

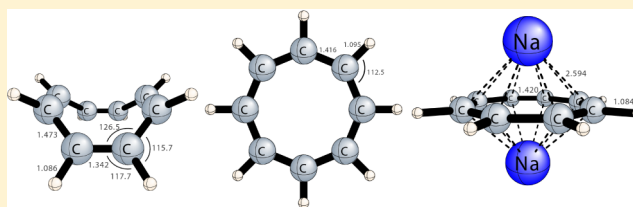
Free Cyclooctatetraene Dianion: Planarity, Aromaticity, and Theoretical Challenges

Alexander Yu. Sokolov,* D. Brandon Magers, Judy I. Wu, Wesley D. Allen,* Paul v. R. Schleyer, and Henry F. Schaefer, III

Center for Computational Quantum Chemistry, The University of Georgia, Athens, Georgia 30602, United States

S Supporting Information

ABSTRACT: The planarity and 10 π -electron aromaticity of the free cyclooctatetraene dianion ($C_8H_8^{2-}$, COT^{2-}) have been questioned recently on the basis of conflicting density functional and second-order Møller–Plesset perturbation computations. Rigorous coupled-cluster methods are employed here to establish the structure and properties of COT^{2-} . Like many multiply charged anions, COT^{2-} exists in isolation only as a short-lived resonance state lying above neutral COT. Wave function stability analysis demonstrates that predictions of nonplanar COT^{2-} rings are artifacts of using overly diffuse basis sets. The resulting broken-symmetry wave functions are not characteristic of COT^{2-} but mainly describe COT in a continuum of free electrons. All-electron coupled cluster theory extended through triple excitations [AE-CCSD(T)] yields a planar D_{8h} symmetry COT^{2-} structure. Final focal point analyses place the COT^{2-} resonance state 61.6 kcal mol⁻¹ above neutral COT. Nonetheless, COT^{2-} exhibits structural, magnetic, and energetic properties characteristic of aromatic compounds. Comparison with all-trans octatetraene indicates that COT^{2-} has a substantial aromatic stabilization energy (25 kcal mol⁻¹) approaching that of benzene (33 kcal mol⁻¹), but this favorable influence is swamped by Coulomb repulsion. Charge-compensating complexation of COT^{2-} with two sodium cations results in a thermodynamically stable Na_2COT compound (D_{8h} symmetry), for which high-level structures are also presented.



INTRODUCTION

The association of π -aromaticity with planarity needs qualification. Only a few monocyclic, aromatic $4n+2$ π -electron annulenes are planar. Several charged $[4n+2]$ annulenes, $C_3H_3^+$, $C_5H_5^+$, and $C_7H_7^+$, have planar geometries. But unlike benzene, none of the higher neutral $[4n+2]$ annulenes (e.g., C_nH_n , $n = 10, 14, 18$) are planar. Eight-membered rings with 10 π -electrons might be planar if the putative aromatic stabilization is large enough to overcome the angle strain^{1–6} inherent in such systems. Several planar 10 π -electron 1,4-heterocyclooctatetraene systems are known (e.g., the 1,4-dihydro-1,4-diazocine, C_6H_6XY , $X = Y = NH$) and exhibit the expected Hückel π -aromatic characteristics; while others, such as 1,4-dithiocine ($X = Y = S$) and 1,4-oxathiocine ($X = O$, $Y = S$), prefer distinctly nonplanar geometries,^{7–9} similar to the parent cyclooctatetraene (COT).

Recently, the planarity and aromaticity of the 10 π -electron cyclooctatetraene dianion (COT^{2-}) in isolation have been subjects of controversy.^{10–15} Early applications of Hückel theory,^{16,17} semiempirical methods,^{17,18} as well as self-consistent field (SCF) theory^{19,20} suggested that isolated COT^{2-} is planar and aromatic. However, density functional (DFT) and Møller–Plesset second-order perturbation (MP2) computations yield either planar^{10,14} or nonplanar^{11,13,15} COT^{2-} geometries, depending on the basis set used. The 10 π Hückel aromaticity of COT^{2-} has also been questioned.^{10–13} In 2011, Dominikowska et al.¹³ reported

that DFT and MP2 methods with small basis sets (e.g., 6-311G or cc-pVDZ) predicted the COT^{2-} structure to be planar with various symmetries (C_{4h} , C_{8h} , or D_{4h}). When larger basis sets with diffuse functions were employed, B3LYP/6-311++G(d,p) and MP2/aug-cc-pVDZ geometry optimizations converged to distinctly nonplanar, tub-shaped D_{2d} and C_{2v} COT^{2-} minima. SCF convergence failed in other cases.¹³

Like many multiply charged anions (MCAs),^{21–24} COT^{2-} exists in condensed phases stabilized by counterions and polar solvent molecules.^{25–30} For example, COT is reduced easily to COT^{2-} by alkali and transition metals.^{26–28} Notably, the detection of COT^{2-} in the gas phase has never been reported. Many isolated MCAs, like free COT^{2-} , are metastable and exist in short-lived resonance states that decay by electron emission.^{22–24,31,32} While the metastable nature of MCAs can be understood using simple semiclassical concepts, such as repulsive Coulomb barriers (RCBs),^{33–38} the accurate quantum mechanical description of such species is challenging, since a balanced treatment of their resonance properties (i.e., electron-molecule scattering) and electron correlation is required.^{31,32}

Sommerfeld and co-workers predicted the COT^{2-} lifetime to be 6 fs using a configuration interaction method with a complex absorbing potential (CAP/CI).³⁹ However, many questions about this evanescent molecule remain unanswered. Relative to

Received: July 23, 2013

Table 1. Absolute Energies, Smallest Eigenvalues of the Basis Set Overlap Matrix, and the Spatial Extent of the HOMO of the Cyclooctatetraene Dianion COT^{2-} Computed Using the RHF Method and Basis Sets with Varying Diffuse Character at the CCSD(T)/aug(H)-cc-pVTZ Optimized Geometry^a

diffuse functions on carbon	energy, a.u. RHF	overlap matrix smallest eigenvalue	HOMO extent $\langle x^2 \rangle, \langle y^2 \rangle$, a.u.	HOMO extent $\langle z^2 \rangle$, a.u.	RHF→RHF stability	RHF→UHF stability
no diffuse	−307.429844	1.4×10^{-5}	8.31	2.89	S	S
s	−307.429869	1.1×10^{-5}	8.31	2.89	S	N [2]
s, p	−307.440655	1.0×10^{-7}	8.88	3.76	N [4]	N [6]
s, p, d	−307.441106	8.6×10^{-8}	8.92	3.80	N [6]	N [8]
s, p, d, f	−307.441481	8.2×10^{-8}	8.92	3.80	N [6]	N [8]

^aThe COT^{2-} ring was placed in the xy plane. For the hydrogen atom the aug-cc-pVTZ basis was used. For the carbon atoms the cc-pVTZ basis set with either no diffuse functions, or with one diffuse Gaussian function for each angular momentum specified in the first column were employed. In addition, the results of the RHF→RHF or RHF→UHF wavefunction stability analyses are shown (“S” = stable, “N” = not stable). For the unstable wavefunctions the number of negative eigenvalues of the MO Hessian is given in square brackets.

the neutral COT, what is the energy of the COT^{2-} resonance state? Does it have a planar structure? What is the origin of the disparate literature results^{10–15} regarding the planarity of COT^{2-} ? Does the COT^{2-} resonance state have “aromatic” features? We endeavor to answer these questions using state-of-the-art theoretical methods by characterizing the Born–Oppenheimer geometric structure, the minimum energy, and the properties of an eigenstate of the time-independent electronic Schrödinger equation of COT^{2-} that is localized primarily on the molecular framework. We modeled such an eigenstate by employing the basis set confinement (BSC) approach.³⁹ This allows the localized wave function of the unbound state to be described while avoiding variational collapse. In addition to reporting a theoretical estimate of the putative aromatic stabilization energy of COT^{2-} , we present high-level results for neutral COT and the Na_2COT ($\text{Na}_2\text{C}_8\text{H}_8$, D_{8h} symmetry) complex.

■ THEORETICAL METHODOLOGY

Resonance states can be studied using time-dependent methods,^{40–42} stabilization techniques,^{43–45} or can be characterized by a complex energy via complex scaling^{46–51} or complex absorbing potential (CAP)^{52–54} approaches. Unfortunately, these methods have limitations. Many of them can only be applied to small systems, while others do not provide adequate description of electron correlation. The only research of this type reported for COT^{2-} is the aforementioned CAP/CI study.³⁹ Moreover, standard methods well-suited for electron correlation treatment are designed for bound states and should be used cautiously for studying resonance states.^{55–57} Difficulties arising from the use of highly diffuse basis sets, necessary for describing the electron density of anionic species, is a common problem of these methods. Increasing the spatial extent of the basis set by adding diffuse functions favors the states describing a detached electron in a pseudocontinuum. As a result, variational energy minimization may lead to a stationary state no longer corresponding to a resonance, but rather to a mixture of the resonance and continuum states.^{32,31,35,39} In such cases, the electronic resonance state wave function becomes unstable with respect to spin or spatial symmetry breaking. However, such variational collapse can be avoided if one models the resonance state wave function using a spatially compact basis set. In the basis set confinement approach (BSC),³⁹ a basis set is chosen to describe only the part of the resonance state wave function where electrons are bound; the lowest pseudocontinuum state is pushed to a much higher energy.³⁹

We evaluate the effect of basis set confinement on the stability and on the resonance nature of the COT^{2-} restricted Hartree-Fock (RHF) wave function by performing RHF computations for a series of basis sets with increasing diffuse character. The correlation-consistent augmented triple- ζ aug-cc-pVTZ basis set was employed for the hydrogen atoms.⁵⁸ Five different basis sets with varying diffuse character were employed for the carbon atoms. These basis sets were constructed by adding one diffuse Gaussian function sequentially to each of the s, p, d, and f shells in the cc-pVTZ basis set.⁵⁹ This provided a range of basis sets from cc-pVTZ to aug-cc-pVTZ.

Table 1 shows the absolute RHF energies, the spatial extent of the highest-occupied molecular orbital (HOMO), as well as wave function stability analyses⁶⁰ of COT^{2-} . Out of the five basis sets studied, only the one with no carbon diffuse functions gave a stable RHF wave function. Augmenting the cc-pVTZ basis of each carbon atom by a diffuse s-function resulted in a RHF solution susceptible to spin symmetry breaking (RHF→UHF instability, Table 1). The inclusion of diffuse p-functions results in wave function instability from the mixing of doubly occupied and diffuse virtual orbitals (RHF→RHF instability). Significant lowering of the absolute energy and a drastic increase of the radial extension of the COT^{2-} HOMO, especially in the z -direction (perpendicular to the plane of the molecule), resulted as well (Table 1). This strong basis set dependence indicates the increasing pseudocontinuum character of the RHF wave function. Interestingly, removing diffuse p-functions from the aug-cc-pVTZ basis set still results in an electronically unstable wave function.

Augmenting the basis set also introduces numerical instabilities in the iterative solution of the SCF equations, leading to convergence problems. These instabilities arise from unphysical linear dependencies in the nonorthogonal one-electron basis set, in regions where the basis functions overlap significantly.^{61,62} Linear dependencies can be diagnosed by computing the eigenvalues of the basis set overlap matrix;⁶¹ small eigenvalues (usually less than 10^{-7}) indicate numerically unstable solutions. Table 1 shows the smallest eigenvalues of the overlap matrix computed for the five basis sets studied. Adding the carbon diffuse p-functions reduces the smallest eigenvalue by 2 orders of magnitude (from 10^{-5} to 10^{-7}) and results in severe numerical instabilities. Augmenting the carbon basis set with d- and f-diffuse functions has much less effect.

Importantly, basis sets with carbon diffuse functions give numerically and electronically unstable RHF wave functions for COT^{2-} , and thus are ill-suited for further electron correlation

treatments.^{63–66} Moreover, basis set augmentation results in wave functions with significant pseudocontinuum character. We have ascertained the properties of the COT^{2-} resonance state by employing a mixed aug(H)-cc-pCVTZ basis set, constructed from the core–valence aug-cc-pCVTZ and cc-pCVTZ basis sets^{58,59,67} for the hydrogen and carbon atoms, respectively. Our description of metastable COT^{2-} follows the BSC approach, where the wave function is only provided enough freedom to describe a bound part of the resonance state. Such good approximations of the true resonance state wave function are well-suited for electron correlation treatments using efficient high-level theoretical methodology.

■ COMPUTATIONAL DETAILS

Cyclooctatetraene and its dianion were characterized by coupled cluster theory with single and double excitations (CCSD),^{68–71} as well as by perturbative treatment of triple excitations [CCSD(T)].^{72,73} The equilibrium structures of all stationary points were computed at the all-electron (AE-) CCSD(T)/aug(H)-cc-pCVTZ level of theory. Tight convergence criteria were used for the energy ($10^{-9} E_h$) and the root-mean-square of the energy gradient ($10^{-5} E_h/a_0$). The single-reference nature of the molecular wave functions was confirmed by analyzing the T_1 diagnostic⁷⁴ and the largest T_2 coupled-cluster amplitude. Harmonic vibrational frequencies were obtained at the AE-CCSD(T)/aug(H)-cc-pCVTZ level of theory by analytical differentiation of the potential energy. For the triplet state the all-electron unrestricted CCSD(T)/aug(H)-cc-pCVTZ level of theory based on the restricted open-shell Hartree–Fock (ROHF) reference was employed.

The thermodynamic stability of the COT^{2-} resonance state was examined by computing the sum of the first two electron affinities of neutral COT employing the focal point analysis (FPA) technique.^{75–79} The Hartree–Fock (E_{HF}) and the MP2 correlation energies (E_{corr}) computed using the aug(H)-cc-pVXZ ($X = \text{D, T, Q, 5}$) series of basis sets^{58,59} were extrapolated to the complete basis set (CBS) limit. [Hereafter we refer to CBS limit as a complete basis set limit for the idealized confined system, which resembles a complete basis set limit for the true resonance state.] The stability of the RHF wave function for aug(H)-cc-pVXZ basis sets was confirmed by computing and diagonalizing the molecular orbital Hessian.⁶⁰ The eq 1 and 2 functional forms^{80,81} were used for the extrapolation:

$$E_{\text{HF}}(X) = E_{\text{HF}}^{\infty} + ae^{-bX} \quad (X = 3, 4, 5) \quad (1)$$

and

$$E_{\text{corr}}(X) = E_{\text{corr}}^{\infty} + aX^{-3} \quad (X = 4, 5) \quad (2)$$

The FPA computations of COT and COT^{2-} employed AE-CCSD(T)/aug(H)-cc-pCVTZ optimized geometries. In addition to CCSD and CCSD(T), the coupled cluster theory in the FPA incorporated full single, double, and triple excitations⁸² (CCSDT) to take higher-order correlation effects into account. The initial FPA computations did not correlate the carbon 1s orbitals, but core correlation effects (Δ_{core}) were included later as an auxiliary correction by differencing all-electron CCSD(T)/aug(H)-cc-pCVQZ and frozen-core CCSD(T)/aug(H)-cc-pVQZ energies. Zero-point vibrational corrections (Δ_{ZPVE}) were computed at the AE-CCSD(T)/aug(H)-cc-pCVTZ level of theory. The geometries of neutral all-trans octatetraene and its dianion were optimized at B3LYP/6-311+G**. For OT^{2-}

this level of theory yields a planar geometry and a stable electronic wave function, which was confirmed by harmonic frequency and wave function stability analyses, respectively.

A custom aug(H,Na)-cc-pCVTZ basis set was used for Na_2COT . The aug-cc-pCVTZ basis set was employed for H and Na, while the cc-pCVTZ basis was used for C to avoid linear dependencies. Harmonic vibrational frequencies at the AE-CCSD/aug(H,Na)-cc-pCVDZ confirmed that D_{8h} Na_2COT was a genuine minimum. All computations were performed with the Cfour, Molpro, and Psi4 software packages.^{83–85} CCSDT energies were computed using Kállay's program^{82,86} interfaced with Psi4.

■ RESULTS AND DISCUSSION

COT and COT^{2-} : Structures and Energetics. Optimized structures of COT and COT^{2-} computed at AE-CCSD(T)/aug(H)-cc-pCVTZ are shown in Figures 1 and 2. The singlet

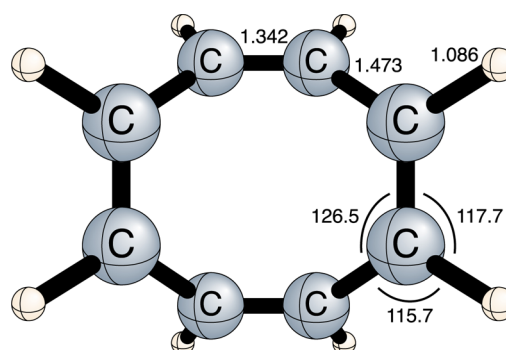


Figure 1. Top view of the neutral cyclooctatetraene structure (C_8H_8 , D_{2d} symmetry) optimized at the AE-CCSD(T)/aug(H)-cc-pCVTZ level of theory. Only unique bond lengths (in Å) and bond angles (in degrees) are shown.

ground-state neutral COT adopts the well-known D_{2d} tub-shaped equilibrium geometry (Figure 1).^{87–90} The computed lengths of the single (1.473 Å) and double (1.342 Å) C–C bonds agree well with equilibrium structures derived from the

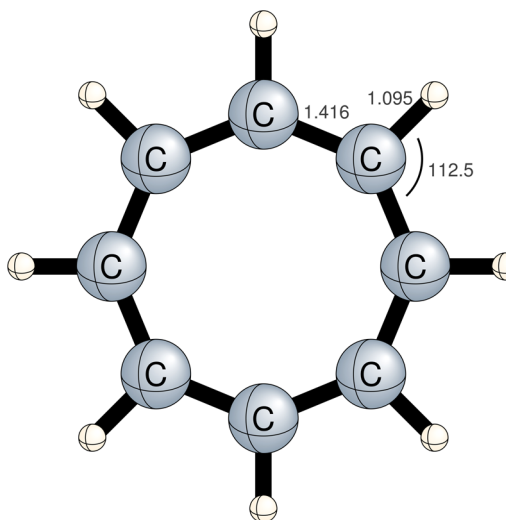


Figure 2. Top view of the cyclooctatetraene dianion structure ($\text{C}_8\text{H}_8^{2-}$, D_{8h} symmetry) optimized at the AE-CCSD(T)/aug(H)-cc-pCVTZ level of theory. Only unique bond lengths (in Å) and bond angle (in degrees) are shown.

femtosecond time-resolved coherence spectroscopy measurements (1.470 Å and 1.337 Å),⁹⁰ as well as from available X-ray crystallographic⁸⁹ and electron diffraction^{87,88} data. In addition, our computations reproduce the ring angles of the X-ray crystal structure⁸⁹ of COT very well; the mean absolute deviations of the (C=C–C) bond and (C=C–C=C) torsional angles are only 0.1° and 0.2°, respectively.

The COT^{2–} dianion has a singlet ground state and an adiabatic singlet–triplet energy gap of 90 kcal mol^{–1}. Geometry optimizations of singlet COT^{2–} with both planar (*D*_{4h}) and nonplanar (tub-shaped, *D*_{8h}) starting geometries led to a planar *D*_{8h} symmetry structure with equal C–C bond lengths (1.416 Å) at AE-CCSD(T)/aug(H)-cc-pCVTZ (Figure 2). This deviates only by about 0.01 Å from the mean of the C–C and C=C bond lengths in neutral COT. The addition of the two anionic electrons lengthens the C–H bonds from 1.086 Å in neutral COT (Figure 1) to 1.095 Å in the dianion (Figure 2). The planarity of COT^{2–} at the equilibrium structure was confirmed by computed harmonic vibrational frequencies and infrared intensities (Table 2).

Table 2. Harmonic Vibrational Frequencies (ω_e , cm^{–1}) and Corresponding Infrared Intensities (km mol^{–1}) of the Cyclooctatetraene Dianion C₈H₈^{2–} Computed at the AE-CCSD(T)/aug(H)-cc-pCVTZ Level of Theory

mode	description	ω_e	intensity
$\omega_1(a_{1g})$	C–H stretch	3035	0.0
$\omega_2(a_{1g})$	C–C stretch	739	0.0
$\omega_3(a_{2g})$	in-plane bend	1376	0.0
$\omega_4(b_{1g})$	C–H stretch	2911	0.0
$\omega_5(b_{1g})$	in-plane bend	988	0.0
$\omega_6(b_{2g})$	C–C stretch	1655	0.0
$\omega_7(b_{2g})$	in-plane bend	1291	0.0
$\omega_8(e_{1g})$	out-of-plane bend	638	0.0
$\omega_9(e_{2g})$	C–H stretch	2961	0.0
$\omega_{10}(e_{2g})$	C–C stretch	1516	0.0
$\omega_{11}(e_{2g})$	C–C stretch	1166	0.0
$\omega_{12}(e_{2g})$	in-plane bend	333	0.0
$\omega_{13}(e_{3g})$	out-of-plane bend	713	0.0
$\omega_{14}(e_{3g})$	out-of-plane bend	459	0.0
$\omega_{15}(a_{2u})$	umbrella motion	608	134.3
$\omega_{16}(b_{2u})$	out-of-plane bend	790	0.0
$\omega_{17}(b_{2u})$	out-of-plane bend	218	0.0
$\omega_{18}(e_{1u})$	C–H stretch	3006	725.0
$\omega_{19}(e_{1u})$	in-plane bend	1440	28.2
$\omega_{20}(e_{1u})$	C–C stretch	887	55.5
$\omega_{21}(e_{2u})$	out-of-plane bend	594	0.0
$\omega_{22}(e_{2u})$	out-of-plane bend	217	0.0
$\omega_{23}(e_{3u})$	C–H stretch	2925	0.0
$\omega_{24}(e_{3u})$	C–C stretch	1490	0.0
$\omega_{25}(e_{3u})$	C–C stretch	1289	0.0
$\omega_{26}(e_{3u})$	in-plane bend	775	0.0

The thermochemical stability of COT^{2–} was assessed by computing the sum of the first two adiabatic electron affinities of COT [$EA_{1+2} = E(C_8H_8) - E(C_8H_8^{2-})$]. Rigorous FPA computations established the –61.6 kcal mol^{–1} COT EA_{1+2} value, based on a consistent convergence of the computed EA_{1+2} energy to the complete basis set (CBS), as well as the electron correlation limit (Table 3). Following the EA sign convention, negative EA values indicate a disfavored (endothermic) electron attachment, while positive EA values

indicate an energetically favored (exothermic) process. At the RHF/CBS limit, the addition of two extra electrons to COT is strongly unfavorable energetically ($EA_{1+2} = -118.8$ kcal mol^{–1}). Including double excitations at the CCSD level of theory lowers EA_{1+2} substantially (by +46.0 kcal mol^{–1}, Table 3). Corrections for triple excitations based on CCSDT computations amount to +6.1 kcal mol^{–1}. Overall, electron correlation effects contribute significantly to stabilizing COT^{2–}, and reduce the EA_{1+2} by roughly a factor of 2, that is, from –118.8 kcal mol^{–1} at the RHF/CBS to –66.6 at the CCSDT/CBS level. The large structural differences between COT and COT^{2–} give rise to a substantial zero-point vibrational energy correction ($\Delta_{ZPVE} = +5.3$ kcal mol^{–1}). Adding the core correlation correction ($\Delta_{core} = -0.3$ kcal mol^{–1}) gives the final EA_{1+2} value of –61.6 kcal mol^{–1} (Table 3) for COT. The second adiabatic electron affinity EA_2 for COT (–74.3 kcal mol^{–1}), derived from the difference of our computed EA_{1+2} value and the experimental first adiabatic electron affinity of COT ($EA_1 = +12.7 \pm 0.5$ kcal mol^{–1}),^{5,91,92} also is highly negative (unfavorable energetically). On this basis, COT^{2–} is extremely unstable thermochemically and prone to electron emission.

Aromatic Stabilization Energy of COT^{2–}. Despite being highly unstable thermodynamically, the planar, highly *D*_{8h} symmetrical geometry of isolated COT^{2–} suggests Hückel π -aromaticity (although not all bond length-equalized $4n+2$ π -electron rings are aromatic, e.g., borazine).^{93–95} Various magnetic criteria, for example, computed nucleus independent chemical shifts (NICS)²⁰ (see below) and the experimental ¹H NMR chemical shifts of the COT^{2–}-fused dimethyldihydropyrène system,⁹⁶ document the magnetic aromaticity of isolated planar COT^{2–}. However, no energetic assessment of the aromatic stabilization energy (ASE) of COT^{2–} has been reported. This is in part because of the difficulty of selecting appropriate acyclic references for deriving ASEs for charged systems. Typically, the ASEs of neutral hydrocarbons are evaluated relative to the energy of reference compounds through carefully chosen isodesmic or homodesmotic reactions.⁹⁷ The number and type of chemical bonds, as well as energetic effects other than aromaticity (e.g., π -conjugation, hyperconjugation, protobranching, or geometric strain) must be balanced on both sides of the equation. Unfortunately, the selection of the appropriate reference compounds for multiply charged molecules, like COT^{2–}, is complicated further by unbalanced Coulomb repulsion.

We estimated the ASE of COT^{2–} by comparing the sum of the first two adiabatic electron affinities EA_{1+2} of COT to that of all-trans octatetraene (OT, C₈H₁₀). Remarkably, at the AE-CCSD(T)/aug(H)-cc-pCVTZ level of theory, the formation of the dianion from the neutral precursor is 8.9 kcal mol^{–1} more favorable energetically for COT^{2–} than for OT^{2–} (COT $EA_{1+2} = -74.8$ kcal mol^{–1} versus –83.7 kcal mol^{–1} for OT). This 8.9 kcal mol^{–1} energy difference is a lower bound for the ASE of COT^{2–}, since the computed EA_{1+2} for COT^{2–} (–74.8 kcal mol^{–1}) includes the planarization energy (12.7 ± 0.5 kcal mol^{–1}, from experiment)^{5,91} and the bond equalization energy (3–4 kcal mol^{–1})^{98–100} required to achieve planar *D*_{8h} COT^{2–}. Compared to OT^{2–}, COT^{2–} anticipates modestly greater Coulomb repulsion because of its more compact, cyclic rather than linear, shape. Considering these effects, the ASE of COT^{2–} is at least 25–26 kcal mol^{–1}. This approaches the estimated ASE of benzene¹⁰¹ (33 kcal mol^{–1})! Hence, COT^{2–} is energetically “more favorable than it ought to be” and fulfills the energetic criteria for aromaticity. The most sophisticated

Table 3. FPA of the Sum of First Two Electron Affinities of the Cyclooctatetraene Molecule^a

basis set	EA ₁₊₂ [RHF]	δ[MP2]	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]	EA ₁₊₂ [CCSDT]
aug(H)-cc-pVDZ	−129.96	+53.32	−17.17	+4.60	−0.72	[−89.93]
aug(H)-cc-pVTZ	−123.85	+62.31	−19.28	+6.41	[−0.72]	[−75.13]
aug(H)-cc-pVQZ	−120.98	+64.28	−20.03	+6.86	[−0.72]	[−70.59]
aug(H)-cc-pV5Z	−119.59	+65.16	[−20.03]	[+6.86]	[−0.72]	[−68.32]
CBS limit	[−118.81]	[+66.09]	[−20.03]	[+6.86]	[−0.72]	[−66.60]
EA ₁₊₂ (final) = EA ₁₊₂ [CCSDT/CBS] + Δ _{core} [AE-CCSD(T)/aug(H)-cc-pCVQZ] + Δ _{ZPVE} [AE-CCSD(T)/aug(H)-cc-pCVTZ] = −66.60 − 0.29 + 5.34 = −61.55 kcal mol^{−1}						
fit function	$a+be^{-cX}$	$a+bX^{-3}$	additive	additive	additive	additive
points (X)	3,4,5	4,5				

^aEA₁₊₂ = E(C₈H₈) − E(C₈H₈^{2−}), in kcal mol^{−1}. The symbol δ denotes the increment of the EA₁₊₂ value with respect to the preceding level of theory in the hierarchy RHF→MP2→CCSD→CCSD(T)→CCSDT. Square brackets signify results obtained from basis set extrapolations or additivity assumptions. Final predictions are boldfaced.

dissected NICS(0)_{πzz} index^{102–104} (−49.9 ppm, compared to benzene: −35.6 ppm) also confirms the aromaticity of planar in COT^{2−} isolation.

Importantly, aromatic molecules are not always thermochemically stable in the absolute sense and may not even be kinetically persistent (e.g., [10]annulene),^{105,106} but are only expected to be thermochemically more stable “than they ought to be”, that is, when compared to appropriate nonaromatic acyclic references. Despite its significant three-membered ring strain, the 2 π-electron aromatic cyclopropenyl cation (C₃H₃⁺) exhibits considerably higher delocalization energy than the allyl cation, based, for example, on simple Hückel computations.¹⁰⁷ The frequently (but erroneously) employed aromaticity criteria based on reactivity or kinetic persistence of molecules are flawed. We stress that the term aromaticity refers here only to a ground state molecular property. Thus, the energies of transition and excited states (however interesting they may be) are immaterial. The fleeting existence and metastable nature of isolated COT^{2−} do not preclude aromaticity, but merely reflect the large Coulombic repulsion and other energetic effects present in this dianion. Relative to COT, the energy of COT^{2−} (ΔE = −EA₁₊₂) can be expressed as a sum of COT^{2−} ASE (ΔE_{ASE}), planarization of the COT^{2−} ring energy (ΔE_{planar}), bond equalization (ΔE_{bond-eq}), and Coulomb repulsion (ΔE_{CR})

$$\Delta E = E(\text{COT}^{2-}) - E(\text{COT})$$

$$\approx \Delta E_{\text{CR}} + \Delta E_{\text{ASE}} + \Delta E_{\text{planar}} + \Delta E_{\text{bond-eq}} \quad (3)$$

According to eq 3, ΔE_{CR} is 71 kcal mol^{−1}. Thus, the contribution of Coulomb repulsion to the relative energy exceeds the ASE (~25 kcal mol^{−1}) by almost a factor of 3. This substantial destabilization energy must be compensated to obtain a thermodynamically stable species.

Na₂COT Sandwich Complex. Our high-level thermochemical data for COT → COT^{2−} reveal that the isolated COT^{2−} is indeed highly unstable with respect to electron emission, and supports earlier theoretical evidence of its short lifetime.³⁹ Thus, the possible gas-phase detection of this evanescent molecule would require sophisticated experiments capable of forming and detecting metastable species on the femtosecond time scale. A much simpler, commonly employed experimental strategy is to stabilize MCAs with counterions. A sandwich complex of planar COT^{2−} capped with two sodium atoms in D_{8h} symmetry, Na₂COT, is illustrative. Na₂COT has been studied both experimentally (by calorimetric^{108,109} and mass-spectrometric methods¹¹⁰) and computationally.^{14,111} The

CCSD(T)/6-311++G** geometry was reported most recently.¹⁴

Figure 3 shows the equilibrium structure of Na₂COT optimized at the AE-CCSD(T)/aug(H,Na)-cc-pCVTZ level.

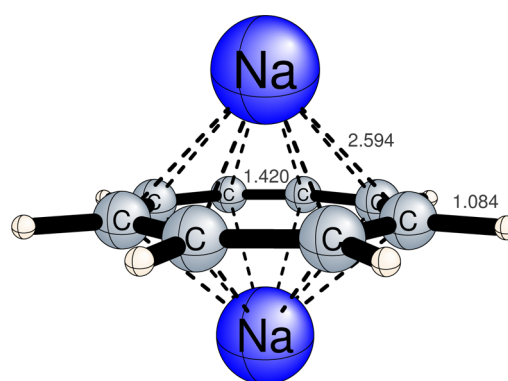
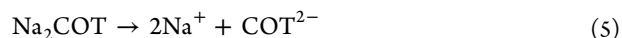


Figure 3. Side view of the Na₂C₈H₈ (Na₂COT) structure (D_{8h} symmetry) optimized at the AE-CCSD(T)/aug(H,Na)-cc-pCVTZ level of theory. Only unique bond lengths (in Å) and bond angles (in degrees) are shown. The Na–Na distance is 3.626 Å.

The two Na atoms are located 1.813 Å above and below the ring center (a prior lower-level study reported a much greater distance, 1.864 Å).¹⁴ As expected, coordination of the two Na⁺ cations does not affect the geometry of the COT^{2−} moiety significantly. The C–C (1.420 Å) and C–H (1.084 Å) bond lengths of Na₂COT (Figure 3) differ by only 0.004 Å and 0.011 Å, respectively, from those of isolated COT^{2−} (Figure 2). This agreement validates the theoretical methodology used here to compute COT^{2−}. The computed value of NICS(0)_{πzz} index (−47.63 ppm) for Na₂COT is also very similar to that of COT^{2−}, which confirms the aromaticity of the COT ring.

The thermodynamic stability of Na₂COT is evaluated by the computed dissociation energies (DEs) for the homo- (eq 4) and heterolytic cleavage (eq 5) reactions.



Both dissociation reactions are endothermic with computed 82.0 (eq 4) and 391.3 kcal mol^{−1} (eq 5) DEs at AE-CCSD(T)/aug(H,Na)-cc-pCVTZ without zero-point vibrational corrections.

■ CONCLUSIONS

We have reported a high-level theoretical study of the cyclooctatetraene dianion (COT^{2-}) using reliable coupled-cluster methods. Like many MCAs, free COT^{2-} is thermodynamically unstable; only a short-lived resonance state might exist in the gas phase. Such states present severe challenges to electronic structure theory. Recently, DFT and MP2 methods with large diffuse basis sets were reported to yield nonplanar (tub-shaped) geometries for COT^{2-} , while planar structures were obtained for basis sets without diffuse character.^{11,13,15} Our stability analysis of the COT^{2-} RHF wave function identified the origin of these discrepancies. Addition of diffuse basis functions to the carbon atoms results in an electronic wave function unstable with respect to mixing of doubly occupied and diffuse virtual orbitals (RHF \rightarrow RHF instability). Such mixing yields wave functions having a significant contribution from states involving neutral COT with a continuum of unattached free electrons ($\text{COT} + 2e^-$). Thus, unlimited spatial expansion of the basis set leads inevitably to an electronic wave function and nonplanar geometry characteristic of neutral COT and not the COT^{2-} resonance state. Such variational collapse was circumvented by means of a basis set confinement (BSC) approach. We employed a mixed aug(H)-cc-pCVTZ basis set utilizing an augmented correlation-consistent aug-cc-pCVTZ basis for hydrogens and the cc-pCVTZ basis for carbons to study the properties of the resulting wave function localized on the COT^{2-} molecular framework.

The Born–Oppenheimer minimum energy structure of the COT^{2-} resonance state has a planar geometry with D_{8h} symmetry and equivalent C–C bond lengths at the AE-CCSD(T)/aug(H)-cc-pCVTZ level of theory. Coordination with two sodium cations forms the D_{8h} symmetry Na_2COT complex and does not affect the structure of the eight-membered COT^{2-} ring significantly. Our computed equilibrium structure for the neutral tub-shaped COT molecule (D_{2d} symmetry) agrees very well with recent experimental femtosecond time-resolved coherence spectroscopy measurements.⁹⁰

The FPA-derived sum of the first two adiabatic electron affinities of the COT molecule [$\text{EA}_{1+2} = E(\text{COT}) - E(\text{COT}^{2-})$] indicates that isolated COT^{2-} is extremely thermodynamically unstable with respect to spontaneous electron loss. After extrapolating to the complete basis set limit and correcting for core correlation and zero-point vibrational effects, we obtained $\text{EA}_{1+2} = -61.6 \text{ kcal mol}^{-1}$ at the CCSDT level of theory. Combining this result with the experimental first adiabatic electron affinity ($\text{EA}_1 = +12.7 \pm 0.5 \text{ kcal mol}^{-1}$),^{5,91,92} gave the second adiabatic electron affinity ($\text{EA}_2 = -74.3 \text{ kcal mol}^{-1}$) of COT.

Our computational results confirm the aromaticity of isolated COT^{2-} by its planar D_{8h} geometry, negative nucleus independent chemical shift [$\text{NICS}(0)_{\text{zz}} = -49.9 \text{ ppm}$] value, and moderately large (25 kcal mol^{-1}) aromatic stabilization energy (ASE). Despite being aromatic, COT^{2-} is highly unstable thermodynamically because of the strong Coulomb repulsion between the two excess electrons. The charge-balancing complexation of COT^{2-} with two sodium cations overcomes the Coulomb repulsion and produces an energetically stable Na_2COT molecule. Another possibility for the experimental study of aromatic COT^{2-} species is investigation of its derivatives with strongly electron-withdrawing groups. Alternatively, polycyclic derivatives having planar COT^{2-}

moieties¹¹² may be viable candidates for experimental detection in the gas phase.

■ ASSOCIATED CONTENT

Supporting Information

Cartesian geometries for all optimized structures, as well as harmonic vibrational frequencies for COT and Na_2COT . This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: alex@ccqc.uga.edu (A.Y.S.).

*E-mail: wdallen@uga.edu (W.D.A.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Combustion Program (Grant DEFG02-97-ER14748), as well as U.S. National Science Foundation (Grant CHE-1057466), and used resources of the National Energy Research Scientific Computing Center (NERSC), which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

■ REFERENCES

- (1) Anet, F. J. *Am. Chem. Soc.* **1962**, *84*, 671–672.
- (2) Allinger, N. L.; Sprague, J. T.; Finder, C. J. *Tetrahedron* **1973**, *29*, 2519–2523.
- (3) Roth, W. R.; Lennartz, H.-W.; Vogel, E.; Leiendecker, M.; Oda, M. *Chem. Ber.* **1986**, *119*, 837–843.
- (4) Nevins, N.; Lii, J. H.; Allinger, N. L. *J. Comput. Chem.* **1996**, *17*, 695–729.
- (5) Kato, S.; Lee, H. S.; Gareyev, R.; Wenthold, P. G.; Lineberger, W. C.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1997**, *119*, 7863–7864.
- (6) Wu, J. I.; Fernández, I.; Mo, Y.; Schleyer, P. v. R. *J. Chem. Theory Comput.* **2012**, *8*, 1280–1287.
- (7) Rzepa, H. S.; Sanderson, N. *Phys. Chem. Chem. Phys.* **2004**, *6*, 310.
- (8) Rzepa, H. S.; Sanderson, N. *Mol. Phys.* **2005**, *103*, 401–405.
- (9) Rzepa, H. S. The butterfly effect in chemistry: aromaticity on the edge of chaos. 2013; <http://www.ch.imperial.ac.uk/rzepa/blog/?p=10870>, (accessed August 28, 2013)
- (10) Feixas, F.; Matito, E.; Solà, M.; Poater, J. J. *Phys. Chem. A* **2008**, *112*, 13231–13238.
- (11) Cao, T.; Ma, Y.; Yan, X.; Cheng, J.; Luo, Y.; He, L.; Zhu, W. *Chin. J. Chem.* **2009**, *27*, 1914–1918.
- (12) Dominikowska, J.; Palusiak, M. *Phys. Chem. Chem. Phys.* **2010**, *34*, 1855–1861.
- (13) Dominikowska, J.; Palusiak, M. *J. Comput. Chem.* **2011**, *32*, 1441–1448.
- (14) Gnanasekaran, R. *Vib. Spectrosc.* **2011**, *57*, 288–293.
- (15) Badri, Z.; Foroutan-Nejad, C.; Rashidi-Ranjbar, P. *Phys. Chem. Chem. Phys.* **2012**, *14*, 3471–3481.
- (16) Coulson, C. A. *Chem. Phys.* **1961**, *12*, 193–195.
- (17) Dewar, M. J. S.; Harget, A. J.; Haselbach, E. *J. Am. Chem. Soc.* **1969**, *91*, 7521–7523.
- (18) Trindle, C.; Wolfskill, T. *J. Org. Chem.* **1991**, *56*, 5426–5436.
- (19) Wipff, G.; Wahlgren, U.; Kochanski, E.; Lehn, J. M. *Chem. Phys.* **1971**, *11*, 350–352.
- (20) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.
- (21) Dougherty, R. C. *J. Chem. Phys.* **1969**, *50*, 1896–1897.

- (22) Scheller, M. K.; Compton, R. N.; Cederbaum, L. S. *Science* **1995**, *270*, 1160–1166.
- (23) Boldyrev, A. I.; Gutowski, M.; Simons, J. *Acc. Chem. Res.* **1996**, *29*, 497–502.
- (24) Dreuw, A.; Cederbaum, L. S. *Chem. Rev.* **2002**, *102*, 181–200.
- (25) Elofson, R. M. *Anal. Chem.* **1949**, *21*, 917–919.
- (26) Katz, T. J.; Strauss, H. L. *J. Chem. Phys.* **1960**, *32*, 1873–1875.
- (27) Katz, T. J. *J. Am. Chem. Soc.* **1960**, *82*, 3784–3785.
- (28) Katz, T. J. *J. Am. Chem. Soc.* **1960**, *82*, 3785–3786.
- (29) Allendoerfer, R. D.; Rieger, P. H. *J. Am. Chem. Soc.* **1965**, *87*, 2336–2344.
- (30) Thielen, D. R.; Anderson, L. B. *J. Am. Chem. Soc.* **1972**, *94*, 2521–2523.
- (31) Sommerfeld, T.; Tarantelli, F.; Meyer, H. D.; Cederbaum, L. S. *J. Chem. Phys.* **2000**, *112*, 6635–6642.
- (32) Sommerfeld, T. *J. Phys. Chem. A* **2000**, *104*, 8806–8813.
- (33) Wang, X.-B.; Ding, C.-F.; Wang, L.-S. *Phys. Rev. Lett.* **1998**, *81*, 3351–3354.
- (34) Wang, L.-S.; Wang, X.-B. *Nature* **1999**, *400*, 245–248.
- (35) Dreuw, A.; Cederbaum, L. S. *Phys. Rev. A* **2000**, *63*, 049904(E).
- (36) Xing, X.-P.; Wang, X.-B.; Wang, L.-S. *Phys. Rev. Lett.* **2008**, *101*, 83003.
- (37) Xing, X.-P.; Wang, X.-B.; Wang, L.-S. *J. Chem. Phys.* **2009**, *130*, 074301.
- (38) Xing, X.-P.; Wang, X.-B.; Wang, L.-S. *J. Phys. Chem. A* **2009**, *113*, 945–948.
- (39) Sommerfeld, T. *J. Am. Chem. Soc.* **2002**, *124*, 1119–1124.
- (40) Heller, E. J. *Acc. Chem. Res.* **1981**, *14*, 368–375.
- (41) Neuhauser, D. *J. Chem. Phys.* **1991**, *95*, 4927–4932.
- (42) Grossmann, F. *Chem. Phys. Lett.* **1996**, *262*, 470–476.
- (43) Hazi, A.; Taylor, H. *Phys. Rev. A* **1970**, *1*, 1109–1120.
- (44) Mandelshtam, V. A.; Ravuri, T. R.; Taylor, H. S. *J. Chem. Phys.* **1994**, *101*, 8792–8799.
- (45) Mandelshtam, V. A.; Taylor, H. S. *J. Chem. Phys.* **1995**, *102*, 7390–7399.
- (46) Balslev, E.; Combes, J.-M. *Commun. Math. Phys.* **1971**, *22*, 280–294.
- (47) Aguilar, J.; Combes, J.-M. *Commun. Math. Phys.* **1971**, *22*, 269–279.
- (48) Simon, B. *Commun. Math. Phys.* **1972**, *27*, 1–9.
- (49) Reinhardt, W. P. *Annu. Rev. Phys. Chem.* **1982**, *33*, 223–255.
- (50) Moiseyev, N. *Phys. Rep.* **1998**, *302*, 212–293.
- (51) Bravaya, K. B.; Zuev, D.; Epifanovsky, E.; Krylov, A. J. *Chem. Phys.* **2013**, *138*, 124106–124120.
- (52) Jolicard, G.; Austin, E. J. *Chem. Phys. Lett.* **1985**, *121*, 106–110.
- (53) Sommerfeld, T.; Riss, U. V.; Meyer, H. D.; Cederbaum, L. S.; Engels, B.; Suter, H. U. *J. Phys. B: At. Mol. Opt. Phys.* **1999**, *31*, 4107–4122.
- (54) Riss, U. V.; Meyer, H. D. *J. Phys. B: At. Mol. Opt. Phys.* **1999**, *26*, 4503–4535.
- (55) Lambrecht, D. S.; Fleig, T.; Sommerfeld, T. *J. Phys. Chem. A* **2008**, *112*, 2855–2862.
- (56) Zubarev, D. Y.; Boldyrev, A. I. *J. Phys. Chem. A* **2008**, *112*, 7984–7985.
- (57) Lambrecht, D. S.; Fleig, T.; Sommerfeld, T. *J. Phys. Chem. A* **2008**, *112*, 7986–7986.
- (58) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.
- (59) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (60) Burton, N. A.; Yamaguchi, Y.; Alberts, I. L.; Schaefer, H. F. *J. Chem. Phys.* **1991**, *95*, 7466.
- (61) Lowdin, P. O. *Annu. Rev. Phys. Chem.* **1960**, *11*, 107–132.
- (62) Lykos, P. G.; Schmeising, H. N. *J. Chem. Phys.* **1961**, *35*, 288.
- (63) Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783–4790.
- (64) Allen, W. D.; Horner, D. A.; Dekock, R. L.; Remington, R. B.; Schaefer, H. F. *Chem. Phys.* **1989**, *133*, 11–45.
- (65) Crawford, T. D.; Stanton, J. F.; Allen, W. D.; Schaefer, H. F. *J. Chem. Phys.* **1997**, *107*, 10626.
- (66) Russ, N. J.; Crawford, T. D.; Tschumper, G. S. *J. Chem. Phys.* **2004**, *120*, 7298–7306.
- (67) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1995**, *103*, 4572–4585.
- (68) Rittby, M.; Bartlett, R. J. *J. Phys. Chem.* **1988**, *92*, 3033–3036.
- (69) Stanton, J. F.; Gauss, J.; Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1991**, *94*, 4334–4345.
- (70) Hampel, C.; Peterson, K. A.; Werner, H.-J. *Chem. Phys. Lett.* **1992**, *190*, 1–12.
- (71) Watts, J. D.; Gauss, J.; Bartlett, R. J. *Chem. Phys. Lett.* **1992**, *200*, 1–7.
- (72) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479–483.
- (73) Stanton, J. F. *Chem. Phys. Lett.* **1997**, *281*, 130–134.
- (74) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem.* **1989**, *36*, 199–207.
- (75) East, A. L. L.; Allen, W. D. *J. Chem. Phys.* **1993**, *99*, 4638–4650.
- (76) Császár, A. G.; Allen, W. D.; Schaefer, H. F. *J. Chem. Phys.* **1998**, *108*, 9751.
- (77) Császár, A. G.; Tarczay, G.; Leininger, M. L.; Polyansky, O. L.; Tennyson, J.; Allen, W. D. In *Spectroscopy from Space*; Demaison, J., Sarka, K., Cohen, E. A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001; NATO Science Series, Vol. 20; pp 317–339.
- (78) Gonzales, J. M.; Pak, C.; Cox, R. S.; Allen, W. D.; Schaefer, H. F.; Császár, A. G.; Tarczay, G. *Chem.—Eur. J.* **2003**, *9*, 2173–2192.
- (79) Schuurman, M. S.; Muir, S. R.; Allen, W. D.; Schaefer, H. F. *J. Chem. Phys.* **2004**, *120*, 11586–11599.
- (80) Feller, D. *J. Chem. Phys.* **1993**, *98*, 7059–7071.
- (81) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639–9646.
- (82) Kállay, M.; Surján, P. *J. Chem. Phys.* **2001**, *115*, 2945–2954.
- (83) CFOUR, a quantum chemical program package written by Stanton, J. F.; Gauss, J.; Watts, J. D.; Szalay, P. G.; Bartlett, R. J. with contributions from Auer, A. A.; Bernholdt, D. E.; Christiansen, O.; Harding, M. E.; Heckert, M.; Heun, O.; Huber, C.; Jonsson, D.; Jusélius, J.; Lauderdale, W. J.; Metzroth, T.; Michauk, C.; O'Neill, D. P.; Price, D. R.; Ruud, K.; Schiffmann, F.; Tajti, A.; Varner, M. E.; Vázquez, J. and the integral packages: Molecule (Almlöf, J.; Taylor, P. R.), Props (Taylor, P. R.), Abacus (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.), and ECP routines by Mitin, A. V. and van Wüllen, C. For the current version see, <http://www.cfour.de> (accessed August 28, 2013).
- (84) Werner, H.-J. et al. MOLPRO, version 2010.1, a package of *ab initio* programs. 2010; see <http://www.molpro.net> (accessed August 28, 2013).
- (85) Turney, J. M.; Simmonett, A. C.; Parrish, R. M.; Hohenstein, E. G.; Evangelista, F. A.; Fermann, J. T.; Mintz, B. J.; Burns, L. A.; Wilke, J. J.; Abrams, M. L.; Russ, N. J.; Leininger, M. L.; Janssen, C. L.; Seidl, E. T.; Allen, W. D.; Schaefer, H. F.; King, R. A.; Valeev, E. F.; Sherrill, C. D.; Crawford, T. D. *WIREs Comput. Mol. Sci.* **2012**, *2*, 556–565.
- (86) Kállay, M.; Gauss, J. *J. Chem. Phys.* **2005**, *123*, 214105–214105–13.
- (87) Bastiansen, O.; Hedberg, L.; Hedberg, K. *J. Chem. Phys.* **1957**, *27*, 1311–1317.
- (88) Traetteberg, M. *Acta Chem. Scand.* **1966**, *20*, 1724–1726.
- (89) Claus, K. H.; Kruger, C. *Acta Crystallogr. Sect. C* **1988**, *44*, 1632–1634.
- (90) Kummli, D. S.; Lobsiger, S.; Frey, H.-M.; Leutwyler, S.; Stanton, J. F. *J. Phys. Chem. A* **2008**, *112*, 9134–9143.
- (91) Wenthold, P. G.; Hrovat, D. A.; Borden, W. T.; Lineberger, W. C. *Science* **1996**, *272*, 1456.
- (92) Miller, T. M.; Viggiano, A. A.; Miller, A. E. S. *J. Phys. Chem. A* **2002**, *106*, 10200–10204.
- (93) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209–218.
- (94) Madura, I. D.; Krygowski, T. M.; Cyran'ski, M. K. *Tetrahedron* **1998**, *54*, 14913–14918.
- (95) Jemmis, E. D.; Kiran, B. *Inorg. Chem.* **1998**, *37*, 2110–2116.
- (96) Mitchell, R. H.; Zhang, P.; Berg, D. J.; Williams, R. V. *Chem. Commun.* **2012**, *48*, 8144–8146.

- (97) Wheeler, S. E.; Houk, K. N.; Schleyer, P. v. R.; Allen, W. D. *J. Am. Chem. Soc.* **2009**, *131*, 2547–2560.
- (98) Anet, F.; Bourn, A.; Lin, Y. S. *J. Am. Chem. Soc.* **1964**, *86*, 3576–3577.
- (99) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573–622.
- (100) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 5879–5881.
- (101) Schleyer, P. v. R.; Pühhöfer, F. *Org. Lett.* **2002**, *4*, 2873–2876.
- (102) Corminboeuf, C.; Heine, T.; Seifert, G.; Schleyer, P. v. R.; Weber, J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 273.
- (103) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842–3888.
- (104) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863–866.
- (105) Sulzbach, H. M.; Schleyer, P. v. R.; Jiao, H.; Xie, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1995**, *117*, 1369–1373.
- (106) Spitler, E. L.; Johnson, C. A.; Haley, M. M. *Chem. Rev.* **2006**, *106*, 5344–5386.
- (107) Wiberg, K. B.; Bartley, W. J.; Lossing, F. P. *J. Am. Chem. Soc.* **1962**, *84*, 3980–3981.
- (108) Stevenson, G. R.; Ocasio, I.; Bonilla, A. *J. Am. Chem. Soc.* **1976**, *98*, 5469–5473.
- (109) Stevenson, G. R.; Valentin, J.; Williams, E., Jr; Caldwell, G.; Alegria, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 515–519.
- (110) Miyajima, K.; Kurikawa, T.; Hashimoto, M.; Nakajima, A.; Kaya, K. *Chem. Phys. Lett.* **1999**, *306*, 256–262.
- (111) Han, J.-G.; Pang, W.-M.; Shi, Y.-Y. *Chem. Phys.* **2000**, *257*, 21–28.
- (112) Ohmae, T.; Nishinaga, T.; Wu, M.; Iyoda, M. *J. Am. Chem. Soc.* **2010**, *132*, 1066–1074.