

# Localized and delocalized perfluorosemibullvalenes

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**Abstract** On the basis of the experimental Gibbs free-energy barrier of the degenerate Cope arrangement in semibullvalene, B3P86 shows the best agreement, while B3LYP and MP2 underestimate and CCSD(T) overestimates the barrier. The substituent effect proposal by Hoffmann has been verified. In contrast to semibullvalenes with either localized energy-minimum structures or delocalized transition-state structures, perfluorosemibullvalene has both localized and delocalized energy-minimum structures that are very close in energy.

**Keywords** Semibullvalenes · DFT · Ab initio · Energy barrier

## Introduction

In 1966 Zimmerman synthesized semibullvalene (**1**, C<sub>8</sub>H<sub>8</sub>) and predicted a rather low barrier for the degenerate Cope rearrangement [1, 2]. The barrier estimated by experiments at low temperature was  $\Delta G^\ddagger=5.5$  kcal mol<sup>-1</sup> [3, 4]. Since then, semibullvalene has been thought as a potential candidate for the realization of neutral bishomoaromatic systems [5, 6]. On

the basis of a theoretical analysis, Hoffmann and Stohrer [7] concluded that a  $\pi$ -electron-accepting group (-CN) at C<sub>2,8</sub> and C<sub>4,6</sub>, and a  $\pi$ -electron-donating group (-F) at C<sub>1,5</sub> could stabilize the bishomoaromatic transition state ITS into an energy-minimum structure (Fig. 1), while a  $\pi$ -electron-accepting group (-CN) at C<sub>1,5</sub> and a  $\pi$ -electron-donating group (-F) at C<sub>2,4</sub> and C<sub>6,8</sub> could destabilize the transition state (ITS) and raise the barrier. On the basis of AM1 semiempirical calculations, however, Dewar and Jie [8] obtained the opposite conclusion and found that a  $\pi$ -electron-donating group (-F) at C<sub>2,8</sub> and C<sub>4,6</sub>, and a  $\pi$ -electron-accepting group (-CN) at C<sub>1,5</sub> could also stabilize the transition state ITS into an energy-minimum structure. Apart from electronic effects, strain-induced destabilization of the localized structure **1** through annelated small rings at C<sub>2,8</sub> or/and C<sub>4,6</sub> [9–11], as well as stabilization of the delocalized structure through Li<sup>+</sup> coordination [12] and heteroatom substitutions [13] have been explored. Recently, the isolobal analogue of boron carbonyl semibullvalene (BCO)<sub>8</sub> has been computed to have a bishomoaromatic energy-minimum structure [14]. Despite these extensive experimental and theoretical studies, no definitive neutral bishomoaromatic semibullvalenes have yet been realized experimentally yet [15–18].

In this paper, we present our computations on the degenerate Cope rearrangement of semibullvalene at various levels of theory. The quality and reliability of these methods have been validated. In addition, the predicted electronic substitution effects by Hoffmann and Dewar have been verified accordingly. Finally, the structure and stability of perfluorosemibullvalene have been studied.

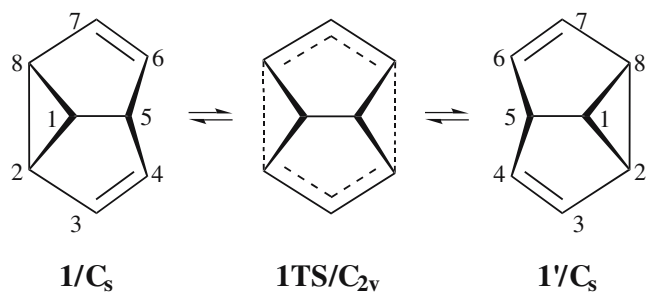
## Computational methods

Structures were fully optimized at the B3LYP [19, 20] and B3P86 [21] B3P86 specifies the same Becke three

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**Fig. 1** Degenerate Cope rearrangement of semibullvalene (**1**)

parameter hybrid functional (Reference [19]) with the non-local correlation provided by Perdew 86. density functional levels of theory and the ab initio MP2 [22–25] level of theory by using the 6–311+G(d,p) basis set. The optimized structures were characterized as either energy minima (NImag=0) without imaginary frequencies or transition states (TS) with only one imaginary frequency (NImag=1) at both B3LYP and B3P86 levels of theory [26]. For discussion and comparison we used the Gibbs free energies scaled at 298 K. In addition, CCSD(T) [27] single-point calculations were carried out to test the performance of this method. All calculations were done with the Gaussian 03 program [28]. All data are summarized in the electronic supporting information.

## Results and discussion

Table 1 lists the calculated results for **1**. At the B3LYP, MP2 and B3P86 levels of theory, the localized structure (**1**) is an energy minimum, and the delocalized structure (**1TS**) is the transition state for the corresponding Cope arrangement. For **1**, all three methods give nearly the same C<sub>2</sub>–C<sub>8</sub> and C<sub>4</sub>–C<sub>6</sub> distances. For **1TS**, however, the B3LYP C<sub>2</sub>–C<sub>8</sub> distance of 2.122 Å is longer than those at B3P86 (2.064 Å)

**Table 1** Computed Gibbs free energy barrier ( $\Delta G^\ddagger$ ), and the C<sub>2</sub>–C<sub>8</sub> and C<sub>4</sub>–C<sub>6</sub> distances (Å)

Method	<b>1</b> (C <sub>s</sub> )	<b>1TS</b> (C <sub>2v</sub> )	$\Delta G^\ddagger$ <sup>a</sup>
	C <sub>2</sub> –C <sub>8</sub> /C <sub>4</sub> –C <sub>6</sub>	C <sub>2</sub> –C <sub>8</sub>	
B3LYP/6-311+G(d,p)	1.610/2.363	2.122	4.0
MP2/6-311+G(d,p) <sup>b</sup>	1.614/2.322	2.055	2.2
B3P86/6-311+G(d,p)	1.601/2.335	2.064	5.0
CCSD(T)/6-311+G(d,p) <sup>c</sup>			7.4
CCSD(T)/6-311+G(d,p) <sup>d</sup>			7.5

<sup>a</sup> Scaled at 298 K, kcal mol<sup>-1</sup>

<sup>b</sup> Using the B3LYP/6-311+G(d,p) Gibbs free energy correction

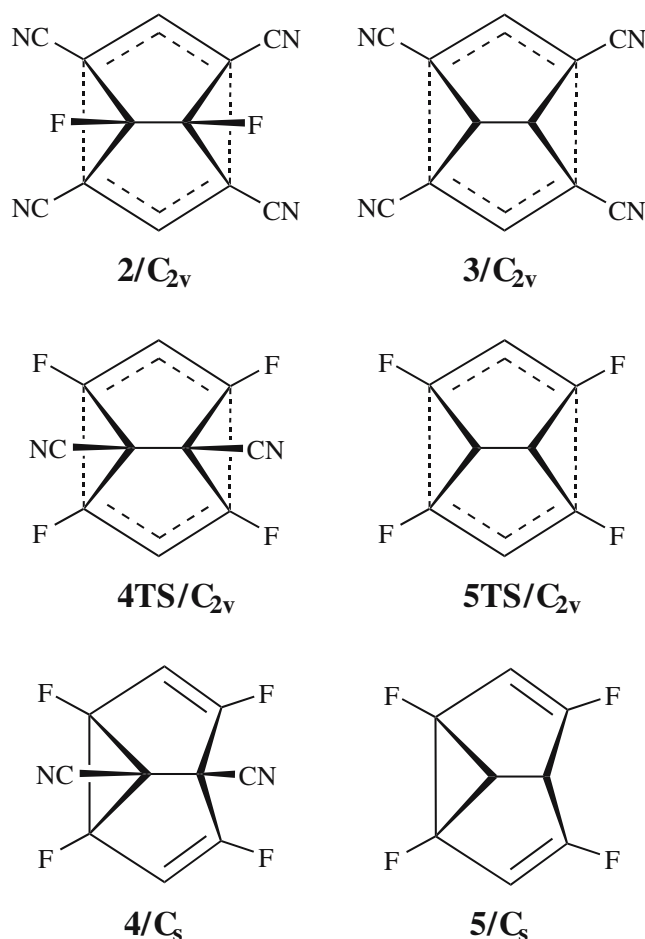
<sup>c</sup> Using the B3LYP/6-311+G(d,p) geometries and Gibbs free energy correction

<sup>d</sup> Using the B3P86/6-311+G(d,p) geometries and Gibbs free energy correction

and MP2 (2.055). Taking the reported Gibbs free energy barrier ( $\Delta G^\ddagger=5.5$  kcal mol<sup>-1</sup> [3, 4]) as reference, MP2/6–311+G(d,p) and B3LYP/6–311+G(d,p) underestimate the barrier (2.2 and 4.0 kcal mol<sup>-1</sup>, respectively) and in turn overestimate the stability of the delocalized **1TS** to a large extent. The closest agreement (5.0 kcal mol<sup>-1</sup>) is found at the B3P86/6–311+G\*\* level.

In addition, we also have tested the performance for the correlated CCSD(T) method. As given in Table 1, the calculated Gibbs free energy barrier is 7.4 and 7.5 kcal mol<sup>-1</sup> using the B3LYP/6–311+G(d,p) and B3P86/6–311+G(d,p) geometries, respectively, higher than the experimental value. These indicate that CCSD(T) overestimates the Gibbs free energy barrier and underestimates the stability of the delocalized structure (**1TS**). Note that there is no energetic effect due to the different transition-state geometries. Thus, B3P86/6–311+G(d,p) shows the best performance for calculating the Gibbs free-energy barrier.

On the basis of our results, we also have carried out calculations on the most favored structures (**2** and **3**) by Hofmann and those (**4** and **5**) by Dewar in Fig. 2 to verify the electronic stabilization. The calculated results are given



**Fig. 2** Hoffmann (**2** and **3**) and Dewar (**4** and **5**) structures

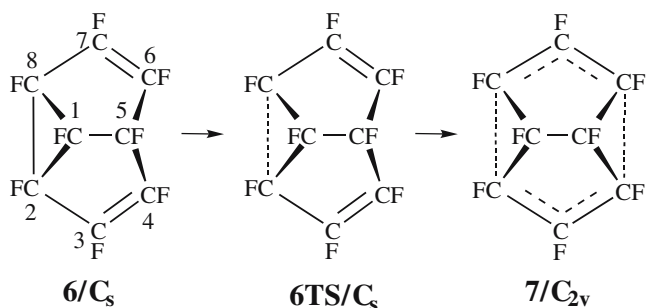
**Table 2** Computed Gibbs free energy barrier ( $\Delta G^\ddagger$ ) and the C<sub>2</sub>–C<sub>8</sub> (C<sub>4</sub>–C<sub>6</sub>) distances (Å)

	C <sub>2</sub> –C <sub>8</sub> /C <sub>4</sub> –C <sub>6</sub>	C <sub>2</sub> –C <sub>8</sub> /C <sub>4</sub> –C <sub>6</sub> 2 (C <sub>s</sub> →C <sub>2v</sub> )	$\Delta G^\ddagger$ <sup>a</sup>
B3LYP/6-311+G(d,p)		2.361	
MP2/6-31G(d) <sup>b</sup>		2.276	
B3P86/6-311+G(d,p)		2.306	
		3 (C <sub>s</sub> →C <sub>2v</sub> )	
B3LYP/6-311+G(d,p)		2.285	
MP2/6-31G(d) <sup>b</sup>		2.205	
B3P86/6-311+G(d,p)		2.239	
	4 (C <sub>s</sub> )	4TS (C <sub>2v</sub> )	
B3LYP/6-311+G(d,p)	1.560/2.425	2.228	11.6
MP2/6-311+G(d,p)	1.557/2.396	2.198	10.6 <sup>c</sup>
B3P86/6-311+G(d,p)	1.552/2.406	2.182	13.2
	5 (C <sub>s</sub> )	5TS (C <sub>2v</sub> )	
B3LYP/6-311+G(d,p)	1.573/2.408	2.241	10.4
MP2/6-311+G(d,p)	1.563/2.376	2.152	9.8 <sup>c</sup>
B3P86/6-311+G(d,p)	1.565/2.388	2.164	11.8

<sup>a</sup> Scaled at 298 K, kcal mol<sup>-1</sup><sup>b</sup> No convergence at MP2/6-311+G(d,p) due to oscillating<sup>c</sup> Using the B3LYP/6-311+G(d,p) Gibbs free energy correction

in Table 2. At the B3LYP, B3P86 and MP2 levels of theory, only delocalized minimum structures (**2** and **3**) are obtained, despite the localized starting geometries. The results for **3** are especially interesting, since only four  $\pi$ -electron-accepting –CN substituents at C<sub>2,8</sub> and C<sub>4,6</sub> are strong enough to stabilize the delocalized structure (**3**), and it is not necessary to have  $\pi$ -electron-donating –F substituents at C<sub>1,5</sub> for further stabilization.

In contrast to the conclusion by Dewar and Jie [8], the most stable localized structures for **4** and **5** have been found at the B3LYP, B3P86 and MP2 levels of theory, and the corresponding delocalized structures (**4TS** and **5TS**) are transition states. Moreover, the computed Gibbs free-energy barriers (Table 2, kcal mol<sup>-1</sup>) for **4** and **5** are much higher than that for **1**, e.g.; 11.6 (B3LYP), 13.2 (B3P86) and 10.6 (MP2) for **4**, as well as 10.4 (B3LYP), 11.8 (B3P86) and 9.8 (MP2) for **5**. These results clearly verify the prediction by Hoffmann and Stohrer [7], i.e.;  $\pi$ -electron-accepting

**Fig. 3** Degenerate Cope rearrangement of **6** and **7**

groups (–CN) at C<sub>1,5</sub> and  $\pi$ -electron-donating groups (–F) at C<sub>2,4</sub> and C<sub>6,8</sub> could destabilize the transition state (**1TS**) and raise the barrier. In addition, the destabilization effect of  $\pi$ -electron-accepting groups (–CN) at C<sub>1,5</sub> is also estimated by comparing the free energy barriers for **4** and **5**, i.e.; 1.2, 1.4 and 0.8 kcal mol<sup>-1</sup> at the B3LYP, B3P86 and MP2 levels of theory, respectively.

Finally, we are interested in the electronic effect of perfluorosemibullvalene (**6**) (Fig. 3). The calculated results are given in Table 3. At MP2/6-31G(d) and MP2/6-311+G(d,p), both **6** and **7** are energy minima, but no transition state **6TS** could be located. At the MP2/6-311+G(d,p) level including the Gibbs free energy correction at MP2/6-31G(d), **7** is more stable than **6** by 3.1 kcal mol<sup>-1</sup>, indicating that perfluorination stabilizes the delocalized transition state structure into an energy minimum structure.

At the B3LYP/6-311+G(d,p) level, both localized (**6**) and delocalized (**7**) structures are energy minima, and **7** is more stable than **6** by 2.5 kcal mol<sup>-1</sup> in Gibbs free energy. In addition, the corresponding transition state (**6TS**) has been located, and the computed Gibbs free energy barrier is only 0.8 kcal mol<sup>-1</sup>.

Similarly, at B3LYP, both **6** and **7** are energy minima and **6TS** is the corresponding transition state at B3P86. At B3P86/6-311+G(d,p), **7** is only 0.3 kcal mol<sup>-1</sup> more stable than **6**, and the energy barrier is 1.7 kcal mol<sup>-1</sup>. Considering this small energy difference, both energy-minimum structures **6** and **7** could have equilibrium at defined temperature without any detectable barrier.

## Conclusions

In conclusion, B3P86 shows the best performance for calculating the stability of the delocalized structure of semibullvalene (**1TS**), while MP2 and B3LYP overestimate the stability of **1TS** and CCSD(T) underestimates the stability of **1TS**. The predicted electronic effect by Hoffmann has been verified clearly. In contrast to these semibullvalenes, which have either localized minimum

**Table 3** Computed Gibbs free energy barrier ( $\Delta G^\ddagger$ ) and the C<sub>2</sub>–C<sub>8</sub>, C<sub>4</sub>–C<sub>6</sub> distances (Å)

	B3LYP	MP2	B3P86
<b>6</b> (C <sub>s</sub> )	1.649/2.439	1.636/2.409	1.634/2.421
<b>6TS</b> (C <sub>s</sub> )	1.922/2.411		1.959/2.381
<b>7</b> (C <sub>2v</sub> )	2.339	2.319	2.305
$\Delta G^\ddagger$ <sup>a</sup>	0.8	–	1.7
$\Delta G$	–2.5	–3.1 <sup>b</sup>	–0.3

<sup>a</sup> Scaled at 298 K, kcal mol<sup>-1</sup><sup>b</sup> Using the MP2/6-31G(d) Gibbs free energy correction

structures or delocalized transition-state structures, perfluorosemibullvalene has both localized (**6**) and delocalized (**7**) structures very close in energy.

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