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Structure−Correlation Principles Connecting Ground State Properties and Reaction Barrier Heights for the Cope Rearrangement of Semibullvalenes

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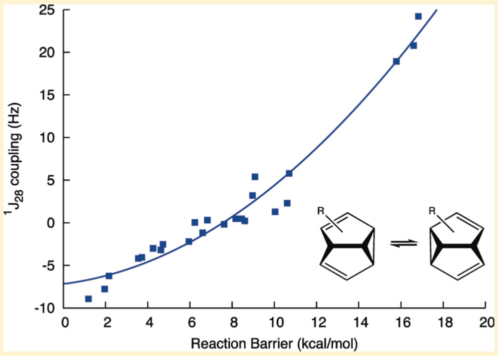
Supporting Information

ABSTRACT: A direct relationship exists between the properties of substituted semibullvalenes and their Cope rearrangement activation barrier. This unique correlation not only enables the determination of kinetic data from ground state information, but also provides a rationalization for the extent to which ground state properties are altered with respect to their "normal" values (i.e., that of their localized Lewis structure). Examination of electron density distribution, geometrical parameters, and *J*-coupling constant differences between canonical and Lewis structures deliver quantitative evidence for the structure−correlation principle.



A fascinating situation exists in pericyclic reactions, in which transition state characteristics directly correlate with the properties of the ground state. This effect is known as the structure−correlation principle.[1] As an example, density redistribution toward the *retro*-Diels−Alder transition state accounts for the peculiar ^1J-coupling constants (i.e., the abnormally large/small values for C—C/C═C bonds) of unsaturated bicyclic systems, such as norbornene and its derivatives.[2−6] This note further expands this phenomenon by establishing a direct correlation between the activation barriers and ground state properties of sigmatropic rearrangements. This unique relationship not only enables the determination of kinetic data from ground state information, but also provides a rationalization for the extent to which ground state properties are altered with respect to their "normal" values. The degenerate Cope rearrangement (CR) of semibullvalene constitutes an ideal proof-of-principle example: the transition state barrier height can be altered by strategic placement of various electron-donating/withdrawing substituents and strain-inducing annelations[7−10] to the point of eventual stabilization of a bishomoaromatic ground state[11−16] as recently experimentally realized.[11] Furthermore, the rigid tricyclic molecular structure (boat conformation) goes through a typical pericyclic homoaromatic transition state and lacks "chameleonic"[17−22] nature, thus simplifying the controversial picture of the reaction mechanism (i.e., the diradical character of the transition state is modest).

In semibullvalene (**1**), the net structural outcome of the degenerate Cope rearrangement is the breaking/formation of the C_2−C_8/C_4−C_6 bonds. **1** features an elongated 1.61 Å C_2−C_8 bond (Figure 1A) as compared to the C−C bond of ethane (1.53 Å), cyclopropane (1.51 Å), or even the parent CR prototype, gauche hexa-1,5-diene (1.54 Å) computed at the B3LYP/6-311+G(d,p) level. Alternatively, **1** possesses shorter/longer C_2C_3/C_3C_4 (1.47/1.34 Å) than hexa-1,5-diene (1.51/1.33 Å). A similarly insightful picture is provided by both the Wiberg bond orders and the $^1J_{28}$ coupling constants. The $^1J_{28}$ coupling constant of **1** (Figure 2), for instance, is abnormally low (−0.2 Hz) when compared to the C−C single bonds in ethane (30.9 Hz), cyclopropane (10.1 Hz[23]), or even a distorted cyclopropane [imposed into the C_1−C_2−C_8 conformation (5.0 Hz)]. In fact, the $^1J_{28}$ coupling constant more closely matches the $^2J_{CC}$ coupling computed for propane (−1.3 Hz). These structural deviations, associated with electronic anomalies, arise from an intramolecular effect that can be attributed to redistribution of the density of semibullvalene toward its CR transition state. In other words, the geometrical parameters and electron density of **1** resembles its Cope rearrangement TS more than expected in a localized Lewis structure.

To prevent this density redistribution (i.e., electron delocalization) and verify its effect on the properties of semibullvalene, we constructed and optimized a truly localized Lewis structure, in which one double bond is confined entirely between two carbon atoms, using the block-localized wave function (BLW) approach of Mo.[24−27] For the nonsymmetric molecules (i.e., non-C_s), the double bond further away from the substituent was blocked, although the two alternative localizations led to the same effect. Comparisons of the density,

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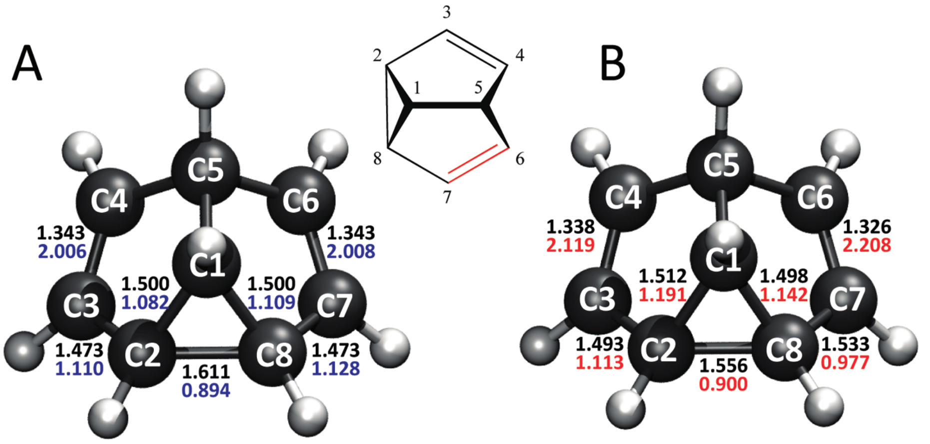

Figure 1. Carbon numbering used for semibullvalene throughout the text (top). Canonical (A) and BLW-localized (B) (BLW-)B3LYP/6-311+G(d,p) geometries. The C_6–C_7 bond indicated in red is localized in the BLW optimized geometry B. The bond lengths (Å) computed at the same level are given in black. The Wiberg bond orders are given in blue for the canonical (A) and in red for the BLW-localized geometries and density (B).

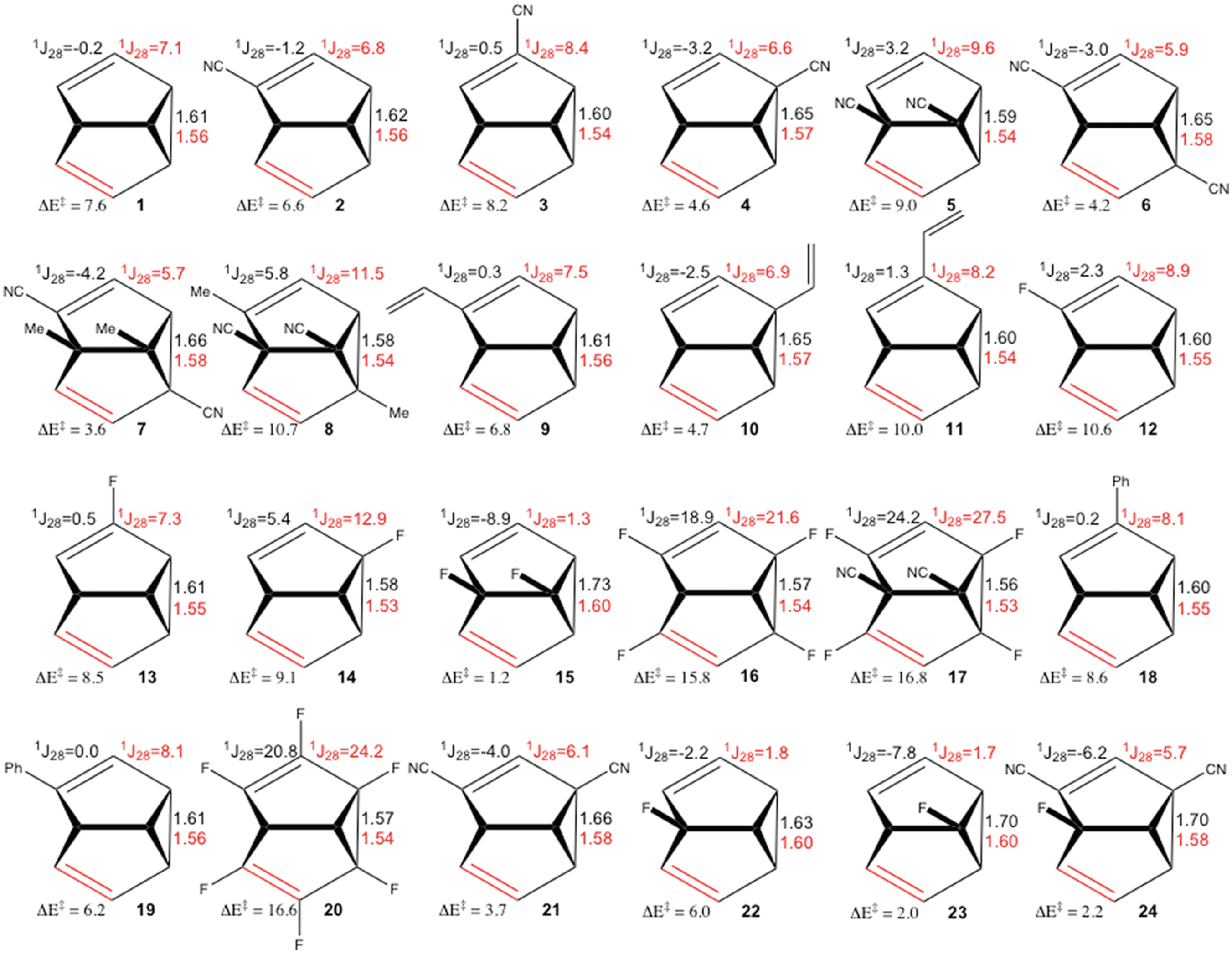

Figure 2. Semibullvalene and 23 substituted derivatives. Red double bonds were localized using the BLW method and geometries optimized at the BLW-B3LYP/6-311+G(d,p) level. C_2–C_8 ^1J-couplings constants (above) computed at the PBE/IGLO-III//(BLW)-B3LYP/6-311+G(d,p) level and bond lengths (Å right side) are given for both for the canonical (black) and the block-localized (red) geometries. The CCSD(T)/cc-pVTZ//B3LYP/6-311+G(d,p) activation barriers (kcal/mol) (lower left) are not corrected for zero-point energies.

geometrical parameters, and *J*-coupling constants of both the BLW-localized (i.e., block-localized) and canonical (i.e., delocalized) states allow direct probing of the fingerprints of the Cope rearrangement on the ground state properties in an unbiased and direct manner. This procedure has already provided unique quantitative insight in a related context highlighting the peculiarity of norbornene[2] and served to demonstrate the magnetic anomalies of conjugated molecules.[28,29]

Localization of the C_6–C_7 double bond (via the BLW procedure) results in a drastic shortening of the C_2–C_8 bond (R_{28}) to a typical C–C single bond distance (1.56 Å, Figure 1B). This shortening is accompanied by a slight decrease/increase in the C_3–C_4 double bond distance/order (0.005 Å/0.202). Thus, localization of the C_6–C_7 double bond delivers the idealized Lewis structure (with "normal" bond distances), represented by Figure 1B. The drastic geometry changes induced upon localization of the π-electron bond corroborate the large degree of structural deformation toward the TS present in the ground state (GS) of semibullvalene. The extent is well illustrated by Figure 3, which shows the electron density difference (EDD) between the canonical and BLW-localized wave function. The red and yellow regions, corresponding to the C_2–C_8 bond, indicate increased electron density upon localization (reduced interaction in the GS) of the C_6–C_7 π-electrons. The blue/green areas between the C_1–C_2 and C_1–C_8 bonds indicate decreased density imposed by the restitution of cyclopropane character. In a sense, the localization of the π system restores the typical σ-delocalized cyclopropane moiety with a stronger C_2–C_8 bond and a normal $^1J_{28}$ coupling value (as compared to cyclopropane, 10 Hz).

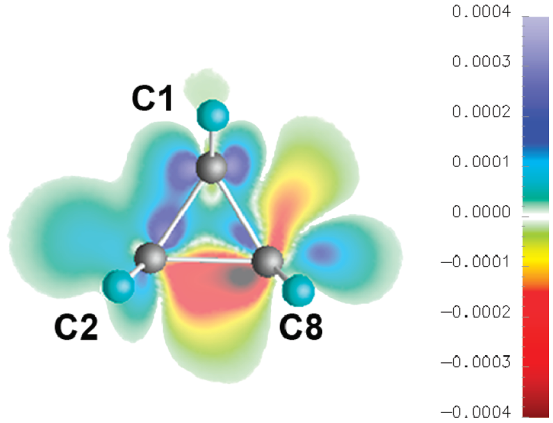

Figure 3. The electron density difference (EDD) between canonical and BLW-localized wave functions of semibullvalene computed at the PBE/IGLO-III level using the B3LYP/6-311+G(d,p) geometries. The blue zone represents higher density in the ground state, while red indicates higher density in the BLW-localized state.

The structure–correlation principle can be further exploited by analyzing the influence of substituents (Figure 2) on the $^1J_{28}$ and R_{28} values as a function of the activation barrier. Placement of electron-withdrawing/donating substituents at selected semibullvalene positions are known to influence the CR activation barrier.[7−10] If the TS does affect the structure of semibullvalene, one should expect a correlation between reaction barrier height and ground state properties for a series of semibullvalene derivatives. π-withdrawing (e.g., cyano and vinyl groups) substitution at the 2/8- and 4/6-positions reduce the barrier height, while donating groups (e.g., fluorine, methyl) placed in those same positions have the opposite effect. Placing these substituents at positions 1 and 5 lead to a reversed trend, (as compared to substituting at positions 2/8 and 4/6), while substitutions at positions 3 and 7 have a minimal effect on the reaction rate.

The activation barrier associated with the Cope rearrangement of 24 substituted semibullvalenes are given in Figure 2 together with the $^1J_{28}$(BLW) coupling constants and C_2–C_8 bond distance of both the standard and BLW-localized forms. Structures **2** and **4** (as well as **22** and **23**) share a common transition state; thus, the difference in activation energies simply reflects the overall reaction energy of the Cope rearrangement between the two systems. The accumulation of substituent effects is illustrated by two contrasting derivatives, **17** (1,5-dicyano-2,4,6,8-tetrafluorosemibullvalene) and **15** (1,5-difluorosemibullvalene), characterized by the highest (16.8 kcal/mol) and lowest (1.2 kcal/mol) activation barriers, respectively. The substitution patterns associated with decreased activation barriers relative to **1** each possess a smaller/larger J_{28} or R_{28} than the semibullvalene reference. Inversely, the compounds with increased activation barriers as compared to **1** exhibit larger/shorter C_2–C_8 $^1J_{CC}$ coupling constant/bond distance. Thus, a strong (inverse) relationship exists between the TS barrier height and the ground state properties (i.e., the $^1J_{28}$ coupling constants and the R_{28} bond distances). Examination of Figure 4 illustrates the high-degree

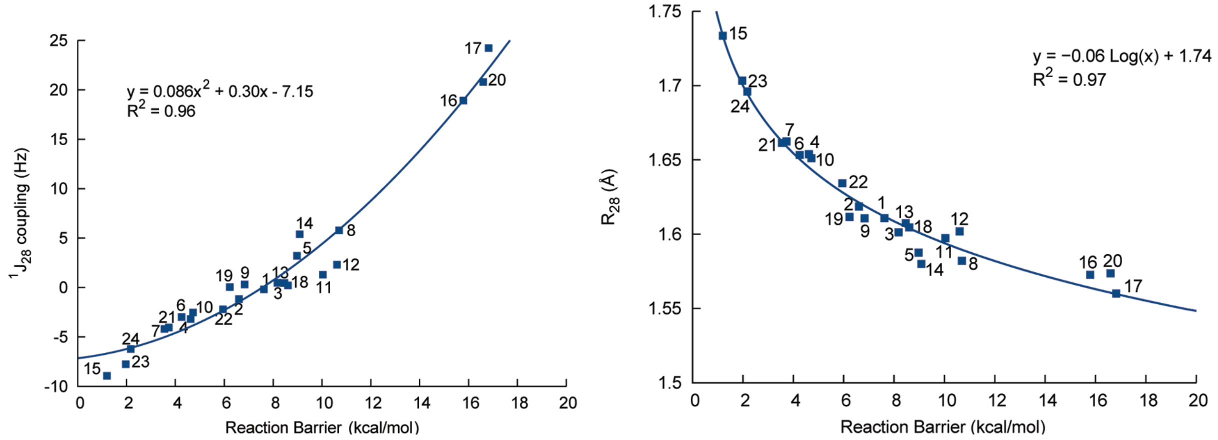

Figure 4. Correlation plots of the Cope rearrangement activation barrier (at the CCSD(T)/cc-pVTZ//B3LYP/6-311+G(d,p) level) with the PBE/IGLO-III//B3LYP/6-311+G(d,p) $^1J_{28}$ canonical coupling constant (left) and the B3LYP/6-311+G(d,p) R_{28} bond distances (right). Data are taken from Figure 2.

of curvilinear relationships between the activation barrier and the C_2-C_8 ^1J coupling constant/bond distance. Similar correlations exist when considering changes in the $^1J_{28}$ coupling constant and C_2-C_8 bond distance between canonical and BLW-localized structures (i.e., Δ^1J_{28} and ΔR_{28}; see Figures S2 and S3 in the Supporting Information) as well as the difference between the R_{28} and R_{46} bond distances (Figure S6, Supporting Information). These relationships show, unequivocally, that the TS energetics of this pericyclic reaction directly correlates with the ground state properties. This phenomenon is in line with the X-ray diffraction analysis of substituted semibullvalenes by Quast et al., who reported that small variations of the apparent C_2-C_8 and $C_4\cdots C_6$ atomic distances are observed in more rapidly rearranging derivatives.[30] Unlike the geometries of the majority of derivatives included in the test sets (Figure 2), those (1,5-difluoro-2,4,6,8-tetracyanosemibullvalene and 2,4,6,8-tetracyanosemibullvalene) that are characterized by a bishomoaromatic ground state (see Figure S7, Supporting Information, and ref 16) are highly sensitive to the theoretical level used in the optimization (e.g., 2,4,6,8-tetracyanosemibullvalene has a bishomoaromatic ground state at the B3LYP but not at the M06-2X geometry). For this reason, they have been excluded from Figure 4 but are given in the Supporting Information (Figures S8 and S9).

This work examines the Cope rearrangement of a series of semibullvalene derivatives to demonstrate a clear relationship between the transition state energy and the ground state properties of the C−C bond being broken. The fingerprint of transition states in the ground state properties can occur in bicyclic and tricyclic products of diverse pericyclic reactions such as Diels−Alder, Cope, and Claisen. Similar to the Bell−Evans−Polanyi relation,[31,32] the Burgi−Dunitz correlation principle, and the Hammond postulate, the link existing between the reaction kinetics and ground state characteristics could permit facile assessment of activation barriers based solely on the ground state geometry.[1] Using the kinetic details of reference compounds, structure−property relationships, such as those presented herein, could be utilized as the last step of a hierarchical screening of novel derivatives to assess their kinetic feasibility and persistence. In particular, it could serve as a measure of dynamics and robustness of shape-shifting organic molecules (e.g., based on bullvalene).[33]

■ COMPUTATIONAL DETAILS

The Cope rearrangement transition states and adducts shown in Figures 1 and 2 were optimized at the (BLW)-B3LYP[34,35]/6-311+G(d,p) level using a modified version of GAMESS-US 2008-R1.[36] Diabatic states were obtained from BLW[24−26] computations where the C_6-C_7 π-bond that is displayed in red was localized. Using the block-localized wave function approach, one can construct the wave function of an electron-localized reference Lewis structure by partitioning the system into several mutually interacting subgroups and restricting the expansion of each MO in only one subspace. The block-localized state can be self-consistently optimized and used in molecular property computations. Note that our version of the BLW module only allows the simultaneous blocking of orthogonal or parallel bonds, thus excluding the simultaneous blocking of two double bonds in semibullvalene derivatives. The geometry of the block-localized structures can additionally be optimized. The diradical character of the transition states was found to be negligible (T1 diagnostic smaller than 0.014 at the CCSD level).[37,38] The activation barriers were computed at the CCSD(T)/cc-pVTZ level (single-point) in Molpro using the B3LYP/6-311+G(d,p) geometries. Note that activation barriers computed at the B3LYP/6-311G(d,p) level correlate well with those computed at the CCSD(T)/cc-pVTZ level (see Figure S11, Supporting Information).

The J-coupling computations were performed using the gauge-including atomic orbitals (GIAO)[39] approximation at the (BLW)-PBE[40]/IGLO-III level as implemented in our version of Dalton.[41] The electron density difference plots were computed at this same level on the canonical B3LYP/6-311+G(d,p) geometry. The BLW formalism has already been shown[42] to be rather insensitive to the level of theory used, as it relies on the difference between the properties of a resonance structure and that of adiabatic state computed at the same level.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cartesian coordinates of all structures (canonical, BLW, TS, and GS); additional correlation figures between ^1J-coupling, C_2-C_8 and C_4-C_6 bond distances with activation barriers (Figures S1−S6, S8); energy and structural parameters of **1**, **15**, 1,5-difluoro-2,4,6,8-tetracyanosemibullvalene, and 2,4,6,8-tetracyanosemibullvalene at different energy levels (Figure S7); correlation plots of the activation barriers computed at the B3LYP/6-311G(d,p) with CCSD(T)/cc-pVTZ (Figure S10). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153.
(2) Steinmann, S. N.; Vogel, P.; Mo, Y.; Corminboeuf, C. *Chem. Commun.* **2011**, *47*, 227.
(3) Goh, Y. W.; Danczak, S. M.; Lim, T. K.; White, J. M. *J. Org. Chem.* **2007**, *72*, 2929.
(4) Unruh, G. R.; Birney, D. M. *J. Am. Chem. Soc.* **2003**, *125*, 8529.
(5) Birney, D.; Lim, T. K.; Koh, J. H. P.; Pool, B. R.; White, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 5091.
(6) Jones, G. R.; Caldarelli, S.; Vogel, P. *Helv. Chim. Acta* **1997**, *80*, 59.
(7) Hoffmann, R.; Stohrer, W. D. *J. Am. Chem. Soc.* **1971**, *93*, 6941.
(8) Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 7201.
(9) Dewar, M. J. S.; Jie, C. *Tetrahedron* **1988**, *44*, 1351.
(10) Miller, L. S.; Grohmann, K.; Dannenberg, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 6862.
(11) Griffiths, P. R.; Pivonka, D. E.; Williams, R. V. *Chem.—Eur. J.* **2011**, *17*, 9193.
(12) Williams, R. V. *Chem. Rev.* **2001**, *101*, 1185.
(13) Jiao, H.; Nagelkerke, R.; Kurtz, H. A.; Williams, R. V.; Borden, W. T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1997**, *119*, 5921.
(14) Paquette, L. A.; Liao, C. C.; Burson, R. L.; Wingard, J., R. E.; Shih, C. N.; Fayos, J.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 6935.
(15) Dewar, M. J. S.; Wade, J., L. E. *J. Am. Chem. Soc.* **1977**, *99*, 4417.
(16) Wu, H. S.; Jia, J. F.; Jiao, H. J. *J. Mol. Model.* **2007**, *13*, 133.
(17) Hrovat, D. A.; Chen, J.; Houk, K. N.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 7456.
(18) Doering, W. v. E.; Wang, Y. *J. Am. Chem. Soc.* **1999**, *121*, 10112.

(19) Hrovat, D. A.; Beno, B. R.; Lange, H.; Yoo, H.-Y.; Houk, K. N.; Borden, W. T. *J. Am. Chem. Soc.* **1999**, *121*, 10529.
(20) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 334.
(21) Kozlowski, P. M.; Dupuis, M.; Davidson, E. R. *J. Am. Chem. Soc.* **1995**, *117*, 774.
(22) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67.
(23) Strain is known to influence *J*-coupling constants by altering the relative s-character of a bond. See: Frei, K.; Bernstein, H. J. *J. Chem. Phys.* **1963**, *38*, 1216.
(24) Mo, Y. *J. Chem. Phys.* **2003**, *119*, 1300.
(25) Mo, Y.; Gao, J. L.; Peyerimhoff, S. D. *J. Chem. Phys.* **2000**, *112*, 5530.
(26) Mo, Y.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687.
(27) The BLW method allows for the construction and optimization of a block-localized wave function self-consistently. The BLW state represents a specific resonance structure (i.e., a diabatic state), which then serves as an ideal reference for the energies or properties of the fully delocalized states. See refs 2, 24−26, 28, and 29 for details and examples.
(28) Steinmann, S. N.; Jana, D. F.; Wu, J. I. C.; Schleyer, P. v. R.; Mo, Y.; Corminboeuf, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 9829.
(29) Steinmann, S. N.; Mo, Y.; Corminboeuf, C. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20584.
(30) Quast, H.; Carlsen, J.; Janiak, R.; Peters, E.-M.; Peters, K.; Schnering, H. G. V. *Chem. Ber.* **1992**, *125*, 955.
(31) Bell, R. P. *Proc. R. Soc. London, Ser. A* **1936**, *154*, 414.
(32) Evans, D. J.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11.
(33) He, M.; Bode, J. W. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 14752.
(34) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(35) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785.
(36) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
(37) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem., Symp.* **1989**, *23*, 199.
(38) Lee, T. J. *Chem. Phys. Lett.* **2003**, *372*, 362.
(39) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.
(40) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
(41) *DALTON, A Molecular Electronic Structure Program*, Release 2.0; University of Southern Denmark, 2005; http://www.kjemi.uio.no/software/dalton/dalton.html.
(42) Mo, Y.; Hiberty, P. C.; Schleyer, P. v. R. *Theor. Chem. Acc.* **2010**, *127*, 27.