

A Theoretical Study of C₄B Isomers. The Interconversion of CCBCC and CCCCB via Cyclic C₄B

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Theory suggests that CCBCC (**1**) will rearrange to planar cyclo-C₄B (**19**) if the excess energy of **1** is ≥ 16.1 kcal mol⁻¹ [calculations at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-31G(d) level of theory]. Cyclo-C₄B lies only 1.1 kcal mol⁻¹ above CCBCC. The planar nature of symmetrical cyclo-C₄B is attributed to multicentered bonding involving boron. If cyclo-C₄B (**19**) has an excess energy of ≥ 24.4 kcal mol⁻¹, it may ring open to form CCCCB (**3**).

Introduction

Carbon clusters (cumulenes) have been studied in great detail because of their importance in flame chemistry and astrochemistry.¹ Studies on similar compounds containing boron and carbon have been mainly concentrated on borocumulenes with boron occupying a terminal position in such molecules. An early mass spectrometric study showed strong bonding between carbon and boron.² Since that time, a number of studies have involved heating boron/carbon mixtures at high temperatures or by laser irradiation of carbon/boron layers on metal surfaces. The products of these processes are generally trapped in low-temperature matrixes (e.g., solid argon), and the structures of the major products are determined using various spectroscopic methods including infrared spectroscopy and electron spin resonance spectroscopy. The following species have been reported: (i) the anion, neutral, and cation of BC,^{3–9} (ii) neutral BC₂ of which the cyclic form is some 6 kcal mol⁻¹ lower in energy than the linear structure,^{10–12} linear BC₂[–],^{9,13–15} and cyclic BC₂⁺,¹⁶ (iii) linear BC₃[–] and linear BC₃⁺¹⁷ and rhombic BC₃⁺,¹⁶ (iv) linear BC₄[–]¹³ and cyclic BC₄⁺,¹⁶ (v) bent (distorted “linear”) BC_n[–] ($n = 5–13$),¹³ (vi) linear BCCB,¹⁷ and (vii) various species containing B, CO, and O, for example, BCO, B(CO)₂, (CBO)₂,^{14,18–20} C_{2n}BO[–] [$(n = 1–5)$; no data concerning the structures are available],¹⁴ and OCBBCO (a molecule reported to have significant triple bond BB character).²¹ Solid-state rare earth borocarbides are also known; they may produce two-dimensional layers, infinite one-dimensional chains, or finite groups of B and C.²²

Our interest in borocumulenes follows earlier studies of cumulenes, for example, the formation of neutral linear and rhombic C₄²³ and C₅,²⁴ together with reports of stable neutral CCBO²⁵ and of the anions [CH₂=B=CH₂][–] and [CH₂=B=O][–].²⁶ In this paper, we report the results of a theoretical investigation of C₄B isomers, in particular, the stable species CCBCC, CCCCB, and cyclo-C₄B.

Methods

Theoretical Methods. Geometry optimizations were carried out with the Becke 3LYP method^{27,28} using a modest 6-31G(d) basis set within the Gaussian 98 suite of programs.²⁹ Stationary

points were characterized as either minima (no imaginary frequencies) or transition structures (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations. The calculated frequencies were also used to determine zero-point vibrational energies, which were then scaled³⁰ by 0.9661 and used as a zero-point correction for the electronic energies calculated at this and higher levels of theory. Higher-level single-point energies were initially calculated using the CCSD(T) method,^{31,32} together with the Dunning aug-cc-pVDZ basis set,^{33,34} that is, at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. A reviewer questioned the accuracy of these results and suggested that calculations should be recalculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-31G(d) level of theory. This has been done, and the data in Tables 1 and 2 contain relative values of energies of minima and transition states on the C₄B potential surface at both levels of theory. All calculations were carried out using the alpha server of the Australian Partnership for Advanced Computing National Facility (Canberra).

Results and Discussion

The original aims of this project were to make a borocumylene with a central boron atom and to compare the chemistry of these compounds with those of cumulenes we had studied previously. We have used the neutralization/reionization technique^{36–38} to convert either negative ions or positive ions into neutrals in collision cells in a mass spectrometer and to investigate the structures of those neutrals by an investigation of their positive ion spectra [–NR⁺ (from a negative ion precursor) or +NR⁺ (from a positive ion precursor)] or negative ion spectra [–NR[–] or +NR[–]] spectra. In particular, neutral CC¹³CCC was formed from [CC¹³CCC]^{–•}, and a combination of experiment and theory showed that the energized neutral and its radical cation both underwent partial rearrangement of the carbon skeleton and scrambled the carbon atoms through the intermediacy of degenerate carbon-substituted rhombic structures.²⁴ The key steps for the cation rearrangement involve equilibration of two rhombic intermediates via an unusual planar intermediate (Scheme 1). Cation C₅^{+•} is isoelectronic with neutral C₄B. Could we make neutral CCBCC, and if so, would it rearrange the skeleton in a fashion similar to [CCCC]^{+•}?

We attempted to make precursor ions that following vertical

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TABLE 1: Details of Stable C₄B Isomers

	C ₁ C ₂ BC ₃ C ₄	C ₁ C ₂ C ₄ BC ₃	C ₂ C ₁ C ₄ C ₃ B						
	1	2	3	8	15	16	17	18	19
State	² B ₂	² Σ	² Σ	² A'	² A'	² A ₁	² A ₁	² A ₁	² A ₁
Symmetry	C _{2v}	C _{∞v}	C _{∞v}	C _s	C _s	C _{2v}	C _{2v}	C _{2v}	C _{2v}
Rel. Energy (a)	0.0	38.0	-4.5	56.3	19.3	25.7	62.5	36.8	3.9
(kcal mol ⁻¹) (b)	0.0	40.8	-4.6	57.9	17.0	25.6	63.5	37.6	1.1
Dipole Moment (Debye)	0.92	2.75	4.72	3.68	1.98	1.87	3.07	4.24	1.12
C ₁ C ₂ (Å)	1.278	1.306	1.285	1.310	1.307	1.461		1.441	1.301
C ₂ C ₃				1.443		1.442	1.502	1.485	
C ₃ C ₄	1.278		1.276	1.391	1.333	1.315	1.353	1.428	1.301
C ₁ C ₄		1.282	1.297						1.412
C ₂ C ₄					1.656		1.353		
C ₁ B	1.413				1.515	1.466	1.452	1.395	1.576
C ₂ B	1.413					1.466	1.554		1.606
C ₃ B		1.373	1.367		1.481				
C ₄ B		1.405		1.043	1.580				
C ₁ C ₂ B (°)	164.1							149.0	
C ₃ C ₁ B						119.7			
C ₃ C ₄ B				164.9					
C ₄ C ₃ B					68.1				65.7
C ₁ BC ₂					110.9	59.7	151.1		
C ₁ BC ₃									
C ₂ BC ₃	177.2								149.7
C ₁ C ₂ C ₃				164.2					
C ₁ C ₂ C ₄							117.4	117.7	
C ₁ C ₄ C ₃					118.6				130.5
C ₂ C ₁ C ₄					70.8				130.5
C ₂ C ₃ C ₄				64.4		149.6			
C ₂ C ₄ C ₃							67.6	62.6	

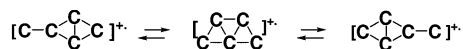
^a Energies are calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory and are relative to **1** (-176.453 758 hartree). ^b Energies are calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-31G(d) level of theory and are relative to **1** (-176.571 083 hartree). ^c B3LYP/6-31G(d) geometries.

TABLE 2: Transition States from Figure 1 and Scheme 1

	TS1	TS2	TS3	11	12	14
State	-	² A'	-	² A ₁	² A ₁	² A ₁
Symmetry	C ₁	C _s	C ₁	C _{2v}	C _{2v}	C _{2v}
Rel. Energy (a)	19.0	19.6	27.1	86.5	23.2	23.2
(kcal mol ⁻¹) (b)	16.1	18.0	25.5	88.6	20.4	22.1
C ₁ C ₂ (Å) ^c	1.287	1.304	1.298	1.330	1.275	1.300
C ₂ C ₃			1.381	1.418		1.468
C ₃ C ₄	1.330	1.319	1.295		1.224	1.293
C ₁ B	1.647					
C ₂ B	1.509	1.506			1.518	
C ₃ B	1.453	1.488	1.740	1.456	1.476	
C ₄ B	1.741	1.576	1.451	1.364		1.365
C ₁ C ₂ B (°)	71.7	155.0			65.2	
C ₄ C ₃ B	77.3	68.0			180.0	
C ₃ C ₄ B			78.4			
C ₂ C ₃ B				152.0		
C ₁ C ₂ C ₃			87.9	62.0		63.7
C ₂ C ₃ C ₄			166.2			153.7
C ₂ BC ₃	148.6	109.8			155.2	
C ₁ C ₂ BC ₃	-17.6					
C ₂ C ₃ BC ₄			-177.0			
C ₂ BC ₃ C ₄	-4.0					
C ₁ C ₂ C ₃ C ₄			16.9			

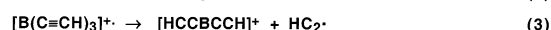
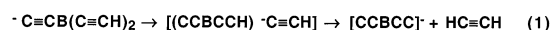
^a Energies are calculated at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory and are relative to CCBCC (-176.453 758 hartree). ^b Energies are calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-31G(d) level of theory and are relative to CCBCC (-176.571 083 hartree). ^c B3LYP/6-31G(d) geometries.

SCHEME 1



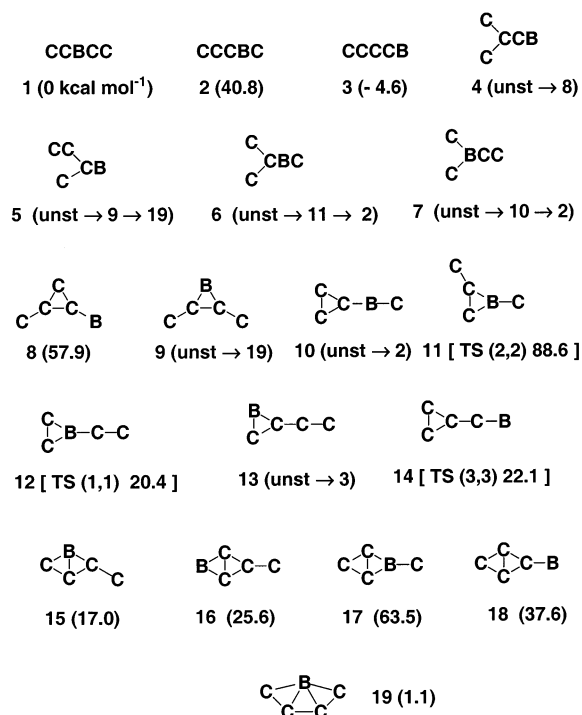
Franck Condon processes would furnish CCBCC. The first attempt was to deprotonate B(C≡CH)₃³⁵ using HO⁻ in the source of the mass spectrometer²⁴ and then to effect the process shown in eq 1 (Scheme 2). The neutral precursor gave only the radical anion [B(C≡CH)₃]^{-•}, which did not furnish [CCBCC]^{-•}.

SCHEME 2



The second approach used the Squires³⁹ multiple desilylation process between B(C≡CSiMe₃)₃ and F⁻ to yield [B(C≡C)₃]⁻, which should yield [CCBCC]^{-•} as shown in eq 2 (Scheme 2).

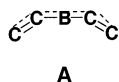
SCHEME 3



This requires a triple desilylation; unfortunately, no source formed [CCBCC]^{•+} ion by this process. Finally, it was hoped that the cation radical precursor [B(C≡CH)₃]^{•+} may yield [CCBCC]⁺; in this case, the only borocumulene cation formed is that shown in eq 3 (Scheme 2).

Theoretical Investigation of the Neutral C₄B Potential Surface. Because we were unable to prepare CCBCC experimentally, we undertook a theoretical investigation to find all C₄B isomers that could, in principle, be involved (directly or indirectly) in possible rearrangements of CCBCC. These are shown in Scheme 3. Geometries have been calculated at the B3LYP/6-31G(d) level of theory and energies at both the CCCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) and CCCSD(T)/aug-cc-pVTZ//B3LYP/6-31G(d) levels as explained in the Theoretical Methods section. Full details of stable structures are listed in Table 1 (including a comparison of the relative energies at the two levels of theory) with bond connectivities and relative energies (at the higher CCCSD(T)/aug-cc-pVTZ//B3LYP/6-31G(d) level of theory) of the stable isomers summarized in Scheme 3.

Doublet CCCCCB (3) is the global minimum on the neutral potential surface. This species is linear with a ²Σ electronic state. Doublet CCBCC (1) has C_{2v} symmetry, a ²B₂ electronic state, and an adiabatic electron affinity of 5.26 eV.⁴⁰ This is a most unusual molecule. The CC and CB bonds (1.28 and 1.41 Å, respectively) have significant triple and double bond character, respectively.⁴¹ The molecule is essentially linear around CBC but bent around CCB, which has an angle of 158° (see data in Table 1). The closest valence bond representation is that shown in A (where each dotted line indicates a partial bond between



two atoms). There are a number of other stable isomers, namely, (i) one mono-substituted three-membered ring system (8), (ii) four undistorted yet planar rhombic isomers (15–18), and (iii) the unusual cyclic planar system 19. Other potential isomers

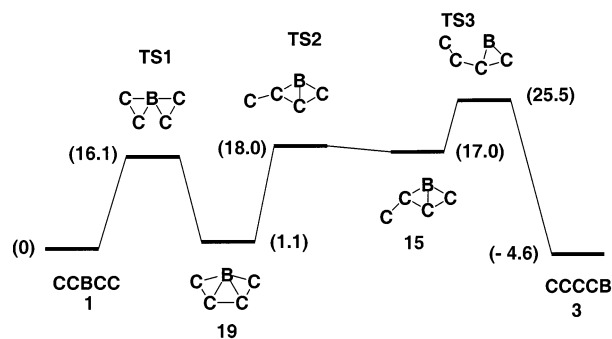


Figure 1. Rearrangement of CCBCC (1) to CCCCCB (3) via cyclic C₄B (19). Energies were calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-31G(d) level of theory. Relative energies are given in kcal mol⁻¹. For full details of individual structures, see Tables 1 and 2.

TABLE 3: Thermochemistry (kcal mol⁻¹) of Some Decomposition Processes of CCBCC and CCCCCB Calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-31G(d) Level of Theory

CCBCC → CC + BCC	118.3
CCBCC → C + CBCC	230.8
CCCCB → CCCC + B	122.3
CCCCB → CCC + CB	156.2
CCCCB → CC + CCCC	122.9

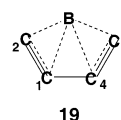
that are either unstable or transition states are identified in Scheme 3. It is of interest that all of the branched chain acyclic systems (4–7) are unstable.

The data collected in Scheme 3 and Table 1 show that there are three low-energy isomers; CCBCC (1), CCCCCB (3), and cyclic 19. Possible rearrangement pathways of CCBCC are shown in Figure 1. Full details of stable species and transition states shown in Figure 1 are recorded in Tables 1 and 2, respectively, while the thermodynamics of some decomposition pathways of selected neutrals are listed in Table 3. The data in Figure 1 show that the conversion of CCBCC (1) to cyclic 19 is endothermic by only 1.1 kcal mol⁻¹ and occurs in one step with a barrier of 16.1 kcal mol⁻¹ (at the CCCSD(T)/aug-cc-pVTZ//B3LYP/6-31G(d) level of theory). It is likely that the nonlinear nature of CCBCC(1) is a contributing factor in the facile cyclization to 19.

The cyclic species 19 can undergo rearrangement to produce other stable isomers listed in Scheme 1. A particular example is shown in Figure 1. This shows a process proceeding through cyclic species 15, which ring opens to give the linear isomer CCCCCB (3). This process from 19 is exothermic by 3.5 kcal mol⁻¹ and requires an excess energy of 24.4 kcal mol⁻¹.

The energy required to isomerize CCBCC to CCCCCB should be compared with the thermochemistries of some decompositions of these two neutrals (Table 3). These decomposition processes are all endothermic by greater than 118 kcal mol⁻¹ and, as such, do not compete favorably with the rearrangement processes shown in Figure 1. The theoretical data indicate that if doublet CCBCC has an excess energy of (i) (at least) 16.1 kcal mol⁻¹ it will rearrange to the pentacyclic isomer 19 or (ii) (at least) 25.5 kcal mol⁻¹ it may rearrange through 19 to give CCCCCB (3), the global minimum on the neutral potential surface.

The Structure of Cyclic Isomer 19. The facile rearrangement of CCBCC to the cyclic isomer 19 (for a valence bond representation, see structure 19)



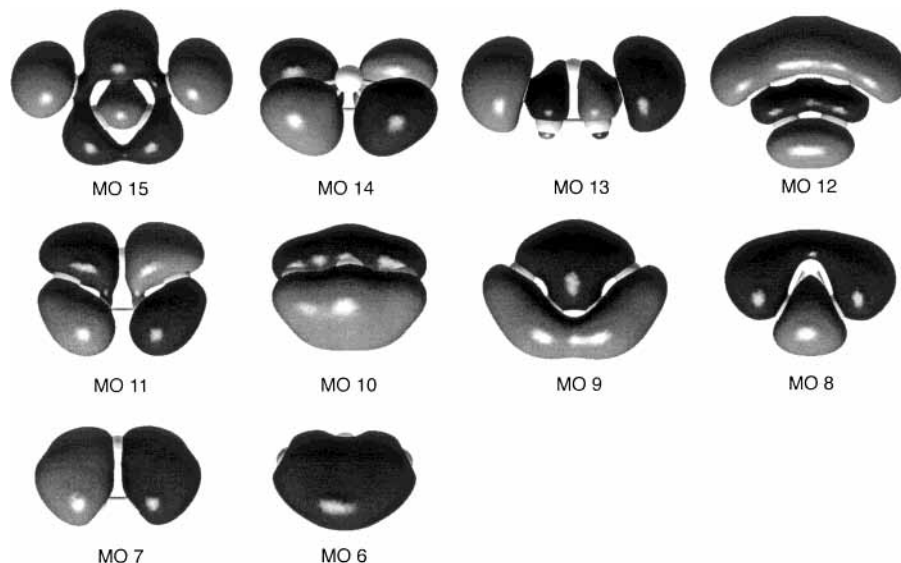


Figure 2. Valence molecular orbitals (MOs) of cyclo- C_4B (**1**) calculated at the B3LYP/6-31G(d) level of theory.

is reminiscent of the behavior of the isoelectronic system $[CCCCC]^+$.²⁴ The linear C_5 radical cation scrambles the carbon atoms by rearrangement through a cyclic C_5 radical cation intermediate, an intermediate that shows structural similarity to **19** (see Scheme 1). For cyclo- C_5^+ , the top CCC angle is 163.8° with each of the four CC “single” bonds being 1.49 Å. For cyclo- C_4B , the CBC angle is 149.7° , and each of the four BC bonds has a bond length within the range 1.58–1.61 Å. The energies of cyclo- C_5^+ and cyclo- C_4B (**19**) are 35.8 and 1.1 kcal mol⁻¹ above $[CCCCC]^+$ and CCBCC, respectively.

How is the boron bound to carbon in symmetrical and planar **19**? The electronic ground state of **19** is 2A_1 . The ground state has four π electrons, which suggests that **19** has no aromatic stabilization. It has been proposed that delocalized σ and π molecular orbitals play significant roles in the stabilization of cyclic B_6 neutral species.⁴² Perhaps multicentered bonding interactions through boron occur as drawn in valence bond representation **19**? Valence molecular orbitals of **19** calculated at the B3LYP/6-31G(d) level of theory are shown in Figure 2. The HOMO (MO15) is a σ molecular orbital occupied by only one electron; this electron is involved in weak three-center bonding between B, C_1 , and C_4 . The other σ bonding MOs, 12 and 9–6, also show σ delocalization. This is most apparent for MOs 12, 9, and 8, which illustrate the multicentered bonding involving boron. The π molecular orbitals 10 and 14 show that the four π electrons are also delocalized through boron. Two nonbonding radical centers on C_2 and C_3 are shown on MO 13. MOs 1–5 are core molecular orbitals and are not shown in Figure 2. From these data, we propose that the multicentered σ and π bonding through boron explain the stability of planar and symmetrical **19**.

Conclusions

(i) Theory suggests that CCBCC (**1**) will rearrange to the cyclic analogue **19** if the excess energy of **1** is ≥ 16.1 kcal mol⁻¹ [calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-31G(d) level of theory]. If **19** has an excess energy of ≥ 24.4 kcal mol⁻¹, this species may ring open to effect formation of CCCCB (**3**).

(ii) There are similarities in the mechanisms of the rearrangements of isoelectronic $[CCCCC]^+$ and CCBCC. Both systems rearrange through the intermediacy of cyclic intermediates. The stabilization of cyclo- C_4B (**19**) is rationalized by multicentered bonding interactions through B.

(iii) The CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory provides adequate relative energies for the C_4B potential surface. The CCSD(T)/aug-cc-pVTZ//B3LYP/6-31G(d) level of theory is very demanding of computer time; both levels of theory give comparable relative energies. Of the 15 calculated structures (both minima and transition states), the maximum difference is 2.9 kcal mol⁻¹ with the average difference being 1.5 kcal mol⁻¹.

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