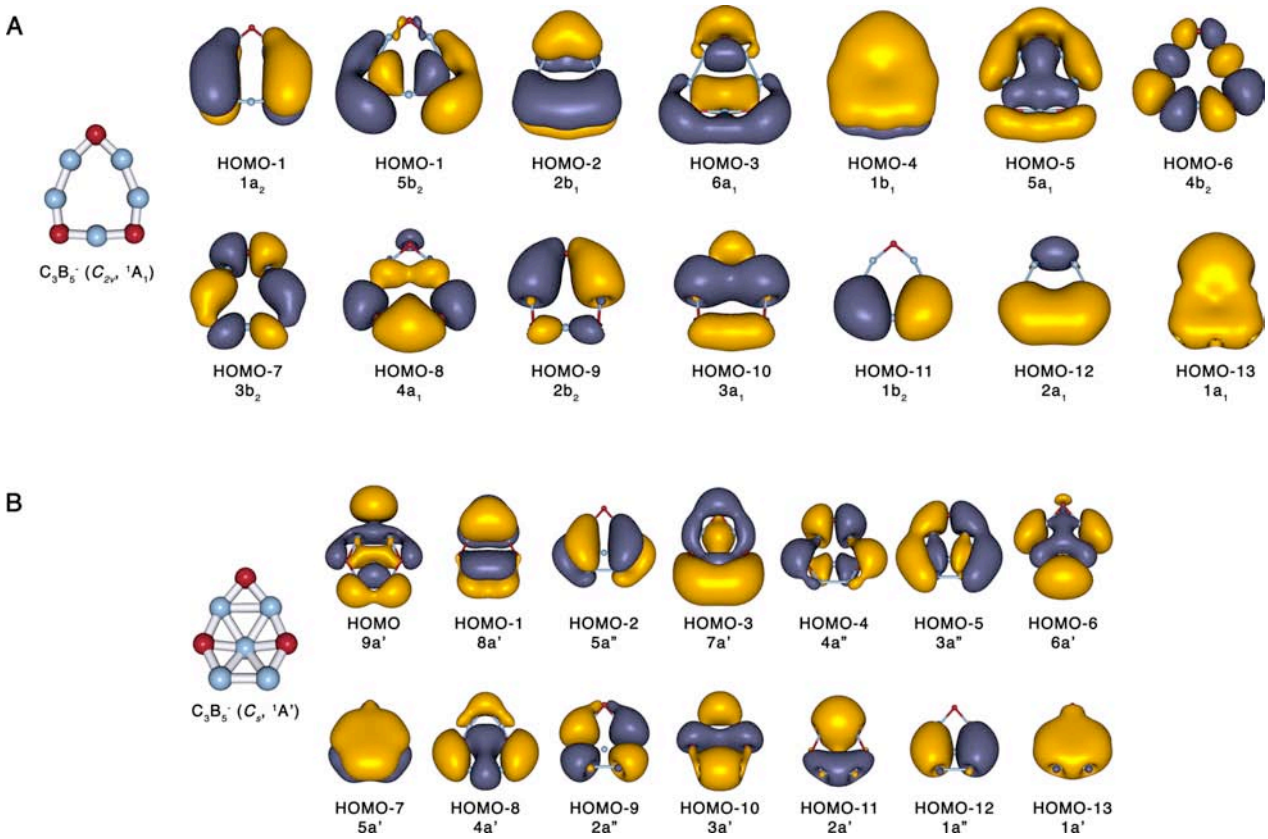

Fig. 5S Valence canonical molecular orbitals (B3LYP/6-311+G*) of the global minimum ring structure II.1 (**A**) and the lowest-lying wheel isomer II.5. (**B**) of the $C_3B_5^-$ cluster. The order of canonical molecular orbitals for the isomer II.1 (**A**) at B3LYP/6-311+G* is different from the order of the spectroscopy states calculated by TD-B3LYP, ROVGF and RCCSD(T) presented in Table 2.