

## Is Cyclobutadiene Really Highly Destabilized by Antiaromaticity?

Judy I-Chia Wu,<sup>a\*</sup> Yirong Mo,<sup>b</sup> Francesco Alfredo Evangelista,<sup>c</sup> and Paul von Ragué Schleyer<sup>a\*</sup>

<sup>a</sup> Department of Chemistry, Center for Computational Quantum Chemistry, University of Georgia, Athens, GA 30602, USA. Fax: (+1) 706 542 0406; E-mail: schleyer@chem.uga.edu <sup>b</sup> Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008, USA. E-mail: yirong.mo@wmich.edu <sup>c</sup> Department of Chemistry, Yale University, New Haven, CT 06520, USA. E-mail: francesco.evangelista@yale.edu

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### Detailed computational procedure for the enthalpy of formation of CBD

The theoretically-derived enthalpy of formation of cyclobutadiene was based on an all-electron focal-point analysis [East, Bak] computation of the reaction enthalpy of the dimerization of acetylene to cyclobutadiene:  $2 \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_4$  [ $\Delta_f H^\circ_0(\text{C}_4\text{H}_4) = 104.23 \text{ kcal mol}^{-1}$ , see below] and the experimental enthalpy of formation of acetylene at 0K [ $\Delta_f H^\circ_0(\text{C}_2\text{H}_2) = 54.69 \pm 0.07 \text{ kcal mol}^{-1}$ ] given in the active thermochemical tables of Ruscic [Bomble]. All computations used the MOLPRO 2006.1, CFOUR, and MRCC program packages [MOLPRO,CFOUR,MRCC]. Highly accurate optimized geometries for acetylene and cyclobutadiene were computed at the all-electron coupled cluster single, double, and perturbative triple [CCSD(T)] level using the correlation-consistent, core-valence polarized, quadruple zeta cc-pCVQZ basis set of Woon and Dunning [Woon]. These geometries were employed for Hartree-Fock and all-electron CCSD(T) computations with the cc-pCVXZ basis set series [Woon] ( $X = \text{D,T,Q,5}$ ). The incremental contribution to the reaction energy at each level of theory is reported in Table S1, together with complete basis set (CBS) extrapolated values. The RHF energy computed using the cc-pCVTZ, cc-pCVQZ, and cc-pCV5Z basis sets was fitted to the equation  $E_{\text{RHF}}(X) = A + Be^{-cX}$ , where  $A$ ,  $B$ , and  $C$  are parameters and  $X$  is the cardinal number corresponding to the maximum angular momentum of the basis set. The correlation energy computed using the cc-pCVQZ and cc-pCV5Z basis sets was fitted instead to the  $E_{\text{corr}}(X) = A + B X^{-3}$  equation. Complete basis set RHF and coupled cluster results are obtained by extrapolating  $X \rightarrow \infty$ . Energy contributions from the coupled cluster full triple (CCSDT) and perturbative quadruple excitations [CCSDT(Q)] were estimated from the incremental contributions computed using the cc-pCVDZ basis set. Harmonic zero-point vibrational energy corrections to the reaction enthalpy were computed at the CCSD(T) level using the cc-pVDZ and cc-pVTZ basis sets [Dunning]. The carbon 1s-like core molecular orbitals were frozen in the correlation energy computations. The final reaction enthalpy is  $-5.15 \text{ kcal mol}^{-1}$  and the estimated uncertainty from the neglect of anharmonic, relativistic, and diagonal Born-Oppenheimer corrections is less than  $0.25 \text{ kcal mol}^{-1}$ . The enthalpy of formation of  $\text{C}_2\text{H}_2$  combined with our accurate dimerization energy gives:  $\Delta_f H^\circ_0(\text{C}_4\text{H}_4) = 2 \Delta_f H^\circ_0(\text{C}_2\text{H}_2) + \Delta_r H^\circ_0(\text{C}_2\text{H}_2) = (109.38 - 5.15) \text{ kcal mol}^{-1} = 104.23 \text{ kcal mol}^{-1}$  ( $= 436.09 \text{ kJ mol}^{-1}$ ). However, note the ca.  $0.5 \text{ kcal/mol}$  uncertainty of the experimental enthalpy of formation of acetylene at 0 K (ranging from 54.19 to 54.69 kcal/mol recommended in various compilations).

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[MOLPRO] MOLPRO, version 2006.1, a package of ab initio programs by H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, G. Rauhut, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, A. W. Lloyd, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni.

[CFOUR] Coupled-Cluster techniques for Computational Chemistry, a quantum-chemical program package by J.F. Stanton, J. Gauss, M.E. Harding, P.G. Szalay with contributions from A.A. Auer, R.J. Bartlett, U. Benedikt, C. Berger, D.E. Bernholdt, Y.J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W.J. Lauderdale, D.A. Matthews, T. Metzroth, D.P. O'Neill, D.R. Price, E. Prochnow, K. Ruud, F. Schiffmann, W. Schwalbach, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J.D. Watts and the integral packages MOLECULE (J. Almlöf and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see <http://www.cfour.de>.

[MRCC] Y. J. Bomble, J. F. Stanton, M. Kállay, and J. Gauss, *J. Chem. Phys.* **123**, 054101 (2005); M. Kállay and J. Gauss, *J. Chem. Phys.* **123**, 214105 (2005).

**Table S1.** The all-electron focal point analysis of the acetylene to cyclobutadiene dimerization. All results are in kcal mol<sup>-1</sup>. The symbol  $\delta$  denotes the increment in the relative energy ( $\Delta E_e$ ) with respect to each preceding level of theory in the RHF→MP2→CCSD→CCSD(T)→CCSDT→CCSDT(Q) hierarchy. Results obtained from basis set extrapolations are shown in square brackets. Parentheses indicate estimated CCSDT and CCSDT(Q) corrections. Harmonic vibrational energy corrections ( $\Delta_{ZPVE}$ ) were computed at the CCSD(T) level.

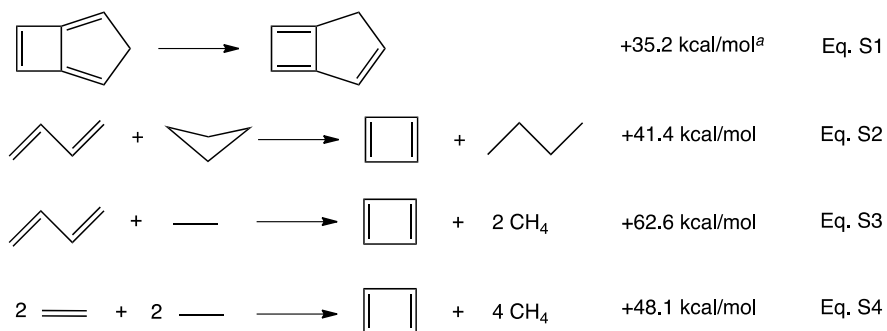
Basis Set	$\Delta E_e$	$+\delta$	$+\delta$	$+\delta$	$+\delta$	$+\delta$	NET $\Delta E$
	RHF	MP2	CCSD	CCSD(T)	CCSDT	CCSDT(Q)	
cc-pCVDZ	-1.95	-8.04	-2.01	-1.56	-0.14	-0.12	-13.82
cc-pCVTZ	2.24	-8.24	-1.37	-1.69	(-0.14)	(-0.12)	-9.32
cc-pCVQZ	2.00	-8.35	-1.31	-1.73	(-0.14)	(-0.12)	-9.65
cc-pCV5Z	1.89	-8.36	-1.32	-1.76	(-0.14)	(-0.12)	-9.81
CBS limit	[1.78]	[-8.38]	[-1.33]	[-1.78]	(-0.14)	(-0.12)	<b>-9.97</b>

Basis Set	$\Delta_{ZPVE}$
	CCSD(T)
cc-pVDZ	4.91
cc-pVTZ	4.83 <sup>a</sup>

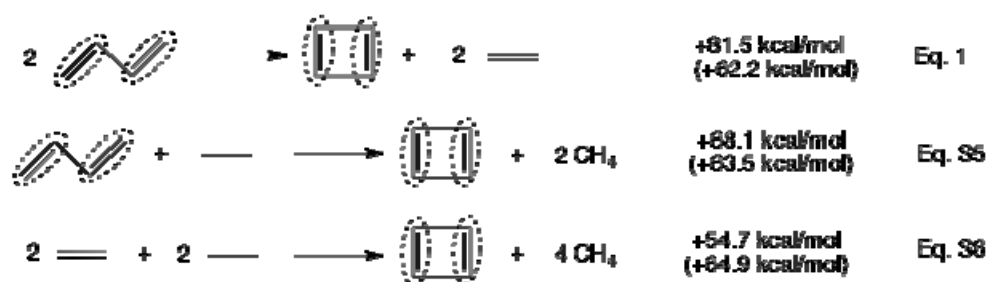
$$\begin{aligned} \Delta_r H(0 \text{ K, final}) &= \Delta E_e[\text{CBD CCSDT(Q)}] + \Delta_{ZPVE} [\text{CCSD(T)/cc-pVTZ}] \\ &= -9.97 + 4.83 = \mathbf{-5.15 \text{ kcal mol}^{-1}} \end{aligned}$$

<sup>a</sup> The zero-point vibration energies of CBD and acetylene computed at CCSD(T)/cc-pVDZ are 37.90 and 16.54 kcal mol<sup>-1</sup>, respectively.



**Figure S1.** Various homodesmotic and isodesmic evaluations of the destabilization energy of CBD. <sup>a</sup>Computed data for Eq. S1 at B3LYP/6-31G\* + ZPE, taken from ref. 19). Data for Eqs. S2-S4 were based on experimental enthalpies of formation, except that 104.3 kcal/mol was employed for CBD.

**Comment:** Interpretations of other homodesmotic and isodesmic equations commonly employed to evaluate the energy of CBD (cf. **Fig. S1**) are complicated by blends of strain,  $\pi$  conjugation, and  $\pi$  antiaromaticity effects (see main text refs. 19, 27-30). The indene-isoindene based (ref. 19) equation S1 does not evaluate the antiaromatic destabilization energy of CBD satisfactorily, since the bismethylenecyclobutene reference molecule lacks parallel  $\pi$  bonds and does not model the strain of CBD adequately. Equation S2 compares CBD with butadiene, but cyclobutane does not compensate for the much higher ring strain of CBD either. Equation S3 does not compensate for the CBD ring strain at all! Nor does Equation S4, which measures a composite of the ring strain and the *net  $\pi$  resonance energy* of CBD relative to *unconjugated* ethane references. However, if one considers CBD to be “unconjugated” (i.e., zero  $\pi$  resonance energy as in Hückel theory), the 48.1 kcal/mol value approximates a lower bound for the strain energy of CBD.



**Figure S2.** Equations 1, S5, and S6 computed at the B3LYP/PVTZ level. The values in parenthesis are computed under applied BLW constraints, in which all  $\pi$  conjugative interactions are “disabled” (the BLW “blocks” are indicated by the dotted circles). Based on this BLW procedure, all three analyses give similar ring strain estimates for CBD.

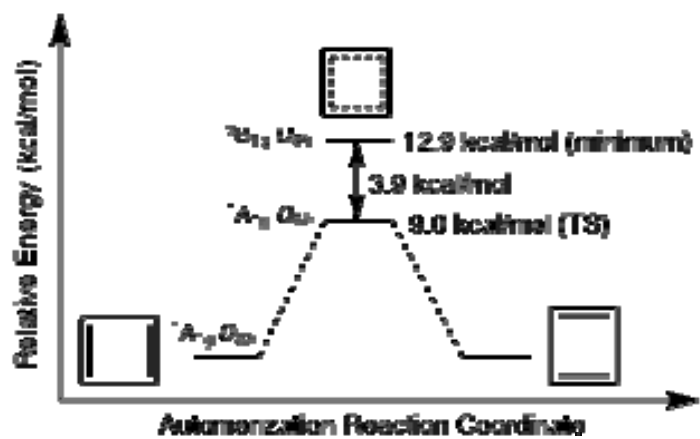


Figure S3. Potential energy surface for CBD at Mk-MRCCSD(T)/cc-pVQZ.

**Resonance energy vs. aromatic stabilization (anti-aromatic destabilization) energy:**

To avoid ambiguity when discussing the energetics of aromatic and antiaromatic molecules, it is important to clearly distinguish the terms “resonance energy,” “aromatic stabilization energy,” and “antiaromatic destabilization energy (or *negative* aromatic stabilization energy).” Following the Pauling-Wheland definition (see ref. 21), “resonance energy” describes the total stabilization due to  $\pi$  conjugation in acyclic or cyclic systems (relative to the energy of the most stable resonance contributor). But the “extra” energetic stabilization (or destabilizations) that arises from the cyclic arrangement of fully conjugated double bonds in an aromatic (or antiaromatic) molecule is called the aromatic stabilization energy (or antiaromatic destabilization energy, see refs. 10 and 22). This is sometimes referred to as the “Dewar resonance energy” (see ref. 22). In short, the resonance energy describes the total  $\pi$  stabilization of a system, of which the aromatic stabilization energy (in cyclically conjugated systems) comprises only a part. Colloquially, aromatic systems are “more stable than they ought to be,” whereas anti-aromatic systems may still be stabilized in an absolute sense, but are “less so than they ought to be.”