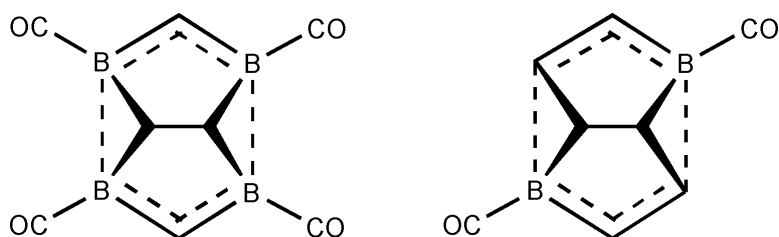


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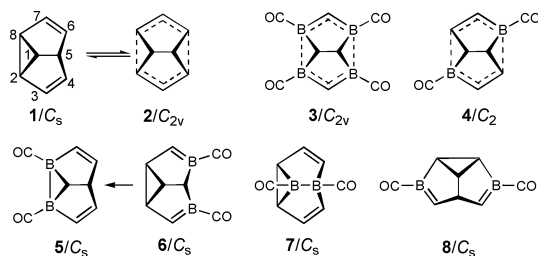
Neutral Bishomoaromatic Semibullvalenes

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Due to its very small degenerate Cope rearrangement barrier ($\Delta G^\ddagger = 5.5$ kcal/mol),¹ semibullvalene (**1**) has been a leading candidate for the realization of neutral bishomoaromaticity² since its preparation by Zimmerman in 1966.³ Theoretical analyses by Hoffmann⁴ and Dewar⁵ suggested that electron-withdrawing groups at C_{2,8} and C_{4,6}, as well as electron-donating groups at C_{1,5}, might stabilize the bishomoaromatic transition state **2** preferentially and eliminate the barrier. In addition to these electronic effects, strain-induced destabilization of the localized structure **1** through small-ring annulations at C_{2,8} or/and C_{4,6},^{2,6,7} as well as stabilization of the delocalized structures through Li⁺ coordination⁸ and heteroatom substitutions,⁹ have been explored. Despite extensive attempts, experimental realization of a definitive neutral bishomoaromatic semibullvalene is still elusive.¹⁰ We called attention to the isolobal



relationship¹¹ of a boron carbonyl (BCO) fragment to a CH group recently.¹² This relationship predicts a number of BCO monocyclic systems, e.g., C₃H₃⁺ ≈ (BCO)₃⁺, C₄H₄²⁺ ≈ (BCO)₄²⁺, C₅H₅⁻ ≈ (BCO)₅⁻, C₆H₆ ≈ (BCO)₆, and C₇H₇⁺ ≈ (BCO)₇⁺,¹³ which mimic the aromaticity of their hydrocarbon counterparts. We now employ the same strategy to convert transition state **2** into bishomoaromatic minima by BCO replacement at appropriate positions.

Structures, optimized at B3P86/6-311+G**¹⁴ with the Gaussian 98 program,¹⁵ either were energy minima (NImag = 0) or transition states (TS) with one imaginary frequency (NImag = 1). Open-shell singlets were computed using the unrestricted “guess = mix” option. Key distances are listed in Table 1.

Despite employing a localized starting geometry, the 2,8,4,6-tetra BCO-substituted structure (**3**) optimizes to a delocalized C_{2v} symmetry minimum. The 1.494 Å R_{2,3} (B–C) bond length is close to that (1.503 Å) of the (1,3,5-C₃H₃(BCO)₃) benzene analogue and the average BC distance between the B–C (1.619 Å) and B=C (1.445 Å) bond lengths in H₃C–BH₂CO and H₂C=BHCO (isolobal with ethane and ethene, respectively). The 2.264 Å R_{2,8} (B–B) distance is much longer than the related 1.817 Å B–B single-bond length in C_s cis-c-CH₂(BHCO)₂ (isolobal with cyclopropane). For comparison, the triplet state (**3T**) is computed to be 6.0 kcal/mol higher in energy, whereas the open-shell singlet state (**3OS**) has

Table 1. Computed Bond Lengths (R, Å)^a and NICS Values (ppm)^b

	NImag	R _{2,8}	R _{2,3}	R _{3,4}	R _{4,6}	NICS
1 /C _s	0	1.601	1.466	1.342	2.335	-10.4
2 /C _{2v}	1	2.064	1.386	1.386	2.064	-22.7
3 (2,8,4,6)/C _{2v}	0	2.264	1.494	1.494	2.264	-16.6
3T (2,8,4,6)/C _{2v}	0	2.715	1.495	1.495	2.715	
4 (2,6)/C ₂	0	2.215	1.503	1.375	2.215	-18.3
4T (2,6)/C ₂	0	2.623	1.526	1.355	2.623	
4OS (2,6)/C ₂	0	2.498	1.521	1.358	2.498	-15.2
5 (2,8)/C _s	0	2.043	1.542	1.347	2.347	-10.1
5T (2,8)/C _s	0	2.735	1.533	1.350	2.513	
7 (1,5)/C _s	0	1.528	1.476	1.342	2.556	-6.9
7T (1,5)/C _{2v}	0	2.844	1.389	1.389	2.844	
7TS (1,5)/C _{2v}	1	2.201	1.389	1.389	2.201	-22.5
8a (3,7)/C _s	0	1.560	1.564	1.465	2.239	-8.2
8b (3,7)/C _{2v}	0	1.669	1.524	1.524	1.669	-14.6
8T (3,7)/C _{2v}	0	1.545	1.560	1.560	1.545	
8OS (3,7)/C _{2v}	0	1.565	1.552	1.552	1.565	-10.2
9 (2-4,6-8)/C _{2v}	0	2.006	1.641	1.641	2.006	-12.7
9T (2-4,6-8)/C _{2v}	0	1.825	1.684	1.684	1.825	
9OS (2-4,6-8)/C _{2v}	0	1.882	1.666	1.666	1.882	-10.2
10 (1-8)/C _{2v}	0	1.816	1.653	1.653	1.816	-10.0
10T (1-8)/C _{2v}	0	1.744	1.686	1.686	1.744	
10OS (1-8)/C _{2v}	0	1.758	1.678	1.678	1.758	-8.8
11 /C _s	0	1.580	1.464	1.341	2.386	-8.3
11TS /C _{2v}	1	2.044	1.387	1.387	2.044	-21.5
12 /C _s	0	1.549	1.469	1.337	2.389	-5.1
12TS /C _{2v}	1	2.017	1.385	1.385	2.017	-20.8
13 /C _{3v}	0	1.529	1.467	1.337	2.487	-3.0
13TS /C _{2v}	1	2.056	1.387	1.387	2.056	-19.6
14 (2,6)/C ₁	0	1.902	1.535	1.352	2.365	-12.3
14TS (2,6)/C ₂	1	2.174	1.505	1.376	2.174	-16.9
15 (2,8,4,6)/C _s	0	2.101	1.514	1.480	2.364	-12.2
15TS (2,8,4,6)/C _{2v}	1	2.235	1.495	1.495	2.235	-14.9
16 (2,6)/C ₁	0	1.822	1.538	1.348	2.365	-9.6
16TS (2,6)/C ₂	1	2.141	1.501	1.375	2.141	-15.9
17 (2,8,4,6)/C _s	0	2.102	1.506	1.481	2.298	-11.8
17TS (2,8,4,6)/C _{2v}	1	2.199	1.492	1.492	2.199	-13.4
18 (2,6)/C ₁	0	1.751	1.551	1.344	2.488	-6.0
18TS (2,6)/C ₂	1	2.169	1.506	1.374	2.169	-15.4
19 (2,8,4,6)/C _s	0	1.955	1.528	1.469	2.499	-5.8
19TS (2,8,4,6)/C _{2v}	1	2.220	1.494	1.494	2.220	-13.4

^a At B3P86/6-311+G**. ^b At HF-GIAO/6-31+G**/B3P86/6-311+G** and at the unweighted centers of the Cope systems (atoms 2–4 and 6–8).

the same energy as **3**. C_{2,6} BCO substitution results in a delocalized singlet minimum (**4**, C₂), but the triplet (**4T**) and open-shell singlet (**4OS**) states are slightly more stable (by 0.3 and 1.3 kcal/mol, respectively, at the level of theory employed). The R_{2,8} distance in **4OS** (2.498 Å) is longer than in **4** (2.215 Å), but shorter than in **4T** (2.623 Å).

However, optimization of 2,8- (**5**) and 4,6- (**6**) starting geometries both lead only to **5**, a C_s symmetry minimum, which is 7.0 kcal/mol more stable than triplet **5T**. The structure of **5** is essentially localized: C(4)–C(6) is like that of **1**, while B(2)–B(8) in **5** is ca. 0.22 Å shorter than in **3** (Table 1).

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Table 2. Computed Activation Free Energies (kcal/mol) Compared to the Available Experimental Values (in Parentheses)

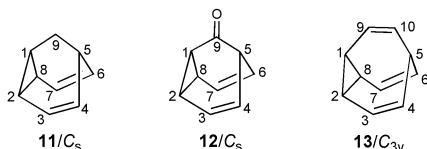
system	ΔG^\ddagger ^a	system	ΔG^\ddagger
1 → 2	5.0 (5.5; ^b 6.2 ^c)	12 → 12TS	9.1 (9.6 ^f)
7 → 7TS	11.7	16 → 16TS	1.3
		17 → 17TS	1.5
11 → 11TS	7.1 (7.8; ^d 7.7 ^e)	13 → 13TS	13.0 (12.8 ^e)
14 → 14TS	1.2	18 → 18TS	3.7
15 → 15TS	1.5	19 → 19TS	2.4

^a At B3P86/6-311+G** corrected at 298 K. ^b Reference 1a. ^c Reference 1b. ^d Reference 18. ^e Reference 10d. ^f Reference 19. ^g Reference 20.

The 1,5-BCO analogue (**7**) has a localized, singlet ground state (the triplet state (**7T**) is 16.7 kcal/mol less stable). The C–C bond lengths in **7** are close to those in **1**, and the B–C and B=C lengths are like those of H₃C–BH₂CO and H₂C=BHCO. Moreover, the BCO substitution at the bridging 1,5-positions in **7** (which are not involved in the delocalization) more than *doubles* the Cope barrier to 11.7 kcal/mol from the 5.0 kcal/mol computed for **1** (Table 2).

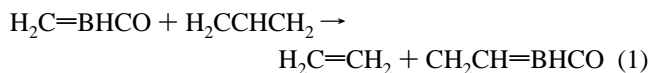
Conversely, 3,7-BCO disubstitution at the central positions of the allyl moieties results in a delocalized, open-shell singlet structure (**8OS**), which is more stable than the triplet (**8T**) and the two singlet states (**8a**/*C_s* and **8b**/*C_{2v}*) by 1.5, 6.5, and 7.9 kcal/mol, respectively. The isolobal set is completed by the 2,3,4,6,7,8-hexasubstituted **9** and by the fully substituted (BCO)₈ (**10**). Both favor delocalized open-shell singlet minima (**9OS** and **10OS**), which are more stable than **9T** (by 3.0) and **9** (by 2.0), as well as **10T** (by 2.0) and **10** (by 6.7 kcal/mol), respectively.

The nucleus-independent chemical shifts (NICS)¹⁶ are in line with the variation of the structural parameters and confirm the delocalization and the neutral bishomoaromaticity of **3**, **4**, and **4OS** (Table 1). In addition, the transition states **2** and **7TS** are aromatic with large negative NICS. While **1**, **5**, **7**, and **8a** are localized in the Cope sense, the σ -aromaticity of their three-membered rings¹⁷ results in moderately large NICS values.⁶ The NICS of **8b**, **9**, **9OS**, **10**, and **10OS** are smaller than those of **3** and **4**. The shorter *R*_{2,8} distances reduce delocalization.



To what extent are these exciting results general? Barbaralane (**11**), barbaralane (**12**), and bullvalene (**13**) have larger Cope barriers than **1** (Table 2). While neither 2,6- nor 2,8,4,6-BCO substitution in **11**–**13** converts the delocalized *C_{2v}* structures into energy minima, the barriers are reduced considerably (Table 2). The 1.2–1.5 kcal/mol barriers of the 2,6- and 2,8,4,6-substituted barbaralanes and barbaralones, **14**–**17**, are much smaller than those of **11** (7.1) and **12** (9.1 kcal/mol). The barriers for the isolobal bullvalenes **18** and **19** enjoy even larger reductions, ca. 10 kcal/mol. All the transition states are delocalized, aromatic, and have large negative NICS values (Table 1). In contrast to **1**, all *C_{2,6}* (**14**, **16** and **18**) and *C_{2,8,4,6}* substitutions (**15**, **17** and **19**) have more stable singlet than triplet states (by 7–8 and 10–11 kcal/mol, respectively; see Supporting Information).

The elimination/reduction of the Cope barriers is due to the enhanced stabilization of the allylic moieties by BCO substitution. This is shown by the homodesmotic stabilization energy (–17.0 kcal/mol, eq 1) of the BCO-substituted allyl radical.



The BCO stabilization effect can be ascribed to the greater radial extension of the orbitals of the more electropositive boron, which favors bridged structures generally, as documented by the prevalence of deltahedral and delocalized bonding.

We conclude that isolobal CH → BCO substitution favors delocalized, neutral bishomoaromatic systems substantially. The barrier to the degenerate Cope rearrangement is eliminated in the substituted semibullvalenes, **3**, **4**, **9**, and **10**, and is strongly reduced in the 2,6- and 2,8,4,6-substituted barbaralanes, barbaralones, and bullvalenes. In addition, BCO substitution can result in low-lying triplet (**T**) and open-shell singlet (**OS**) states as in semibullvalene itself.^{10a} The predicted neutral bishomoaromaticity is documented by the computed diatropic NICS at the Cope rearrangement centers. This study provides conceptual insights and extends the emerging field of boron carbonyl chemistry.^{13,21}

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Supporting Information Available: Energy data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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