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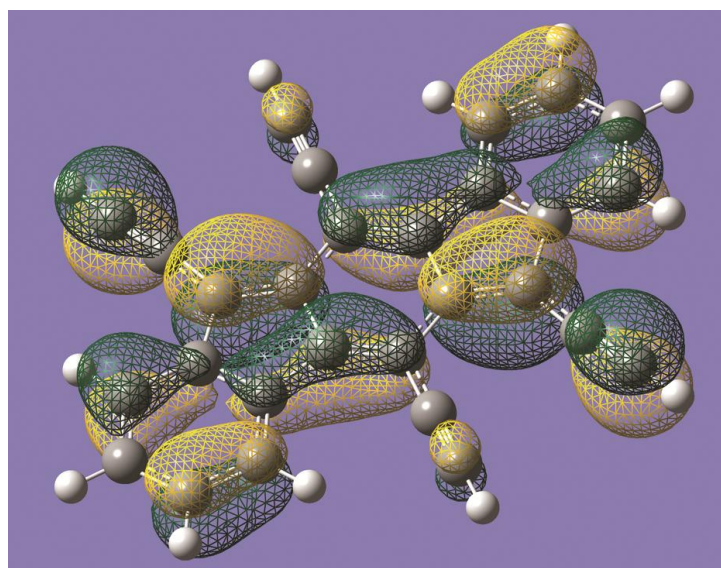
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COMMUNICATION

Is cyclobutadiene really highly destabilized by antiaromaticity?^{†‡§}Judy I-Chia Wu,^{*a} Yirong Mo,^b Francesco Alfredo Evangelista^c and Paul von Ragué Schleyer^{*a}

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The high energy of cyclobutadiene (CBD) is not due primarily to “anti-aromaticity,” but rather to angle strain, torsional strain, and Pauli repulsion between the parallel CC bonds. Estimations including block-localized wavefunction (BLW) computations conclude that the enormous ring strain (ca. 60 kcal mol^{−1}) far exceeds its antiaromatic destabilization (only 16.5 kcal mol^{−1}).

Cyclobutadiene is the organic textbook “anti-aromatic paradigm”, but its peculiar thermochemical instability has not been explained satisfactorily.¹ Cyclic conjugated 4n π electron hydrocarbons originally were called “non-aromatic” or “pseudo aromatic” and were expected to have polyene character. Breslow pointed out that 4n π electron species related to the cyclopropenyl anion and CBD, were highly destabilized and exhibited pronounced bond length alternation.^{13,14} He coined the “antiaromatic” description, which has been in common use ever since. But is CBD really highly destabilized by antiaromaticity? Complexed² and substituted^{3–7} CBD derivatives are known. However, Barbiou *et al.*'s recent claim of “trapping” 1,3-dimethylcyclobutadiene has raised much skepticism and debate.⁸ The parent CBD has only fleeting existence⁹ and is difficult to isolate.^{10–12} Based on Breslow's original definition, “a cyclic conjugated system is considered antiaromatic if its π energy is higher [*i.e.* less stabilizing] than that of a suitable reference compound which is not cyclically delocalized”.¹⁴ Thus, the π resonance stabilization of antiaromatic compounds are expected to be reduced compared to those of fully conjugated but non-aromatic analogs. According to Breslow's estimate of this effect, “the true CBD anti-aromatic destabilization energy is probably of the order of 15–20 kcal mol^{−1}”.¹⁴ While Dewar's 18 kcal mol^{−1} was in line,¹⁵ more recent evaluations give much higher values (see below).

CBD displays many distinct “antiaromaticity” features: *i.e.*, induced paramagnetic ring current in the presence of an externally applied magnetic field⁸ and computed positive NICS (nucleus independent chemical shifts)¹⁶ values (isotropic NICS(0) = +20.8 ppm, see also ref. 17 and 18) at the ring center. Nevertheless, there are good reasons to question the conventional interpretation that CBD is highly antiaromatically destabilized. None of the larger planar 4n π electron annulenes, beginning with cyclooctatetraene show significant antiaromatic destabilization in their bond-alternating ground states or even in their bond-equalized transition states.^{14,19,20} If the “anti-aromaticity” of such systems are not destabilizing, why should antiaromaticity destabilize CBD significantly? (See Supporting Information[§] for the important distinction between the resonance energy²¹ and the antiaromatic destabilization energy²²).

There is no doubt that CBD is highly unstable thermochemically. But is the putative “antiaromaticity” responsible? The enthalpy of formation of CBD is positive and very large.^{9,23,24} We employed the highly accurate all-electron focal-point method²⁵ to compute the enthalpy of formation of CBD ($\Delta_f H_0^\circ = 104.2 \pm 1.0$ kcal mol^{−1}) (see Supporting information[§]). This is well within the bounds of Fattahi *et al.*'s 102.4 ± 3.8 kcal mol^{−1} experimental value.²³ The destabilization of CBD (77.2 kcal mol^{−1}) is very large based on four times the 6.78 kcal mol^{−1} Benson C_d–(C_d)H conjugated increment.²⁶ This analysis is equivalent to eqn (1), where the four =CH– groups of CBD are compared to the energy of the four =CH– groups in two *anti*-butadienes. Since the latter are stabilized by conjugation, the energy associated with the skeletal strain of CBD cannot be differentiated from the π antiaromaticity directly. Bally commented, “there is no unambiguous way to dissect this (ca. 80 kcal mol^{−1}) number”.¹

Interpretations of the energy of CBD largely rely on the assumption that the conventional strain energies of cyclobutane (26.8 kcal mol^{−1})²⁶ and of cyclobutene (29.8 kcal mol^{−1})²⁶ can be extrapolated linearly (based on the consecutive replacement of two sp³ by two sp² ring carbons) to a ca. 33 kcal mol^{−1} value, for CBD (see Fig. 1).^{23,24,27–30} Fattahi *et al.* proposed that the strain energy of 3,4-bismethylenecyclobutene (38.4 kcal mol^{−1}, see Fig. 1) might be an upper bound for the ring strain of CBD, as it also has only sp² ring carbons but exhibits additional 1,4-HH repulsion between the exocyclic double bonds.²³ But the exocyclic C=C bonds of 3,4-bismethylenecyclobutene do not model the closely separated parallel π bonds of CBD satisfactorily.

^a Department of Chemistry, Center for Computational Quantum Chemistry, University of Georgia, Athens, GA 30602, USA.

E-mail: judywu@ccc.uga.edu, schleyer@chem.uga.edu;
Fax: (+1) 706 542 0406

^b Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008, USA. E-mail: yirong.mo@wmich.edu

^c Department of Chemistry, Yale University, New Haven, CT 06520, USA. E-mail: francesco.evangelista@yale.edu

[†] This paper is dedicated to Ron Breslow.

[‡] This article is part of the *ChemComm* ‘Aromaticity’ web themed issue.

[§] Electronic supplementary information (ESI) available: details for the all-electron focal point analysis of the acetylene to cyclobutadiene dimerization, details for the block-localized wavefunction (BLW) evaluations of the ring strain of cyclobutadiene (CBD). See DOI: 10.1039/c2cc33521b

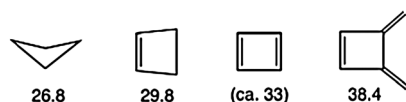


Fig. 1 Conventional ring strain estimates (in kcal mol⁻¹) for cyclobutane, cyclobutene, and 3,4-bismethylenecyclobutene, based on their experimental enthalpies of formation and Benson group increments. The extrapolated ring strain for CBD (see text) also is given.

The *ca.* 44 kcal mol⁻¹ difference between the 33 kcal mol⁻¹ CBD strain estimate and the 77 kcal mol⁻¹ total destabilization energy of CBD (based on eqn (1), Fig. 2) is the most common value attributed to the putative 4n π electron antiaromatic destabilization.^{23,24,27–30} But following the same lines of reasoning, the assumed “strain-balanced” eqn (2) gives a much lower antiaromatic CBD destabilization energy estimate (36.2 kcal mol⁻¹). But eqn (2) suffers from other inherent problems. Hyperconjugation in cyclobutene (13.6 kcal mol⁻¹, see ref. 31) stabilizes the left side of this equation by 27.2 kcal mol⁻¹, but this is not considered in eqn (2). When corrected for this imbalance, the estimated antiaromatic destabilization energy for CBD (9.0 kcal mol⁻¹, see eqn (2), second value) is lowered even more! In view of the resulting large range of antiaromatic destabilization energy estimates for CBD,^{23,24,32,27–30} there are good reasons to doubt that the strain energy of CBD can be estimated accurately from the usual four membered ring reference molecules.

The large ring strain of CBD must be much more than 50 kcal mol⁻¹. CBD suffers from Pauli repulsion of the parallel π and σ bonds as well as from the four highly strained 90° \angle CCC bond angles. Neither cyclobutane nor cyclobutene have or model these features. As it costs 12.8 kcal mol⁻¹ (at B3LYP/PVTZ) to deform a methyl radical \angle HCH angle to 90°, the crudely estimated angle strain in CBD is 4 \times 12.8 = 51.2 kcal mol⁻¹ on this basis alone.

In addition, the longer CC single bonds in CBD (1.576 Å) than in 1,3-butadiene (anti 1.455 Å, syn 1.469 Å) (at B3LYP/PVTZ),³³ document the repulsive π – π interaction between the parallel C=C bonds,³⁴ which contributes to the enormous strain of CBD. Pauli repulsion increases dramatically when two parallel H₂ molecules are brought together in rectangular D_{2h} symmetry.³⁵ The two parallel C–C σ single bonds in CBD also approach each other closely (see TOC and ref. 36). Hence, CBD suffers from *angle strain*, *torsional strain*, as well as π – π and σ – σ repulsion. But no other 4n π electron annulene or four membered ring model exhibits all of these unfavorable features and combinations of compounds do not mimic the CBD strain satisfactorily either (see Supporting Information§).

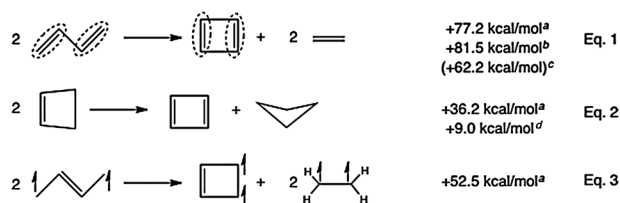


Fig. 2 Energetic evaluations of CBD. ^a Based on $\Delta H_f = 104.3$ kcal mol⁻¹ for CBD and experimental values. ^b Computed at B3LYP/PVTZ. ^c The BLW constraints shown were applied to the π interactions (see text). ^d Corrected for hyperconjugation (see ref. 31).

However, triplet (D_{4h}) cyclobutadiene is nearly an ideal model for the ring strain of singlet CBD! The triplet has many of the skeletal features of singlet CBD (*i.e.*, 90° \angle CCC bond angles, fully eclipsed CH bonds around the ring, and closely separated parallel CC bonds), but is considered to be triplet aromatic^{37,38} with equal CC lengths (1.438 Å, at B3LYP/PVTZ), close to the 1.454 Å CC average for the singlet. Akin to eqn (1), which evaluates the strain and antiaromaticity of CBD, eqn (3) evaluates the strain energy of triplet CBD and its inherent aromatic stabilization energy. Since the aromatic triplet CBD is expected to exhibit “excess” π resonance stabilization,³⁷ the 52.5 kcal mol⁻¹ endothermicity of eqn (3) serves as a lower bound for the strain energy of singlet D_{2h} CBD.

Like D_{8h} COT,³⁹ CBD is a typical “disjoint diradical”,⁴⁰ in which dynamic spin polarization favors the open-shell singlet transition state over the D_{4h} aromatic triplet state minimum. At the Mk-MRCCSD(T)/cc-pVQZ level,⁴¹ the D_{4h} open-shell singlet transition state has the same MO occupancy as the triplet, but is 3.9 kcal mol⁻¹ lower in energy (see Fig. 3).

Alternatively, the ring strain of CBD can be evaluated *directly* by applying the block-localized wavefunction (BLW) method⁴² to exclude π conjugation effects from the homodesmotic or isodesmic equations commonly employed for estimating the energies of CBD. For example, when the π conjugations of CBD and *anti*-butadiene are “disabled” in eqn (1) (*via* BLW, see below), only energetic imbalances due to differences in the skeletal frameworks of CBD, ethylene, and butadiene are considered. Since both ethylene and *anti*-butadiene are *strain free*, the resulting 62.2 kcal mol⁻¹ (eqn (1), third value in parenthesis) measures the ring strain of CBD (including *angle strain*, π – π repulsion strain, and *torsional strain* of CBD). Similar ring strain estimates for CBD (*ca.* 60 kcal mol⁻¹) result when the same BLW procedure is applied to evaluate other equations where the energy of CBD is based on strain free references (see Supporting information§). Clearly, the *ca.* 33 kcal mol⁻¹ literature estimate for the CBD ring strain, depending on the naive assumption that the strain energies of cyclobutane, cyclobutene, and CBD increase linearly, is much too low.

Based on the BLW method, the π resonance energy (RE) and antiaromatic destabilization energy (see below) of CBD also can be computed directly. The adiabatic BLW-RE of CBD (10.1 kcal mol⁻¹, at B3LYP/PVTZ) is evaluated by the energy difference between its fully delocalized and completely optimized Ψ^{Deloc} and an artificially localized Ψ^{Loc} (optimized under the imposed BLW constraint), in which the electrons and basis functions used for constructing the two π orbitals

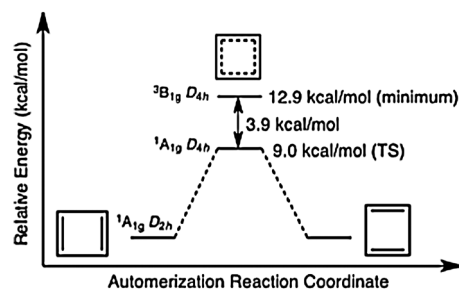


Fig. 3 Potential energy surface for CBD (at Mk-MRCCSD(T)/cc-pVQZ).⁴¹

of CBD are assigned to separate subspaces to “disable” π conjugation. Like the other planar 4n annulenes, the π resonance energy of CBD is *net stabilizing*.¹⁹ By the same procedure, the computed BLW-RE's for *syn*-butadiene (13.3 kcal mol⁻¹) and *anti*-butadiene (14.7 kcal mol⁻¹) are not much higher.

Evaluations of the antiaromatic destabilization energy of CBD depend on the “acyclic non-aromatic” reference compound chosen. Ideally, the best acyclic reference should exhibit similar electronic and geometric features to CBD, and differ only in the absence of “antiaromaticity”. Thus, *syn*- rather than *anti*-butadiene is a better choice as a reference. Based on the computed BLW-RE difference between CBD and two *syn*-butadienes (to have the same number of π conjugations),³⁵ the antiaromatic destabilization energy of CBD is 16.5 kcal mol⁻¹ (see also ref. 43). On this basis, the antiaromatic destabilization energy of CBD is at most only *ca.* 1/5 of its overall *ca.* 77 kcal mol⁻¹ destabilization energy (based on eqn (1))! Our finding contradicts the widely supported view that CBD is highly destabilized by antiaromaticity,^{23,24,27–30,32} but agrees with Breslow's¹⁴ and Dewar's¹⁵ much earlier estimates. Nevertheless, there is no doubt that CBD is *magnetically* antiaromatic.¹⁷ The higher 4n annulenes also display distinct magnetic antiaromaticity features but have negligible antiaromatic destabilization energies.¹⁹

We re-emphasize our earlier conclusion, “instead of the conventional interpretation of CBD as the antiaromatic paradigm, it should be regarded as a unique molecule”. The high energy of singlet CBD is not representative of “antiaromatic” compounds (e.g. the higher [4n]annulenes) generally,^{19,34} but is due primarily to its skeletal strain.

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