Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Three-center two-electron bonds from the quantum interference perspective

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This supplementary material contains 8 supplemental figures (S1-S8) and 1 supplemental table.

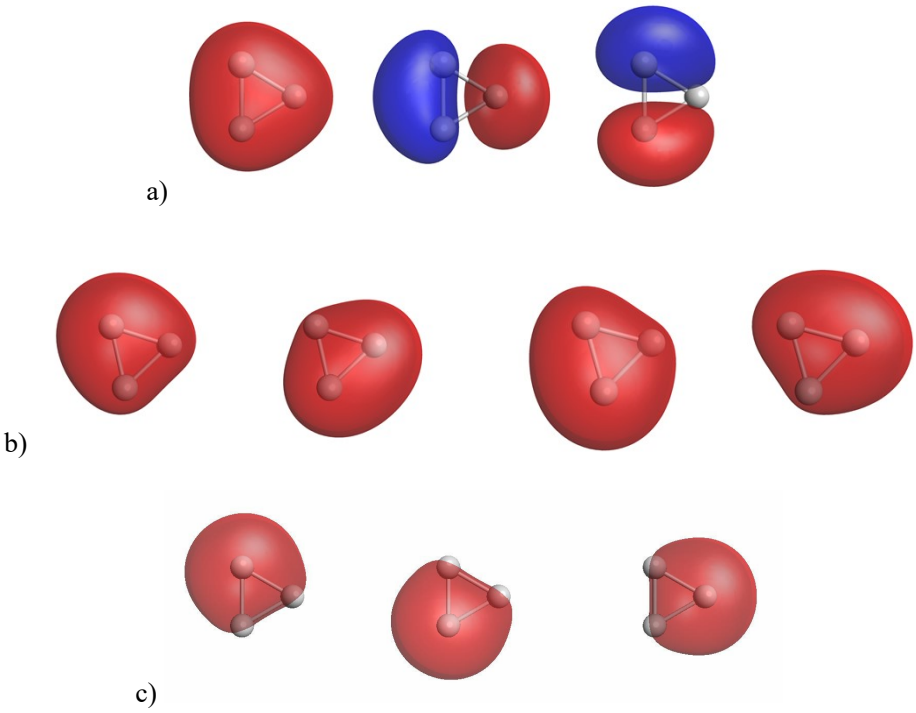

Figure S1. Orbitals of the H_3^+ molecule at the CASSCF level (a), GVB-PP structures 1 and 2 (b) and SC(2,3). MC-SC orbitals are equivalent to the combination of GVB-PP structures. The contour value is 0.1 for all the orbitals.

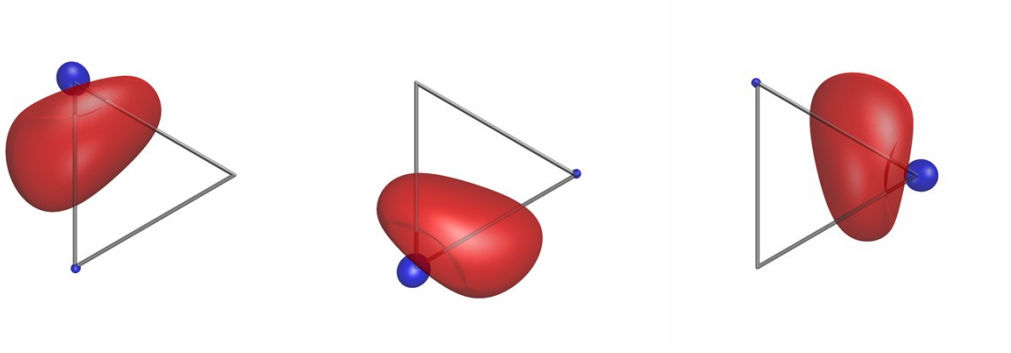

Figure S2. Orbitals for the Li_3^+ molecule at the SC(2,3)/cc-pVTZ level. The contour value is 0.1 for all the orbitals.

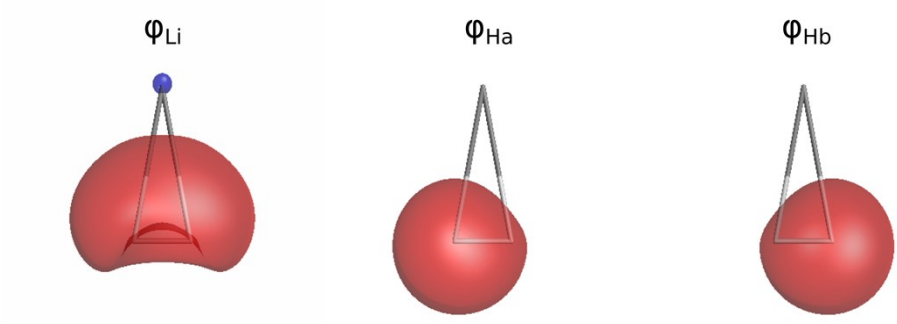

Figure S3. Orbitals for LiH_2^+ calculated at SC(2,3)/cc-pVTZ level. The contour value is 0.1 for all the orbitals.

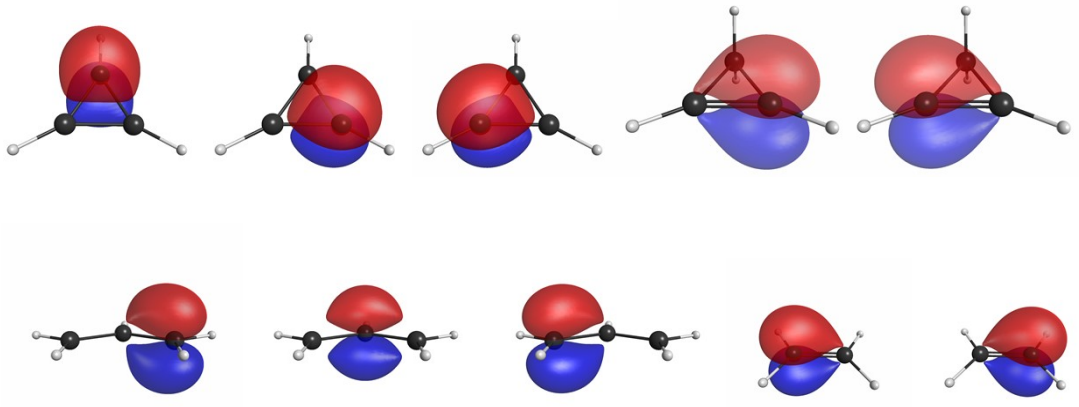

Figure S4. Orbitals of the π system fot the species $C_3H_3^+$ (top left), C_3H_4 (top right), $C_3H_5^+$ (bottom left), and C_2H_4 (bottom right). The contour value is 0.1 for all the orbitals.

Table S1. Selected molecular parameters of the species R_2CBeCR_2 (R = H, CH_3), H_2CBe, **a**, and **b** at the CASSCF/cc-pVTZ level.

	R(C-Be) (Å)	θ(C-Be-C) (º)	R(C-C) (Å)	R(C-H) (Å)	θ(H-C-H) (º)
H_2CBeCH_2	1.6712	179.82	-	1.0794	111.37
$(CH_3)_2CBeC(CH_3)_2$	1.6739	180.00	1.5112	-	-
H_2CBe ($^1A_1$)	1.5808	-	-	1.0752	117.01
H_2CBe ($^3B_1$)	1.6797	-	-	1.0796	111.73
Compound a[a]	1.664 / 1.659	180.0	1.541	-	-
Compound b[a]	1.659 / 1.657	179.3	-	-	-

[a]: M. Arrowsmith, H. Braunschweig, M.A. Celik, T. Dellermann, R. D. Dewhurst, W. C. Ewing, K. Hammond, T. Kramer, I. Krummenacher, J. Mies, K. Radacki and J. K. Schuster, Neutral Zero-Valent s-Block Complexes with Strong Multiple Bonding, *Nat. Chem.,* 2016, **8** (9), 890–894. https://doi.org/10.1038/nchem.2542.

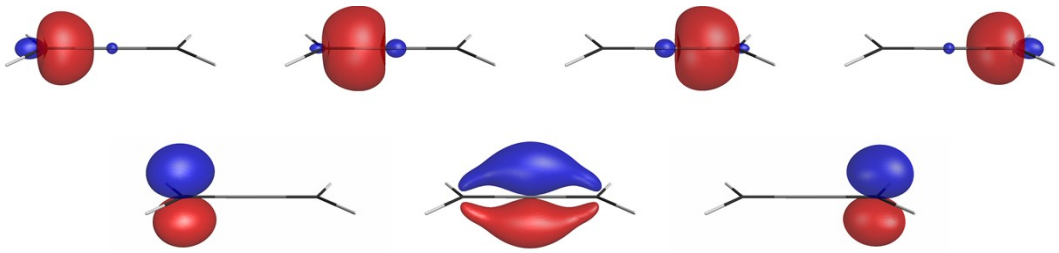

Figure S5. Calculated orbitals for H_2CBeCH_2. The contour value is 0.1 for all the orbitals.

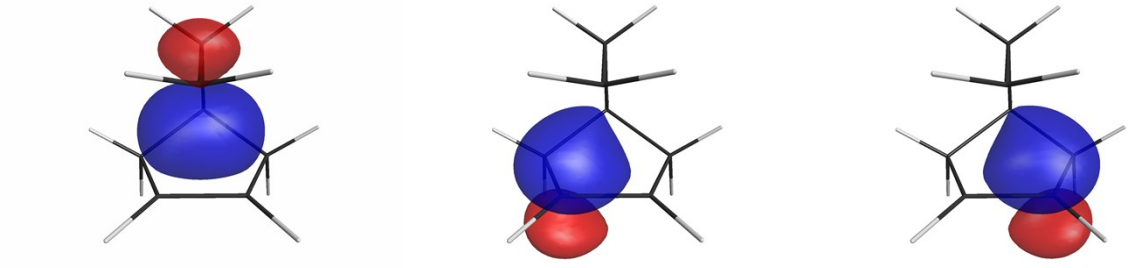

Figure S6. Calculated orbitals for the 3c2e bond of the nonclassical structure of the 2-norbornyl cation. The contour value is 0.1 for all the orbitals.

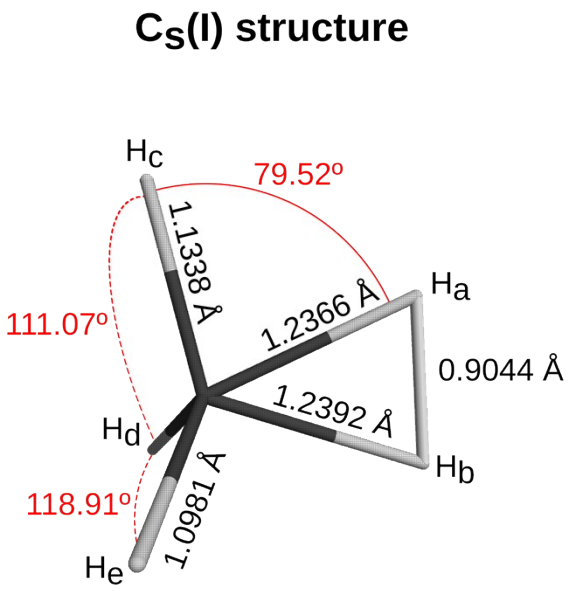

Figure S7. CAS(8,9)/aug-cc-pVTZ global minimum of CH_5^+.

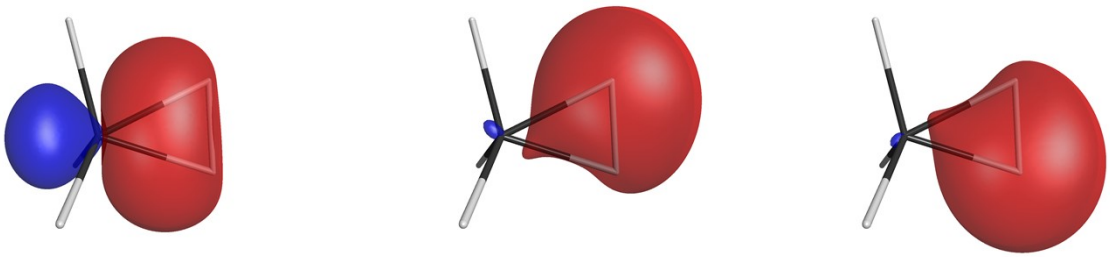

Figure S8. Calculated orbitals for the 3c2e bond of the global minimum of CH_5^+. The contour value is 0.1 for all the orbitals.