

Cope rearrangements in shapeshifting molecules re-examined by means of high-level CCSDT(Q) composite ab initio methods

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ABSTRACT

Benchmark reaction barrier heights for the degenerate Cope rearrangements in the highly fluxional bullvalene and semibullvalene hydrocarbon cages are obtained at the CCSDT(Q) level close to the one-particle basis set limit and include inner-shell, scalar-relativistic, and Born–Oppenheimer corrections. Our best theoretical CCSDT(Q) Gibbs free reaction barrier height for semibullvalene ($\Delta G_{298}^\ddagger = 27.9 \text{ kJ mol}^{-1}$) is in good agreement with the most recent experimental value of 25.9 kJ mol^{-1} . However, our CCSDT(Q) reaction barrier height for bullvalene ($\Delta G_{298}^\ddagger = 62.2 \text{ kJ mol}^{-1}$) indicates that the most recent gas-phase experimental value of 54.8 ± 0.8 should be revised upward.

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Introduction

Highly fluxional ‘shapeshifting’ molecules have attracted renewed attention in recent years and have found several applications in functional materials, sensors, and biologically active compounds.^{1,2,3,4} Following the synthesis of the archetypical ‘shapeshifting’ molecule bullvalene ($C_{10}H_{10}$, Figure 1) semibullvalene (C_8H_8) was synthesized, and the chemical properties and applications of both systems have been extensively studied.^{1,2,3,4,5,6,7,8,9,10} Nevertheless, the most fundamental chemical property underlying their fluxional behaviour – the reaction barrier height for the degenerate Cope rearrangements – remains elusive. For bullvalene gas-phase and solution NMR measurements predict reaction barrier heights ranging from $\Delta G^\ddagger = 49.4$ to 54.8 kJ mol^{-1} (*vide infra*). The variation of 5.4 kJ mol^{-1} in the measured reaction barrier height amounts to $\sim 10\%$ of the reaction barrier height and corresponds to a change of about one order of magnitude in the reaction rate at 298 K according to the Eyring equation. For semibullvalene the two experimental predictions span a somewhat narrower range of 2.9 kJ mol^{-1} , i.e., they are $\Delta G^\ddagger = 23.0$ and 25.9 kJ mol^{-1} (*vide infra*).

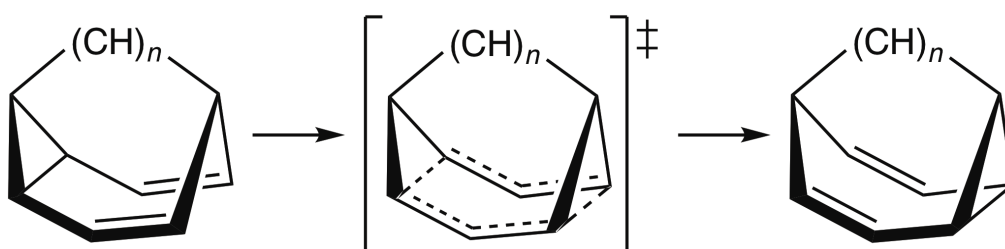


Figure 1. Schematic representation of the Cope rearrangements in semibullvalene C_8H_8 ($n = 0$) and bullvalene $C_{10}H_{10}$ ($n = 2$).

A number of computational studies obtained the reaction barrier heights for the Cope rearrangements in bullvalene and semibullvalene at various levels of theory.^{5,7,8,9,10} For bullvalene the theoretical ΔH^\ddagger values range between 47.1 (CBS-QB3)⁵ and 52.3 (B3LYP/6-31G(d))¹⁰ kJ

mol⁻¹. For semibullvalene the computational predictions spread over a wider range of $\Delta H^\ddagger = 18.7$ (B3PW91/6-311+G(2d,p))⁹ and 30.5 (CCSD(T)/cc-pVDZ)⁷ kJ mol⁻¹. It should be noted in this context that pericyclic reaction barrier heights, including sigmatropic shifts and Cope rearrangements, have been found to pose a significant challenge to approximate theoretical procedures.¹¹ For example, for the highly accurate 26 barrier heights of pericyclic reactions in the BHPERI database the computationally economical composite ab initio methods CBS-APNO¹² and CBS-QB3¹³ result in root mean square (RMS) deviations of 10.9 and 10.0 kJ mol⁻¹, respectively (corresponding to RMS percentage errors of 16.2% and 14.4%, respectively).¹¹

In the present work we calculate the reaction barrier heights for the degenerate Cope rearrangements in bullvalene and semibullvalene by means of the W1-F12 thermochemical protocol, which obtains the CCSD(T) energy (coupled cluster with single, double, and quasiperturbative triple excitations) close to the one-particle basis set limit.¹⁴ W1-F12 theory explicitly includes core-valence, relativistic, Born–Oppenheimer, zero-point vibrational energy, and enthalpic temperature corrections. In addition, at great computational expense, post-CCSD(T) correlation effects up to CCSDT(Q) (coupled cluster with single, double, triple, and quasiperturbative quadruple excitations) are considered explicitly. For semibullvalene we were able to run the CCSDT calculations with the cc-pVDZ basis set and the CCSDT(Q) calculations with the sp part of the cc-pVDZ basis set. For bullvalene (C₁₀H₁₀), post-CCSD(T) contributions altogether (CCSDT(Q)–CCSD(T)) are obtained in conjunction with the latter basis set.

Computational Details

The reaction barrier heights for semibullvalene and bullvalene are obtained at the all-electron, relativistic CCSD(T) level close to the complete basis set (CBS) limit by means of the high-level ab initio W1-F12 thermochemical protocol. The computational details of W1-F12 theory have been specified and rationalized in detail in ref. 14. In short, the Hartree–Fock (HF) component is extrapolated from the cc-pVDZ-F12 and cc-pVTZ-F12 basis sets¹⁵ and the complementary auxiliary basis set singles correction is included in the HF energy.^{16,17} The valence CCSD-F12 correlation component is extrapolated from the same basis sets in conjunction with an optimal extrapolation exponent of 3.38 as recommended in ref. 14. Optimal values for the geminal Slater exponents were taken from refs. 15 and 18 and the RI approximation was applied using the OptRI auxiliary basis sets from ref. 19. The diagonal, fixed-amplitude 3C(FIX) ansatz,¹⁶ and the CCSD-F12b approximation are used in all of the explicitly correlated coupled cluster calculations.¹⁷ The valence (T) correlation energy is obtained from the original W1 theory,²⁰ i.e., it is extrapolated from the jul-cc-pVDZ and jul-cc-pVTZ basis sets.^{21,22,23} The CCSD core-valence (CV) contribution is calculated with the core-valence weighted correlation-consistent cc-pwCVTZ basis set²⁴ and the (T) CV contribution is calculated with the cc-pwCVTZ basis set without the f functions. The scalar relativistic contribution, in the second-order Douglas–Kroll–Hess approximation,²⁵ is obtained from relativistic CCSD(T)/jul-cc-pVDZ-DK calculations.²⁶ The energy calculations involved in W1-F12 theory are carried out with the Molpro 2016.1 program suite.²⁷ The diagonal Born–Oppenheimer corrections (DBOCs) are calculated at the HF/cc-pVTZ level of theory and a valence correlation contribution (Δ DBOC) is calculated at the CCSD/cc-pVDZ level of theory, i.e., Δ DBOC = DBOC(CCSD/cc-pVDZ) – DBOC(HF/cc-pVDZ). All DBOC calculations were carried out with the CFOUR program suite.²⁸

For the smaller semibullvalene hydrocarbon cage (C_8H_8) we were able to obtain the higher-order T_3 effects (CCSDT–CCSD(T)) in conjunction with the cc-pVDZ basis set and the

quasiperturbative T_4 effects (CCSDT(Q)–CCSDT) in conjunction with the sp part of the cc-pVDZ basis set, denoted cc-pVDZ(3s2p). For bullvalene ($C_{10}H_{10}$), post-CCSD(T) contributions altogether (CCSDT(Q)–CCSD(T)) are obtained in conjunction with the cc-pVDZ(3s2p) basis set. All post-CCSD(T) calculations were carried out within the frozen-core approximation using the MRCC program suite.²⁹

The geometries and vibrational frequencies were obtained at the B3LYP-D3BJ/Def2-TZVPP level of theory.^{30,31,32} The equilibrium structures were verified to have all real harmonic frequencies and the transition structures to have only one imaginary frequency. The connectivities of the transition structures were confirmed by performing intrinsic reaction coordinate (IRC) calculations.³³ Zero-point vibrational energies (ZPVEs), enthalpic, and entropic corrections are calculated within the rigid rotor-harmonic oscillator (RRHO) approximation at the B3LYP-D3BJ/Def2-TZVPP level of theory. The harmonic ZPVEs were scaled as recommended in ref. 34. All geometry optimizations and frequency calculations were performed using the Gaussian 16 program suite.³⁵

Results and Discussion

High-level CCSD(T) reaction barrier heights from W1-F12 theory. Table 1 gives the component breakdown of the W1-F12 reaction barrier heights for the degenerate Cope rearrangements in semibullvalene and bullvalene. As expected, the reaction barrier heights are severely overestimated at the HF level and both the CCSD and (T) correlation components reduce the reaction barrier heights (see for example refs. 11 and 36 for high-level CCSD(T) and CCSDT(Q) results for barrier height of other systems). The CCSD correlation energy reduces the reaction barrier heights by large amounts of -19.94 (semibullvalene) and -26.69 (bullvalene) kJ mol^{-1} . The (T) correlation component is still very significant and amounts to -17.33 (semibullvalene) and -19.48 (bullvalene) kJ mol^{-1} . Remarkably, the (T) correlation contributions are not substantially smaller than the CCSD correlation contributions. For bullvalene the (T) correlation component amounts to 73% of the CCSD correlation energy and for semibullvalene it amounts to as much as 87%. These large contributions of the (T) correlation component are unusual. For comparison, for the barrier heights of sigmatropic shifts in the BHPERI database, the (T) correlation component amounts to 6–17% of the CCSD correlation component.¹¹ We note, however, that a key difference between the sigmatropic shifts in the BHPERI database and the Cope rearrangements considered here, is the strain energy involved in the $(\text{CH})_n$ cages. As expected, the core-valence correlation contributions are much smaller than the valence correlation contributions and increase the reaction barrier heights by 0.87 (semibullvalene) and 1.34 (bullvalene) kJ mol^{-1} . For comparison, the CV contribution increases the reaction barrier heights in the BHPERI database by up to 2.1 kJ mol^{-1} .¹¹

Table 1. Component breakdown of the all-electron, nonrelativistic CCSD(T) reaction barrier heights (ΔE^\ddagger) for the degenerate Cope rearrangements in semibullvalene and bullvalene (W1-F12 theory, in kJ mol^{-1}).

	Semibullvalene	Bullvalene
HF ^a	68.49	108.11
CCSD-F12 ^a	-19.94	-26.69
(T) ^b	-17.33	-19.48
CV ^c	0.87	1.34
Scalar rel. ^d	-0.15	-0.19
DBOC ^e	0.11	0.10
ΔE_e^\ddagger	32.05	63.21

^aExtrapolated from the cc-pV{D,T}Z-F12 basis set pair. ^bExtrapolated from the jul-cc-pV{D,T}Z basis set pair. ^cCCSD(T) core-valence correction. ^dScalar relativistic CCSD(T) correction. ^eDBOC = DBOC(HF/cc-pVTZ) + DBOC(CCSD/cc-pVDZ) - DBOC(HF/cc-pVDZ).

The scalar relativistic corrections reduce the barrier heights by -0.15 (semibullvalene) and -0.19 (bullvalene) kJ mol^{-1} . The HF/cc-pVTZ DBOC corrections increase the barrier heights by 0.15 kJ mol^{-1} for both systems. We note that the valence CCSD correlation contribution to the DBOC is rather modest and amounts to -0.04 kJ mol^{-1} for both semibullvalene and bullvalene. Overall, the scalar relativistic and DBOC contributions largely cancel each other out and are thermochemically insignificant (Table 1).

Post-CCSD(T) contributions to the reaction barrier heights. Due to the relatively large contributions of the (T) correlation energy to the reaction barrier heights, it is of interest to estimate the magnitude of post-CCSD(T) contributions. Table S1 of the Supporting Information lists a number of diagnostics for nondynamical correlation effects. The %TAE[(T)] diagnostics is defined as the percentage of the total atomization energy accounted for by parenthetical connected triple excitations and has been found to be a reliable energy-based diagnostic for the importance of nondynamical correlation effects.^{37,38} The %TAE[(T)] values for the local minima and transition structures span a narrow range between 2.0% (bullvalene reactant) and 2.3%

(semibullvalene transition structure). These values suggest that these systems are dominated by dynamical correlation effects and that post-CCSD(T) contributions should not exceed $\sim 2 \text{ kJ mol}^{-1}$.³⁸ Likewise, the \mathcal{T}_1 diagnostics of 0.01 for all systems are below the cut off threshold of 0.02 indicating potentially significant multireference character.³⁹ Finally, we note that the largest CCSD T_2 amplitudes of 0.05–0.06 for the reactants and 0.11–0.12 for the transition structures suggest that the transition structures may exhibit a somewhat more pronounced multireference character.

For semibullvalene we were able to calculate the CCSDT–CCSD(T) contribution (T–(T)) to the reaction barrier height in conjunction with the cc-pVDZ basis set. The fully iterative CCSDT/cc-pVDZ calculations involve 3.9×10^9 (reactant, C_s symmetry) and 7.9×10^9 (transition structure, C_1 symmetry) amplitudes. We note that submicrohartree convergence of the CCSDT energy required ~ 15 iterations, where each iteration ran for 11 hours (reactant) and 18 hours (transition structure) on dual Intel Xeon machines with 40 cores and 1024 GB of RAM. The quasiperturbative (Q) contribution was obtained in conjunction with the cc-pVDZ(3s2p) basis set.

Table 2 gives the post-CCSD(T) contributions to the reaction barrier heights for the degenerate Cope rearrangements in semibullvalene. The T–(T)/cc-pVDZ contribution to the reaction barrier height amounts to 1.38 kJ mol^{-1} . Removing the d functions from the cc-pVDZ basis set (i.e., the cc-pVDZ(3s2p) basis set) results in a smaller T–(T) contribution of 0.47 kJ mol^{-1} . The (Q)/cc-pVDZ(3s2p) contribution amounts to $-0.91 \text{ kJ mol}^{-1}$. Overall, our best CCSDT(Q)–CCSD(T) contribution to the reaction barrier height of semibullvalene amounts to merely 0.46 kJ mol^{-1} .

Table 2. CCSDT–CCSD(T) (T–(T)) and CCSDT(Q)–CCSDT ((Q)) contributions to the reaction barrier heights ($\Delta\Delta E^\ddagger$) for the degenerate Cope rearrangements in semibullvalene and bullvalene (in kJ mol^{-1}).

		Semibullvalene	Bullvalene
T–(T)	cc-pVDZ(3s2p)	0.47	0.80
	cc-pVDZ	1.38	2.34 ^a
(Q)	cc-pVDZ(3s2p)	–0.91	–1.13
Best post-CCSD(T) cont. ^b		0.46	1.21

^aEstimated see text. ^bBest overall CCSDT(Q) – CCSD(T) contribution.

The CCSDT/cc-pVDZ calculations for the bullvalene reactant (in C_s symmetry) involves 15.3×10^9 amplitudes which proved to be beyond the available computational resources. With the cc-pVDZ(3s2p) basis set we obtain a T–(T) contribution of 0.80 kJ mol^{-1} . Based on the results for the smaller, but chemically similar, semibullvalene system, the T–(T)/cc-pVDZ(3s2p) likely represents an underestimation of the T–(T)/cc-pVDZ contribution. For semibullvalene, the T–(T)/cc-pVDZ contribution (1.38 kJ mol^{-1}) amounts to 2.9 times the T–(T)/cc-pVDZ(3s2p) contribution (0.47 kJ mol^{-1}). Assuming a similar underestimation for bullvalene, we can estimate a T–(T)/cc-pVDZ contribution of 2.34 kJ mol^{-1} . The (Q)/cc-pVDZ(3s2p) contribution for the reaction barrier height in bullvalene amounts to $-1.13 \text{ kJ mol}^{-1}$. Overall, our best CCSDT(Q)–CCSD(T) contribution to the reaction barrier height of bullvalene is 1.21 kJ mol^{-1} .

Comparison with available experimental reaction barrier heights. Table 3 lists our best all-electron, relativistic, DBOC-inclusive CCSDT(Q) reaction barrier heights (ΔE_e^\ddagger), as well as the ZPVEs, and enthalpy functions ($H_{298} - H_0$). Overall, we obtain reaction barrier heights of $\Delta H_{298}^\ddagger = 27.95$ (semibullvalene) and 59.48 (bullvalene) kJ mol^{-1} on the enthalpic potential energy surface and $\Delta G_{298}^\ddagger = 27.87$ (semibullvalene) and 62.20 (bullvalene) kJ mol^{-1} on the Gibbs free potential energy surface.

Table 3. Best theoretical all-electron, relativistic, CCSDT(Q) reaction barrier heights on the electronic (ΔE_e^\ddagger), enthalpic at 0 K (ΔH_0^\ddagger), enthalpic at 298 K (ΔH_{298}^\ddagger), and Gibbs free (ΔG_{298}^\ddagger) potential energy surfaces along with the available experimental Gibbs free energy barrier heights for the degenerate Cope rearrangements in semibullvalene and bullvalene (in kJ mol^{-1}).

		Semibullvalene	Bullvalene
Theory	$\Delta E_e^\ddagger^a$	32.52	64.42
	ZPVE ^b	-4.45	-4.37
	$H_{298}-H_0^b$	-0.12	-0.57
	$\Delta H_0^\ddagger^c$	28.07	60.05
	$\Delta H_{298}^\ddagger^c$	27.95	59.48
	$\Delta G_{298}^\ddagger^c$	27.87	62.20
Expt. ^d		23.0±0.4, ^e	49.4±4.2, ^f
		25.9 ^g	53.0±0.4, ^h
			52.3, ⁱ
			51.9±0.0, ^j
			51.5±0.4, ^k
			52.7±0.4, ^l
			52.7, ^m
			51.9±0.4, ⁿ
		54.8±0.8 ^o	

^aCCSDT(Q) values calculated from the WI-F12, all-electron, relativistic, DBOC-inclusive CCSD(T) values in Table 1 and best post-CCSD(T) corrections in Table 2. ^bZPVE and $H_{298}-H_0$ corrections calculated at the B3LYP-D3BJ/Def2-TZVPP level of theory within the RRHO approximation. ^cBest theoretical enthalpic at 0 K (ΔH_0^\ddagger), enthalpic at 298 K (ΔH_{298}^\ddagger), and Gibbs free energy (ΔG_{298}^\ddagger) barrier heights. ^dExperimental Gibbs free energy barrier heights. ^eRef. 40 in CF_2Cl_2 solution. ^fRef. 41. ^gRef. 42. ^hRef. 43 in C_2Cl_4 . ⁱRef. 44 in $\text{C}_3\text{D}_6\text{O}$. ^jRef. 45 in CS_2 . ^kRef. 46 in $\text{C}_2\text{H}_2\text{Cl}_4$. ^lRef. 47 in CDCl_3 . ^mRef. 48 in liquid crystal. ⁿRef. 49 in CS_2 . ^oRef. 49 in gas phase.

The reaction barrier heights for semibullvalene and bullvalene have been determined from variable-temperature ^1H and ^{13}C NMR measurements (Table 3). Our best CCSDT(Q) Gibbs free barrier height for semibullvalene ($27.87 \text{ kJ mol}^{-1}$) is in good agreement with the experimental reaction barrier height of $\Delta G_{298}^\ddagger = 25.9 \text{ kJ mol}^{-1}$ obtained from ^{13}C NMR spectroscopy.⁴² However, our theoretical barrier height differs by 4.9 kJ mol^{-1} from the earlier experimental value ($\Delta G_{298}^\ddagger = 23.0 \text{ kJ mol}^{-1}$) which was obtained nearly half a century ago.⁴⁰

The experimental ΔG_{298}^\ddagger determinations for bullvalene range from 49.4 ± 4.2 to $54.8\pm 0.8 \text{ kJ mol}^{-1}$ (Table 3). The most recent gas-phase measurement ($\Delta G_{298,\text{expt}}^\ddagger = 54.8\pm 0.8 \text{ kJ mol}^{-1}$) lies 7.4 kJ mol^{-1} below our best CCSDT(Q) value ($\Delta G_{298,\text{theor}}^\ddagger = 62.2 \text{ kJ mol}^{-1}$). The uncertainty in the

theoretical reaction barrier height for bullvalene should be larger than that for semibullvalene due to the approximate T–(T) component used (*vide supra*). Nevertheless, overall our multireference diagnostics and available explicit post-CCSD(T) contributions for both systems suggest that the uncertainty in the post-CCSD(T) contributions should not exceed ~ 2 kJ mol⁻¹. Apart from the post-CCSD(T) contributions, the weakest link in the theoretical treatment is most likely due to deficiencies in the ZPVE component. However, unlike heats of formation for systems of this size where the neglect of explicit anharmonicity can lead to errors of over 5 kJ mol⁻¹ in the ZPVE correction,⁵⁰ in the calculation of barrier heights of unimolecular reactions such errors should largely cancel out between the reactant and transition structure. Thus, our high-level theoretical reaction barrier height for bullvalene suggests that the gas-phase experimental value should be revised upward. We note that this measurement was conducted nearly 30 years ago and the use of more advanced NMR techniques may resolve the discrepancy between theory and experiment.

Conclusions

Shapeshifting molecules are a fascinating class of hydrocarbon cages in which the carbon skeleton is continuously changing with no ‘permanent’ C–C bonds. This highly fluxional behavior is enabled due to a series of facile degenerate Cope rearrangements at finite temperatures. In this study, we obtain highly accurate reaction barrier heights for the Cope rearrangements in two prototypical shapeshifting molecules – semibullvalene (C₈H₈) and bullvalene (C₁₀H₁₀). Our reaction barrier heights are calculated at the CCSDT(Q) level close to the complete basis set limit and include inner-shell, scalar-relativistic, Born–Oppenheimer, zero-point vibrational energy, enthalpic, and entropic corrections. Our best theoretical Gibbs free reaction barrier height for semibullvalene ($\Delta G_{298}^\ddagger = 27.9$ kJ mol⁻¹) is in good agreement with the most recent experimental value of 25.9 kJ mol⁻¹. However, our CCSDT(Q) reaction barrier height for bullvalene ($\Delta G_{298}^\ddagger = 62.2$ kJ mol⁻¹) indicates that the experimental values should be revised

upward. We hope that these accurate theoretical results will inspire further measurements of the reaction barrier height in bullvalene using advanced NMR techniques.

Supplementary data

Diagnostics for the importance of nondynamical correlation (Table S1); optimized geometries for all structures (Table S2); and full references for quantum chemical software.

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Graphical TOC:

