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:   (DFT),   B3LYP/6-311+G** ,   (ptC)
(ppC)   . $C_3B_2H_4$(ptC)、CB_4H_2(ptC) CB_5H_2(
ppC)   ─CHCH─   .   ,
.   :   ptC   ppC   ,   ,
C_{2v} .   (NICS)   ,
.   ptC   ppC   Wiberg   (WBIs)
ptC   ppC   .

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Unusual Boron-Carbon Compounds Containing Planar Tetracoordinate and Pentacoordinate Carbons

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Abstract   Unusual boron-carbon compounds containing planar tetracoordinate carbon (ptC) and planar pentacoordinate carbon (ppC) were investigated using density functional theory (DFT) at B3LYP/6-311+G** level. These novel compounds are generally assembled with three types of stable structural units $C_3B_2H_4$ with ptC, CB_4H_2 with ptC, and CB_5H_2 with ppC as well as linking elements ─CHCH─. On the basis of calculation results the bonding features, spectroscopic properties, and the aromaticities of these novel boron-carbon compounds were discussed. Results show that as for the lowest-energy compounds contained ptC and ppC without being limited by symmetrical planes, stereo *cis*-structures of C_{2v} symmetry are more stable than the corresponding planar *trans*-structures. Calculated nucleus-independent chemical shift (NICS) values show that the aromaticity of the center of the three-membered rings is the strongest. The total Wiberg bond indices (WBIs) of the ptC and ppC atoms of the most stable structures of the boron-carbon compounds indicate that the ptC and ppC obey the octal rule.

Key Words   Density functional theory;   Planar tetracoordinate carbon;   Planar pentacoordinate carbon;   Aromaticity

Carbon atoms in organic chemistry are generally of tetrahe-   dral, trigonal, and linear coordination configurations, i.e., the

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carbon atoms adopt sp^3-, sp^2-, and sp-hybrids, respectively. Such structural features play an important role in understanding the stereochemistries and properties of organic compounds. Recently, extensively experimental and theoretical studies [1–30] on unusual species with the planar tetracoordinate carbon (ptC) make the structural chemistry of carbon become more rich. This nonclassical valence-bond structure of ptC was initiated by Hoffmann and coworkers[1] in 1970 and its rationalization was established with the rapid development and application of theoretical and computational chemistry[2–28].

In a localized perspective, the ptC structure is normally composed of two two-center two-electron (2c-2e) bonds, one three-center two-electron (3c-2e) bond and one lone pair perpendicular to the plane of ptC. The bonding interactions from σ-donating and π-accepting ligands[2–15], and the delocalization effect enhancement[4,16–24,31] as well as other geometric constraints[25–28] make this planar arrangement stable.

Merino and co-workers[19,20] theoretically proposed the smallest carbon cluster C_5^{2-} containing a ptC and its metallic salts. Pancharatna et al.[21] predicted the existence of multi-C_5^{2-} units in extended structures theoretically. Subsequently, many cyclic hydrocarbons containing C_5 units were constructed and their stabilities and aromaticities were investigated. In calculations by Minyaev et al. [4], a series of multi-ptC in organoboron compounds containing C_3B_2 unit with a ptC have been investigated. More recently, we investigated stabilities, aromaticities, and electronic spectra of various boron-carbon clusters containing multi-ptC atoms by DFT calculations[15]. These theoretical results indicate that the proposed assembling strategies[4,15] are probably an effective method to construct novel compounds with special properties.

Experimentally, since the first successful synthesis of the $V_2(C_8H_9O_2)_4·2C_4H_8O$ compound with two ptC atoms was achieved in 1977[32], other two kinds of ptC-containing clusters were observed and investigated in combination with theoretical calculations in 2000 and 2001, respectively[7,8].

Since the σ-donating and π-accepting bonding interactions and the geometrical constraints can stabilize the cluster with ptC, other compounds with the planar pentacoordinate carbon (ppC) and the planar hexacoordinate carbon (phC) are also possibly stable. These unusual compounds having the high-coordination carbons in a planar environment were indeed constructed theoretically, and they were verified to be stable by calculations and molecular dynamics simulations[14,33,34].
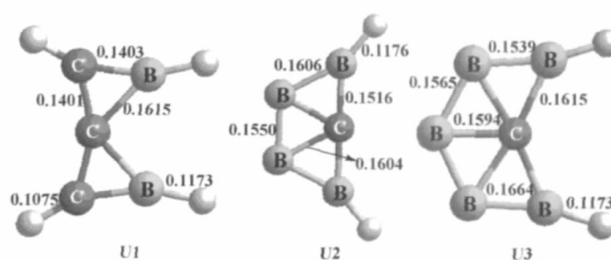
Here we constructed a kind of boron-carbon compounds con-

Fig.1 Optimized geometries of the three kinds of units with ptC or ppC of $C_3B_2H_4$ (U1), CB_4H_2 (U2), and CB_5H_2 (U3) at B3LYP/6-311+G level**

bond length in nm; the atoms without lables are hydrogen atoms.

taining ptC and ppC atoms by assembling the stable structural units $C_3B_2H_4$ (U1), CB_4H_2 (U2), and CB_5H_2 (U3) (Fig.1), as well as linking element —CHCH—. Structures, stabilities, aromaticities, and electronic spectra of these compounds with planar high-coordination carbons were explored by the density functional theory[35].

1 Computational methods

Geometries and stabilities of the three basic units (U1, U2, and U3) have been investigated using the hybrid B3LYP functional[36] with the 6-311+G** basis set. Geometries and vibrational frequencies of these boron-carbon compounds have been determined at B3LYP/6-311+G** level. The Wiberg bond indices (WBIs) for the most stable structures of these boron-carbon compounds were predicted by the natural bond orbital (NBO) approach. The gauge-independent atomic orbital (GIAO) and time-dependent density functional theory (TD-DFT) were used to determine the nucleus-independent chemical shifts (NICS) and excited-state properties, respectively. All calculations were performed by Gaussian 03 program[37].

2 Results and discussion

2.1 Geometries and stabilities of the three basic molecules and their resultant compounds

Fig.1 displays the three basic molecules U1, U2, and U3 optimized at B3LYP/6-311+G** level, in which both U1 and U2 contain one ptC atom, while U3 contains one ppC atom. Predicted electronic states, total energies, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), HOMO-LUMO gaps, and the minimum frequencies of these basic units are summarized in Table 1. As Table 1 shows, the minimum frequencies for these basic structures are

Table 1 Electronic states, total energies (*E*), zero point energies (ZPE), HOMO and LUMO energies (*E*HOMO and *E*LUMO), HOMO-LUMO energy gaps (*E*gap), vertical ionization potentials (VIP), adiabatic ionization potential (AIP), adiabatic electron affinity (AEA), and the minimum vibrational frequencies (Freq) of $C_3B_2H_4$, CB_4H_2, and CB_5H_2

Species	Structure	State	E(a.u.)	ZPE(kJ·mol⁻¹)	E_{HOMO}(a.u.)	E_{LUMO}(a.u.)	E_{gap}/eV	VIP(eV)	AIP(eV)	AEA(eV)	Freq(cm⁻¹)
$C_3B_2H_4$	U1	$^1A_1$	−166.36358	157.36	−0.244	−0.034	5.72				193
CB_4H_2	U2	$^1A_1$	−138.59753	95.23	−0.267	−0.131	3.70				254
CB_5H_2	U3	$^2A_2$	−163.40584	103.72				8.19	8.09	2.08	193

real, indicating that they are minima on the potential energy surface. Structures U1 and U2 have a closed-shell electronic configuration in the singlet $^1A_1$ and their HOMO-LUMO gaps are 5.72 and 3.70 eV at B3LYP/6-311+G** level, respectively. The structure U3 has an open-shell electronic state of $^2A_2$, its vertical ionization potentials (VIP), adiabatic ionization potentials (AIP), and adiabatic electron affinities (AEA) are 8.19, 8.09, and 2.08 eV, respectively. We note that the geometries of U1 in Fig.1 are in good agreement with the previous results[4,15]. The B—ptC bond lengths in U2 are 0.1516 and 0.1604 nm. The B—ppC separations in U3 are 0.1615, 0.1664, and 0.1594 nm.

Two U1 and two —CHCH— units are alternately assembled to form a cyclic compound of $(C_3B_2H_2)_2(C_2H_2)_2$, and it has nine isomers from A1-a to A1-i originating from various building patterns, as shown in Fig.2, the order of stabilities from A1-a to A1-i is A1-b>A1-c>A1-h>A1-e>A1-g>A1-d>A1-i>A1-a>A1-f. The compound A1-b is the most stable isomer among the nine isomers, in which the four boron atoms of two U1 units couple with the carbon atoms of the —CHCH— to form four B—C bonds. Optimized geometries of $(C_3B_2H_2)_2(C_2H_2)_2$ are displayed in Fig.2. As Fig.2 shows, A1-b has a C_{2v} symmetry and the bond lengths of C—B, B—C, and C—C from right to left are 0.1403, 0.1535, and 0.1346 nm, respectively, and the bond lengths of C—ptC and B—ptC are 0.1402 and 0.1642 nm, respectively. The bond length of C-ptC in A1-b is almost identical to that of U1, while the bond length of B—ptC in A1-b is slightly longer
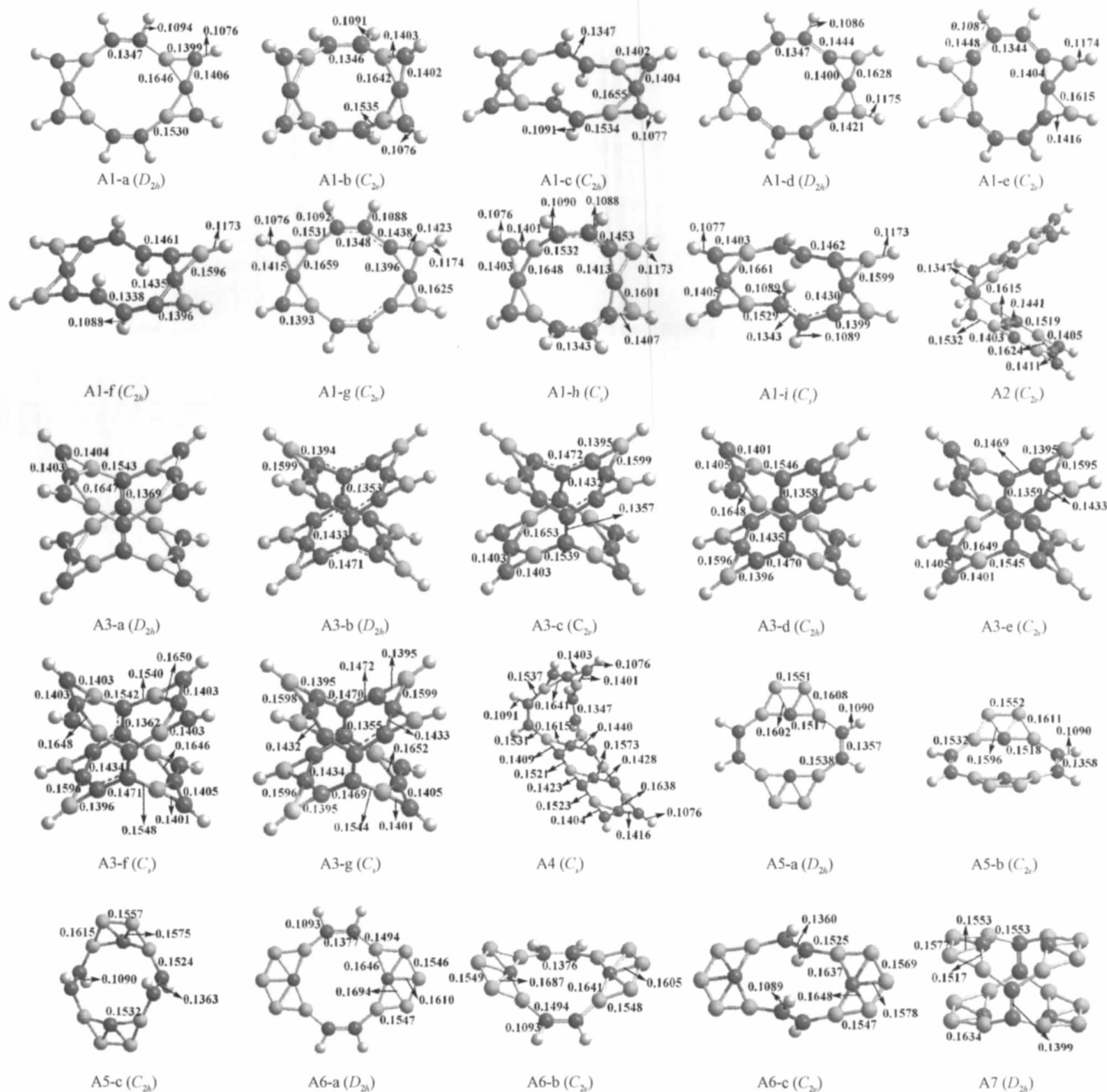

Fig.2   Optimized geometries of $(C_3B_2H_2)_2(C_2H_2)_2$ (A1), $(C_3B_2H_2C_3B_2)_2(C_2H_2)_2$ (A2), $(C_3B_2H_2)_4C_4$ (A3, A4), $(CB_4)_2(C_2H_2)_2$ (A5), and $(CB_4)_4C_4$ (A7) with ptC atoms and $(CB_5)_2(C_2H_2)_2$ (A6) with ppC atoms

than that of U1 by about 0.0027 nm due to the influence of C=C bond.

On the basis of the previous polymerization rule of U1[15], the addition of two U1 units into the most stable structure A1-b may yield nine isomers, A2, A3-a to A3-g, and A4, and their optimized structures are also presented in Fig.2. As Table 2 and Fig. 2 display, the order of stabilities of A2, A3-a to A3-g, and A4 is A2＞A4＞A3-a＞A3-f＞A3-c＞A3-d＞A3-e＞A3-g＞A3-b. The most stable isomer A2 with C_{2v} symmetry (V-sharp) can be considered as a *cis*-dimer of $H_2C_2(B_2C_3)_2H_2$, while the A4 structure with C_s symmetry (tick-like structure) is an adduct of $H_2C_2B_2C_3H_2$ and $H_2C_2(B_2C_3)_3H_2$. The A3-a structure has the relatively high stability among them, where the eight boron atoms connect to four carbon atoms from two —CHCH— elements. The low-energy isomers A3-a and A4 are less stable than A2 by 71.84 and 33.43 kJ·mol⁻¹, respectively, showing that the symmetrical assembling of U1 units along two sides of U1 in A1-b is energetically favorable. The minimum frequencies of A2, A3-a to A3-g, and A4 are real, and thus these structures are stable. The HOMO-LUMO gaps of A2 and A4 are 3.92 and 3.21 eV, respectively, which are smaller than those of isomers A3-a to A3-g. The bond lengths of C—ptC in A2 from left to right are 0.1441 and 0.1411 nm, respectively, slightly longer than those of

U1. The bond lengths of B—ptC in A2 from left to right are 0.1615 and 0.1624 nm, respectively.

Similarly, two U2 or two U3 units with the linking elements of —CHCH— can be assembled to the clusters A5-a, A5-b and A5-c, or A6-a, A6-b and A6-c (Fig.2), respectively. As Table 2 displays, the order of stabilities of A5-a to A5-c is A5-b＞A5-a＞A5-c, and the order of stabilities of A6-a to A6-c is A6-b＞A6-a＞A6-c, the out-of-planar distortions A5-b and A6-b in C_{2v} symmetry are the most stable configurations among their corresponding isomers. Their plane structures lead to the next stable structures A5-a and A6-a in D_{2h} symmetry, and they are slightly higher in energy than their most stable species by 3.35 and 4.18 kJ·mol⁻¹, respectively. We note that the most stable structures A1-b, A5-b, and A6-b have relatively lower symmetries, indicating that the assembling of U1, U2, and U3 units prefers to form the symmetrical *cis*-configuration with the linking element —CHCH—. The further augment of A5-b by two U2 units yields A7. The minimum vibrational frequency of A7 is 79 cm⁻¹. Although the HOMO-LUMO gaps of A5-b and A7 are significantly smaller than that of A1-b by 2.23 and 2.34 eV, respectively, they are remarkably larger than that of A6-b by 1.09 and 0.98 eV.

As seen from Fig.2, the bond lengths of C—C and B—C in

Table 2   Electronic states, total energies (E), relative energies (E_r), HOMO and LUMO energies (E_{HOMO} and E_{LUMO}), HOMO-LUMO energy gaps (E_{gap}) and the minimum vibrational frequencies of $(C_3B_2H_2)_2(C_2H_2)_2$, $(C_3B_2H_2C_3B_2)_2(C_2H_2)_2$, $(C_3B_2H_2)_4C_4$, $(CB_4)_2(C_2H_2)_2$, and $(CB_4)_4C_4$ with ptC atoms and $(CB_5)_2(C_2H_2)_2$ with ppC atoms at B3LYP/6-311+G** level

Species	Isomer	State	E(a.u.)	E_r/(kJ·mol⁻¹)	ZPE(kJ·mol⁻¹)	E_{HOMO}(a.u.)	E_{LUMO}(a.u.)	E_{gap}/eV	Freq(cm⁻¹)
$(C_3B_2H_2)_2(C_2H_2)_2$	A1-a	^1A_g	−485.16645	95.81	395.47	−0.220	−0.091	3.51	76i
	A1-b	$^1A_1$	−485.20296	0.00	397.31	−0.236	−0.051	5.03	31
	A1-c	^1A_g	−485.19356	24.69	396.10	−0.240	−0.052	5.12	79i
	A1-d	^1A_g	−485.17156	82.42	393.80	−0.186	−0.086	2.72	28i
	A1-e	$^1A_1$	−485.17295	78.66	393.17	−0.197	−0.069	3.48	36
	A1-f	^1A_g	−485.13902	167.78	386.69	−0.236	−0.040	5.33	128i
	A1-g	$^1A_1$	−485.17159	82.42	394.38	−0.204	−0.089	3.13	57i
	A1-h	$^1A'$	−485.18614	44.35	393.67	−0.227	−0.053	4.73	48
	A1-i	$^1A'$	−485.16931	88.28	392.42	−0.233	−0.053	4.90	90i
$(C_3B_2H_2C_3B_2)_2(C_2H_2)_2$	A2	$^1A_1$	−813.18663	0.00	524.26	−0.220	−0.076	3.92	20
$(C_3B_2H_2)_4C_4$	A3-a	^1A_g	−813.15927	71.84	519.57	−0.231	−0.076	4.22	64
	A3-b	^1A_g	−813.03972	385.72	497.60	−0.225	−0.059	4.52	80
	A3-c	$^1A_1$	−813.10564	212.63	508.27	−0.229	−0.069	4.35	76
	A3-d	^1A_g	−813.10112	224.51	507.98	−0.229	−0.069	4.35	76
	A3-e	$^1A_1$	−813.10091	225.06	507.85	−0.230	−0.068	4.41	74
	A3-f	$^1A'$	−813.13193	143.59	513.71	−0.230	−0.072	4.30	69
	A3-g	$^1A'$	−813.07206	300.79	502.79	−0.227	−0.064	4.44	82
	A4	C_s	−813.17390	33.43	523.59	−0.207	−0.089	3.21	23
$(CB_4)_2(C_2H_2)_2$	A5-a	^1A_g	−429.69690	3.35	280.29	−0.253	−0.160	2.53	46i
	A5-b	$^1A_1$	−429.69822	0.00	280.50	−0.255	−0.152	2.80	56
	A5-c	^1A_g	−429.63307	167.78	279.16	−0.259	−0.128	3.56	89
$(CB_5)_2(C_2H_2)_2$	A6-a	^1A_g	−479.29757	4.18	294.72	−0.214	−0.143	1.93	34i
	A6-b	$^1A_1$	−479.29922	0.00	294.60	−0.208	−0.145	1.71	12
	A6-c	^1A_g	−479.25742	105.44	292.50	−0.191	−0.169	0.60	53
$(CB_4)_4C_4$	A7	^1A_g	−701.98638	0.00	279.91	−0.248	−0.149	2.69	79

Table 3   WBIs of ptC—B and ppC—B bonds (WBI$_{C-B}$) and total WBIs of the ptC (WBI$_C$) and ppC atoms (WBI$_C$) of the most stable structures of the boron-carbon compounds at B3LYP/6-311+G** level

Structure	WBI$_{C-B}$	WBI$_C$
A1-b	0.6214	3.9103
A2	0.6268, 0.6454	3.8362, 3.9033
A5-b	0.9686, 0.9686	3.7324
A6-b	0.7470, 0.6729, 0.8955	3.7977
A7	0.9063, 0.8719	3.7157

Table 4   Vertical electron transition energies (λ) and oscillator strengths (f) of the most stable boron-carbon compounds with ptC and ppC atoms at B3LYP/6-311+G** level

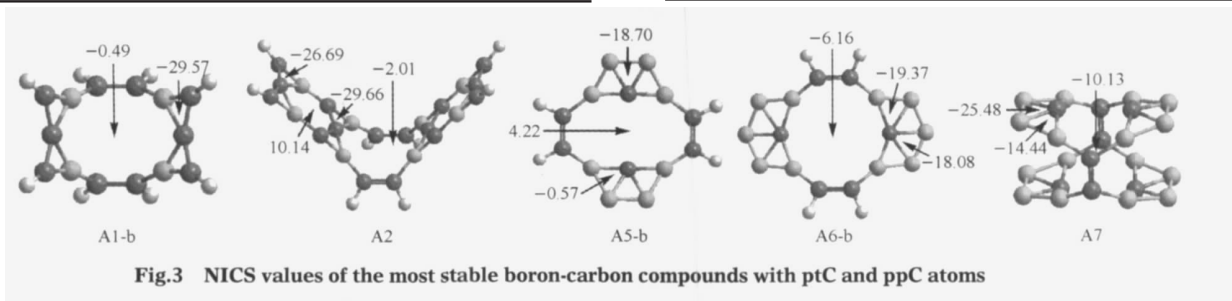| Species	Transition	λ/nm	f
A1-b	$X^1A_1 \rightarrow 1^1B_1$	293.58	0.0015
A2	$X^1A_1 \rightarrow 1^1B_2$	366.50	0.0634
A5-b	$X^1A_1 \rightarrow 1^1B_2$	508.39	0.0463
A6-b	$X^1A_1 \rightarrow 1^1B_1$	680.13	0.0309
A7	$X^1A_g \rightarrow 1^1B_{2u}$	531.86	0.0176

Fig.3   NICS values of the most stable boron-carbon compounds with ptC and ppC atoms

A5-b are 0.1358 and 0.1532 nm, respectively, and the bond lengths of B—ptC in A5-b are 0.1518 and 0.1596 nm, close to those in U2. In A6-b, the bond distances of C—C and B—C are 0.1376 and 0.1494 nm, respectively, and the bond lengths of B—ptC in counter-clockwise are 0.1641, 0.1687, and 0.1605 nm, which are slightly longer than the corresponding bond lengths in U3. The bond lengths of C—C and B—C in A7 are 0.1399 and 0.1553 nm, respectively, and the bond lengths of B—ptC are 0.1517 and 0.1553 nm.

As mentioned above, the bond lengths of C—C bonds in the structures A1-b, A2, A5-b, A6-b and A7 are 0.1346, 0.1347, 0.1358, 0.1376, and 0.1399 nm, respectively, which are typical C=C bonds.

The total bond angles associated with ptC or ppC in A1-b, A2, A5-b, A6-b, and A7 are 360.0, 359.9 and 360.0, 359.6, 359.2, and 336.3°, respectively, indicating that the tetracoordinate or pentacoordinate carbons in the first four structures are almost ideal ptC and ppC, while the tetracoordinate carbon in A7 has an out-of-plane configuration.

2.2   WBIs of selected boron and carbon compounds

Calculated Wiberg bond indices (WBIs) for the most stable compounds are summarized in Table 3. As seen from Table 3, the WBIs of ptC-B and ppC-B in A1-b, A2, A5-b, A6-b, and A7 vary between 0.6214 and 0.9686, and the total WBIs of ptC and ppC atoms are in a range from 3.7157 to 3.9103. Such predicted total WBIs for ptC and ppC suggest that they obey the octal rule in these novel compounds.

2.3   Electronic spectra

The first vertical electron transition energies of the most stable structures of A1-b, A2, A5-b, A6-b, and A7 were determined by the time-dependent (TD)-B3LYP method, which are listed in Table 4. As seen from Table 4, the first vertical electronic excitation energies of A1-b, A2, A5-b, A6-b, and A7 are 293.58, 366.50, 508.39, 680.13, and 531.86 nm, and they are from the

electronic transitions $X^1A_1 \rightarrow 1^1B_1$, $X^1A_1 \rightarrow 1^1B_2$, $X^1A_1 \rightarrow 1^1B_2$, $X^1A_1 \rightarrow 1^1B_1$, and $X^1A_g \rightarrow 1^1B_{2u}$, respectively. The first vertical electronic excitation energy of A2 is lower than that of A1-b by about 73 nm, which results from the increase of conjugated effect. The first vertical electronic excitation energies of the two structures A5-b and A7 with U2 units are remarkably lower than those with U1 units. Moreover, the first vertical electronic excitation energy of A6-b with ppC is the lowest, indicating that more boron atoms involved in the compounds result in lower energy gap.

2.4   Aromaticity of the lower-energy boron-carbon compounds

The NICS values at the centers of the three-, six-, and eight-membered rings, as well as at the mass centers of A1-b, A2, A5-b, A6-b, and A7 were calculated by the GIAO method. As Fig.3 shows, the centers of the three-membered rings of A1-b, A2, A5-b, A6-b, and A7 generally have quite negative NICS values in a range of −29.66 and −14.44 except for the center of one three-membered ring of A5-b (−0.57). The NICS values at the mass centers of A1-b, A2, A5-b, A6-b, and A7 are −0.49, −2.01, 4.22, −6.16, and −10.13, respectively. Therefore, the aromaticity of the three-membered rings are stronger, similar to the previous results[15,16].

3   Conclusions

Using three basic units containing ptC and ppC, we constructed a type of boron-carbon compounds and investigated their structures and related properties by the density functional theory. We obtain a kind of stable stereo *cis*-structures formed by U1, U2, and U3 with ethylene molecules, as well as two extended structures, A2 and A7, which are constructed on the basis of A1-b and A5-b. Calculated WBIs indicated the stable structures in this paper obey octal rule.

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