

## ARTICLE

**Aromaticity of Heterofullerenes  $C_{18}B_xN_y$  ( $x+y=2$ ) and Their Molecular Ions**

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The aromaticity of all possible substituted fullerene isomers of  $C_{18}N_2$ ,  $C_{18}B_2$ ,  $C_{18}BN$ , and their molecular ions which originate from the  $C_{20}$  ( $I_h$ ) cage were studied by the topological resonance energy (TRE) and the percentage topological resonance energy methods. The relationship between the aromaticity of  $C_{18}B_xN_y$  isomers and the sites where the heteroatoms dope at the  $C_{20}$  ( $I_h$ ) cage is discussed. Calculation results show that at the neutral and cationic states all the isomers are predicted to be antiaromatic with negative TREs, but their polyvalent anions are predicted to be aromatic with positive TREs. The most stable isomer is formed by heteroatom doping at the 1,11-sites in  $C_{18}N_2$ ,  $C_{18}B_2$ , and  $C_{18}BN$ . Heterofullerenes are more aromatic than  $C_{20}$ . The stability order in the neutral states is  $C_{18}N_2 > C_{18}BN > C_{18}B_2 > C_{20}$ . The stability order in closed-shell is  $C_{18}B_2^{8-} > C_{20}^{6-} > C_{18}BN^{6-} > C_{18}N_2^{4-}$ . This predicts theoretically that their polyvalent anions have high aromaticity.

**Key words:**  $C_{18}N_2$ ,  $C_{18}B_2$ ,  $C_{18}BN$ , Aromaticity, Topological resonance energy

**I. INTRODUCTION**

Since the discovery of the first fullerene ( $C_{60}$ ) in 1985 [1], the carbon cages known as fullerene have been the focus of much attention. There is continuous interest in the synthesis and characterization of heteroatoms, which have one or more carbon atoms replaced by other elements such as boron or nitrogen. They are expected to be used as semiconductors and building materials for nanometer electronics due to their potential novel properties [2,3]. In 1991 Smalley's group produced the first heterofullerene  $C_{60-n}B_n$  ( $n=1-6$ ) [4]. Later an avalanche of experimental and theoretical studies on boron- or nitrogen-doped carbon clusters were reported [5-9].

The researches of  $C_{20}$  have attracted much attention in recent years.  $C_{20}$  is the smallest possible fullerene. It violates the isolated pentagon rule (IPR) [10] and has only been observed in mass spectrum by Prinzbach *et al.* [11]. In 1991, Parasuk *et al.* predicted that a monocyclic, poly-acetylene structure is the most stable form of  $C_{20}$  clusters by SCF methods [12]. Türker using AM1 method studied the  $C_{20}$  cage and its cationic and anionic forms [13]. Hückel model calculations have been performed for the  $C_{20}$  cage [14,15]. Fourteen structures of  $C_{20}$  have been studied at the DFT/B3LYP/6-31G\* level [16]. Evangelisti investigated the hypothetical system  $C_{12}B_8$  with  $T_h$  symmetry by SCF methods [17]. Yang *et al.* studied the geometry, electronic structure and vibrational spectrum of  $B_8N_{12}$  and  $C_{12}B_8$  [18,19]. Zhang *et al.* studied the structure and stability

of  $C_{18}B_2$  [20]. Chen *et al.* generalized the researches of  $C_{20}$  [21].

Aromaticity is one of the most important and interesting concepts in modern organic chemistry. It has been defined in structural, magnetic and energetic terms. In 1996, Nucleus-independent chemical shift (NICS) was proposed by Schleyer and co-workers [22] as a magnetic index of aromaticity. It is defined as the negative value of the absolute shielding computed at the ring center or at some other interesting point of the system. Rings with negative and positive NICS values are considered aromatic and antiaromatic, respectively. The more negative the NICS values, the more aromatic the molecules are. However, NICS proved not to be a reliable measure of aromaticity when it is applied to polycyclic-system [23-25]. Many investigations revealed that Aihara's topological resonance energy (TRE) and percentage topological resonance energy (%TRE) are an excellent energetic criterion of aromaticity. They can be used to define the aromaticity of neutral and molecule ions, especially in fullerenes. In previous papers we reported the aromaticity of open structure isomers of  $C_{36}X$  ( $X=O, NH, S$ ), hydrogenated isomers of  $C_{36}H_2$  and the homoaromaticity of  $C_{36}CH_2$  formed from fullerene  $C_{36}$ , the initial symmetry of which is  $D_{6h}$  and  $D_{2d}$ , by means of TRE and %TRE methods [26-28]. Herein we report the aromaticity of all possible  $C_{18}B_xN_y$  isomers and their molecular ions formed on the initial  $C_{20}$  cage with  $I_h$  symmetry by TRE and %TRE methods. The relationship between aromaticity of the  $C_{18}B_xN_y$  isomers and the sites where the heteroatoms dope at the  $C_{20}$  cage is discussed, and the aromaticity order of  $C_{18}B_xN_y$  isomers and their molecular ions are established. Finally, the possibility of synthesis of multiply charged anions is also predicted.

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## II. CALCULATION METHODS

TRE is defined as the difference between the  $\pi$ -electron energy of a conjugated molecule and its reference structure [29,30]. In order for the TRE to be obtained, the reference polynomial must first be constructed. The reference polynomial of  $C_{20}$  is:

$$R(X) = X^{20} - 30X^{18} + 375X^{16} - 2540X^{14} + 10155X^{12} - 24474X^{10} + 34805X^8 - 27300X^6 + 10260X^4 - 1400X^2 + 36$$

The tail coefficient of reference polynomial is equal to the number of Kekulé structures. Thus  $C_{20}$  has 36 Kekulé structures. Positive and negative TREs are associated with aromaticity and antiaromaticity, respectively. When aromatic properties of different molecules are compared, the %TRE is very useful. The %TRE is defined as 100 times the TRE, divided by the total  $\pi$ -bonding energy of the polyene reference. We used the computer program published by Ramaraj and Balasubramanian to enumerate the coefficients in the reference polynomials of  $C_{18}B_xN_y$  isomers [31]. In this work we adopted the following heteroatom parameters:  $h_B = -0.45$ ,  $h_N = 1.37$ ,  $k_{C-B} = 0.73$ ,  $k_{C-N} = 0.89$ ,  $k_{B-B} = 0.87$ ,  $k_{B-N} = 0.53$ ,  $k_{N-N} = 0.98$ , which were evaluated by Van-Catledge [32].

## III. RESULTS AND DISCUSSION

### A. Neutral molecules

The Schlegel diagram of  $C_{20}$  ( $I_h$ ) is shown in Fig.1.  $C_{20}$  contains just 12 pentagons and no hexagonal ring. All the carbon atoms are identical. Molecule orbital calculations indicate that there are two unpaired electrons in the nonbonding orbitals, so  $C_{20}$  is an open-shell structure [14,15]. Depending on the different distance between two heteroatoms will produce new isomers, since there are five distinct ways of substitution when two carbon atoms are replaced by nitrogen or boron atom. So,  $C_{18}B_xN_y$  has 15 isomers. The TREs and %TREs of all  $C_{18}N_2$ ,  $C_{18}B_2$ , and  $C_{18}BN$  isomers in neutral and charged states are listed in Ta-

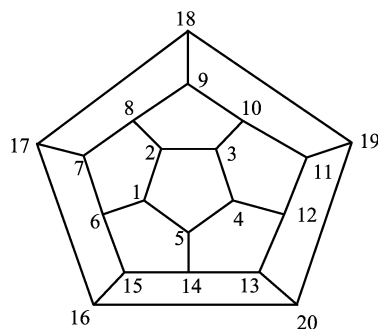


FIG. 1 Schlegel diagram of  $C_{20}$ .

ble I, Table II, and Table III, respectively. The values of  $C_{20}$  were also added in Table III for comparison. As shown in Table III,  $C_{20}$  is predicted to be antiaromatic with negative TRE. In fact,  $C_{20}$  has not been isolated. The %TREs of  $C_{18}B_xN_y$  are larger than  $C_{20}$ . Thus, doping of heteroatoms has a stabilizing effect on  $C_{20}$  to some extent. But all the  $C_{18}B_xN_y$  isomers are also predicted to be antiaromatic with negative TREs. According to the %TREs, the stability order in neutral states is:  $C_{18}N_2 > C_{18}BN > C_{18}B_2 > C_{20}$ . This is different from the stability order of hetero- $C_{40}$ :  $C_{40} > C_{38}B_2 > C_{38}BN > C_{38}N_2$  [33]. Among all the isomers when two heteroatoms are separated by three carbon atoms (**4**, **9**, and **14**), their TREs are the largest. Namely, 1,11-substitution is the most favourable position for them. When four carbon atoms separate two heteroatoms (1,19-substitution), such as for the **5**, **10**, and **15** isomers, they are the least favourable with the largest negative TREs.

Why are the  $C_{18}B_xN_y$  isomers more aromatic than  $C_{20}$ ? Herndon and Randić have shown that for polycyclic aromaticity molecules, relatively small even-membered  $\pi$ -electron rings are the main source of aromaticity [34-36]. For fullerenes, hexagons, and pentagons must be primarily responsible for aromaticity and antiaromaticity, respectively [26]. A nitrogen atom could supply two  $\pi$ -electrons for conjugation. If a nitrogen atom was shared by three pentagons, each of these three pentagons has six  $\pi$ -electrons. This satisfies Hückel's  $4n+2$  rule of aromaticity and warrants the aromaticity of the ring. As a result,  $C_{18}N_2$  isomers are more aromatic than  $C_{20}$ . Namely, nitrogen could stabilize pentagon pairs [37,38]. Boron atom can not supply electrons for conjugation. If three pentagons share a boron atom, each of these three pentagons has four  $\pi$ -electrons. This cannot satisfy Hückel's  $4n+2$  rule of aromaticity and cannot warrant the aromaticity of the ring. After the boron atom substitution, some pentagons turned to be more antiaromatic and contribute much to the destabilization of the molecule,  $C_{18}B_2$  should be more antiaromatic than  $C_{20}$ . But the order of aromaticity is opposite. The  $C_{18}B_2$  isomers are closed-shell structures [14,15]. The aromaticity of the isomers is commonly determined by conjugate effect and closed-shell structure. The aromaticity of  $C_{18}B_2$  is driven mainly by the closed-shell structure effect in the molecule, rather than by the conjugation effect. Therefore the TREs of  $C_{18}B_2$  isomers are slightly larger than  $C_{20}$ .  $C_{18}BN$  isomers are isoelectronic with  $C_{20}$ . The aromaticity of  $C_{18}BN$  isomers were jointly determined by the nitrogen atom and boron atom.  $C_{18}BN$  isomers are also more aromatic than  $C_{20}$ .

### B. Molecular ions

We next examine the aromaticity for molecular ions of  $C_{18}B_xN_y$ . All the molecular cations are predicted to be much more antiaromatic with much smaller neg-

TABLE I TREs and %TREs of  $C_{18}N_2$  molecular ions

|      | No.      | Position | Charge |        |        |        |        |        |       |       |       |
|------|----------|----------|--------|--------|--------|--------|--------|--------|-------|-------|-------|
|      |          |          | +4     | +3     | +2     | +1     | 0      | -1     | -2    | -3    | -4    |
| TRE  | <b>1</b> | 1-2      | -0.740 | -0.767 | -0.794 | -0.590 | -0.387 | -0.059 | 0.268 | 0.910 | 1.552 |
|      | <b>2</b> | 1-3      | -0.713 | -0.730 | -0.746 | -0.572 | -0.397 | -0.069 | 0.259 | 0.915 | 1.571 |
|      | <b>3</b> | 1-9      | -0.726 | -0.683 | -0.639 | -0.503 | -0.367 | -0.047 | 0.274 | 0.927 | 1.580 |
|      | <b>4</b> | 1-11     | -0.722 | -0.792 | -0.862 | -0.601 | -0.340 | -0.023 | 0.294 | 0.937 | 1.580 |
|      | <b>5</b> | 1-19     | -0.934 | -0.688 | -0.443 | -0.418 | -0.394 | -0.076 | 0.242 | 0.904 | 1.567 |
| %TRE | <b>1</b> | 1-2      | -2.251 | -2.311 | -2.371 | -1.764 | -1.157 | -0.170 | 0.818 | 2.872 | 4.926 |
|      | <b>2</b> | 1-3      | -2.174 | -2.204 | -2.234 | -1.712 | -1.191 | -0.199 | 0.793 | 2.900 | 5.007 |
|      | <b>3</b> | 1-9      | -2.217 | -2.066 | -1.914 | -1.507 | -1.101 | -0.132 | 0.836 | 2.934 | 5.031 |
|      | <b>4</b> | 1-11     | -2.203 | -2.391 | -2.579 | -1.799 | -1.019 | -0.060 | 0.900 | 2.965 | 5.031 |
|      | <b>5</b> | 1-19     | -2.851 | -2.088 | -1.325 | -1.254 | -1.182 | -0.221 | 0.740 | 2.865 | 4.991 |

TABLE II TREs and %TREs of  $C_{18}B_2$  molecular ions

|      | No.       | Position | Charge |        |        |        |        |        |        |        |        |       |       |       |       |
|------|-----------|----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|-------|-------|-------|
|      |           |          | +4     | +3     | +2     | +1     | 0      | -1     | -2     | -3     | -4     | -5    | -6    | -7    | -8    |
| TRE  | <b>6</b>  | 1-2      | -1.606 | -1.489 | -1.373 | -1.023 | -0.673 | -0.787 | -0.902 | -0.676 | -0.450 | 0.006 | 0.462 | 1.062 | 1.662 |
|      | <b>7</b>  | 1-3      | -1.539 | -1.440 | -1.341 | -0.997 | -0.653 | -0.746 | -0.840 | -0.599 | -0.357 | 0.062 | 0.480 | 1.064 | 1.648 |
|      | <b>8</b>  | 1-9      | -1.520 | -1.364 | -1.209 | -0.942 | -0.676 | -0.766 | -0.856 | -0.614 | -0.372 | 0.036 | 0.444 | 1.044 | 1.644 |
|      | <b>9</b>  | 1-11     | -1.544 | -1.410 | -1.277 | -0.957 | -0.637 | -0.735 | -0.834 | -0.590 | -0.345 | 0.006 | 0.357 | 1.000 | 1.644 |
|      | <b>10</b> | 1-19     | -1.611 | -1.294 | -0.977 | -0.874 | -0.771 | -0.861 | -0.951 | -0.709 | -0.467 | 0.032 | 0.530 | 1.088 | 1.645 |
| %TRE | <b>6</b>  | 1-2      | -6.144 | -5.566 | -4.989 | -3.684 | -2.378 | -2.770 | -3.161 | -2.382 | -1.603 | 0.051 | 1.705 | 4.118 | 6.531 |
|      | <b>7</b>  | 1-3      | -5.952 | -5.438 | -4.924 | -3.630 | -2.336 | -2.661 | -2.987 | -2.139 | -1.292 | 0.255 | 1.802 | 4.192 | 6.582 |
|      | <b>8</b>  | 1-9      | -5.874 | -5.156 | -4.438 | -3.427 | -2.417 | -2.730 | -3.043 | -2.194 | -1.345 | 0.160 | 1.665 | 4.114 | 6.564 |
|      | <b>9</b>  | 1-11     | -5.963 | -5.327 | -4.692 | -3.485 | -2.278 | -2.620 | -2.963 | -2.106 | -1.249 | 0.045 | 1.338 | 3.951 | 6.564 |
|      | <b>10</b> | 1-19     | -6.227 | -4.906 | -3.586 | -3.171 | -2.757 | -3.069 | -3.381 | -2.534 | -1.688 | 0.151 | 1.989 | 4.279 | 6.569 |

TABLE III TREs and %TREs of  $C_{18}BN$  molecular ions

|      | No.       | Position | Charge |        |        |        |        |        |        |        |        |        |       |       |       |
|------|-----------|----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|-------|-------|
|      |           |          | +6     | +5     | +4     | +3     | +2     | +1     | 0      | -1     | -2     | -3     | -4    | -5    | -6    |
| TRE  | $C_{20}$  |          | -2.237 | -2.027 | -1.817 | -1.275 | -0.733 | -0.915 | -1.096 | -0.915 | -0.733 | -0.275 | 0.183 | 0.973 | 1.763 |
|      | <b>11</b> | 1-2      | -1.677 | -1.482 | -1.288 | -1.002 | -0.716 | -0.694 | -0.672 | -0.528 | -0.384 | 0.028  | 0.440 | 1.010 | 1.579 |
|      | <b>12</b> | 1-3      | -1.643 | -1.445 | -1.246 | -0.986 | -0.726 | -0.713 | -0.700 | -0.563 | -0.425 | -0.011 | 0.403 | 1.006 | 1.609 |
|      | <b>13</b> | 1-9      | -1.63  | -1.437 | -1.245 | -0.962 | -0.679 | -0.691 | -0.704 | -0.564 | -0.423 | -0.006 | 0.412 | 1.007 | 1.601 |
|      | <b>14</b> | 1-11     | -1.631 | -1.447 | -1.263 | -0.994 | -0.725 | -0.686 | -0.647 | -0.516 | -0.386 | 0.031  | 0.447 | 1.025 | 1.603 |
|      | <b>15</b> | 1-19     | -1.978 | -1.776 | -1.575 | -1.066 | -0.557 | -0.757 | -0.957 | -0.817 | -0.677 | -0.258 | 0.162 | 0.882 | 1.602 |
| %TRE | $C_{20}$  |          | -8.091 | -7.153 | -6.216 | -4.323 | -2.430 | -3.011 | -3.593 | -3.011 | -2.430 | -0.902 | 0.626 | 3.500 | 6.374 |
|      | <b>11</b> | 1-2      | -6.024 | -5.198 | -4.373 | -3.365 | -2.356 | -2.269 | -2.181 | -1.719 | -1.257 | 0.113  | 1.483 | 3.537 | 5.591 |
|      | <b>12</b> | 1-3      | -5.904 | -5.069 | -4.234 | -3.312 | -2.390 | -2.331 | -2.272 | -1.833 | -1.394 | -0.018 | 1.358 | 3.529 | 5.700 |
|      | <b>13</b> | 1-9      | -5.857 | -5.043 | -4.230 | -0.999 | 2.232  | -0.026 | -2.284 | -1.835 | -1.386 | 0.001  | 1.388 | 3.529 | 5.67  |
|      | <b>14</b> | 1-11     | -5.863 | -5.075 | -4.287 | -3.335 | -2.383 | -2.242 | -2.100 | -1.682 | -1.263 | 0.120  | 1.504 | 3.591 | 5.678 |
|      | <b>15</b> | 1-19     | -7.105 | -6.229 | -5.352 | -3.592 | -1.832 | -2.469 | -3.106 | -2.662 | -2.217 | -0.836 | 0.545 | 3.110 | 5.675 |

ative %TREs than the anions derived from the same molecule. Molecular cations of any fullerene have not been isolated yet, but molecular anions  $C_{18}B_xN_y$  are markedly aromatized when it acquired two or more electrons to form molecular ions. When the bonding orbits or nonbonding orbits were fully filled by electrons, the

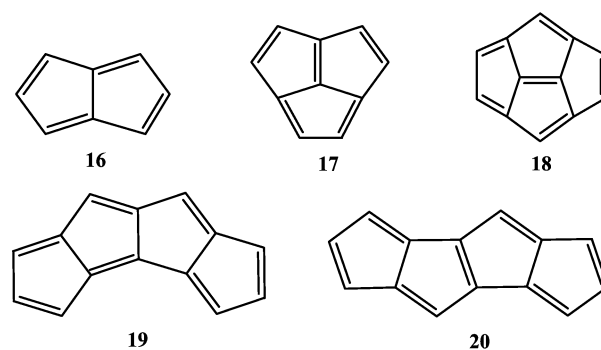
molecule is closed-shell structure and has the highest aromaticity and stability [29,30]. Molecule orbital calculations indicate that,  $C_{20}$  is an open-shell structure [14,15]. If  $C_{20}$  loses two electrons or obtains six  $\pi$ -electrons, it becomes a closed-shell structure. Fullerenes are electron-deficient compounds. The results reveal

TABLE IV TREs and %TREs of compounds **16-20** and their molecular ions

|      | Compound  | Charge |        |        |        |        |        |       |       |       |
|------|-----------|--------|--------|--------|--------|--------|--------|-------|-------|-------|
|      |           | +4     | +3     | +2     | +1     | 0      | -1     | -2    | -3    | -4    |
| TRE  | <b>16</b> | –      | –      | –0.478 | –0.346 | –0.215 | 0.124  | 0.464 | –     | –     |
|      | <b>17</b> | –      | –      | –0.818 | –0.775 | –0.732 | –0.08  | 0.571 | –     | –     |
|      | <b>18</b> | –0.601 | –0.682 | –0.764 | –0.656 | –0.548 | –0.02  | 0.509 | 0.59  | 0.671 |
|      | <b>19</b> | –0.814 | –0.773 | –0.731 | –0.431 | –0.131 | 0.015  | 0.16  | 0.483 | 0.805 |
|      | <b>20</b> | –0.972 | –0.77  | –0.567 | –0.529 | –0.491 | –0.066 | 0.359 | 0.297 | 0.234 |
| %TRE | <b>16</b> | –      | –      | –4.78  | –3.398 | –2.017 | 1.312  | 4.642 | –     | –     |
|      | <b>17</b> | –      | –      | –6.238 | –5.784 | –5.33  | –0.489 | 4.352 | –     | –     |
|      | <b>18</b> | –4.064 | –4.389 | –4.715 | –3.994 | –3.272 | –0.066 | 3.141 | 3.838 | 4.535 |
|      | <b>19</b> | –4.607 | –4.247 | –3.887 | –2.284 | –0.68  | 0.084  | 0.849 | 2.705 | 4.561 |
|      | <b>20</b> | –5.513 | –4.261 | –3.009 | –2.781 | –2.553 | –0.323 | 1.907 | 3.206 | 4.505 |

that  $C_{20}$  has a greater tendency to act as an electron acceptor than a donor. Such a trend in aromaticity is similar to  $C_{36}$  [26].  $C_{18}B_xN_y$  has tendencies to obtain electrons to form closed-shell structures. We can see from Tables I-III, when each  $C_{18}B_xN_y$  isomer has 24  $\pi$ -electrons, all of them are slightly aromatic with small positive TREs. According to the %TREs, the order of aromaticity is:  $C_{18}B_2^{6-} > C_{18}BN^{4-} > C_{18}N_2^{2-} > C_{20}^{4-}$ . If each isomer has 26  $\pi$ -electrons, they achieve closed-shell structures and have the highest aromaticity, and their TREs become large positive values. According to the %TREs, we can get the following stability order:  $C_{18}B_2^{8-} > C_{20}^{6-} > C_{18}BN^{6-} > C_{18}N_2^{4-}$ . In this case, the 1,3-substitution for  $C_{18}B_2^{8-}$  and  $C_{18}BN^{6-}$  are energetically more favourable. But as far as  $C_{18}N_2^{4-}$  isomers are concerned, 1,9- and 1,11-substitution are energetically more favourable. As shown above, all of their %TREs are larger than the %TREs of  $C_{60}$  (1.795) and  $C_{60}^{6-}$  (2.003) [30,39].  $K_6@C_{60}$  has been prepared [40]. Therefore, we can predict that  $C_{20}^{6-}$ ,  $C_{18}BN^{6-}$ ,  $C_{18}B_2^{8-}$ , and  $C_{18}N_2^{4-}$  have high aromaticity and they are even more aromatic than  $C_{60}$ .

As has been seen above, the electrons play an important role in the aromaticity of  $C_{20}$  and  $C_{18}B_xN_y$  isomers. Compounds of **16-20** consist of pentagonal rings only, as shown in Fig.2. They are segment compounds of  $C_{20}$ . The TREs and %TREs of these compounds are listed in Table IV. The neutral and cationic species of compounds are predicted to be antiaromatic with negative TREs. Actually, not all of them have been isolated. But their anions are predicted to be aromatic with positive TREs. Compound **16** is highly reactive and has only been observed as a fugitive species at  $-196^\circ\text{C}$  [41]. In contrast,  $\mathbf{16}^{2-}$  was synthesized in 1964 by Katzetal *et al.* [42], which is a closed-shell structure. **17** is antiaromatic and to date has been observed in mass spectrometry experiments [43], but  $\mathbf{17}^{2-}$  is a stable nonplanar aromatic species which has been prepared by Meijere and co-workers [44]. Attempts to generate compounds of **18-20** have not been successful [45-47]. According to the %TREs, compound **19** is more stable than **20**,

FIG. 2 Five kinds of pentagon segments in  $C_{20}$ .

which is in agreement with the B3LYP/6-31G\* level calculation results [46].

From the Table IV, we can see the following stability trend:  $\mathbf{19} > \mathbf{20} > \mathbf{18}$ .  $\mathbf{18}^{2-}$  and  $\mathbf{18}^{4-}$  are isoelectronic with pyracylene and pyrene, respectively. Pyracylene and pyrene have been isolated [48,49]. Compounds of  $\mathbf{19}^{4-}$  and  $\mathbf{20}^{4-}$  are isoelectronic with naphthacene and chrysene, which have also been isolated [50]. Adding  $\pi$ -electrons to these molecules is likely to create aromaticity in the pentagonal rings, and tend to form aromatic molecular anions. If one or more  $\pi$ -electrons are removed from the pentagons, it would lead to more antiaromaticity of pentagons, and the  $\pi$ -electronic system would be destabilized to a great extent. Therefore, it is highly probable that pentagonal rings in  $C_{20}$  are responsible for the aromaticity of the molecular anions. We might say that  $C_{20}$  has the propensity to form highly charged molecular anions since the molecule has many local pentagons structure.

#### IV. CONCLUSION

Hexagons and pentagons are main sources of aromaticity and antiaromaticity in fullerene molecules, respectively. The aromaticity of  $C_{20}$  and  $C_{18}B_xN_y$  are

jointly determined by the conjugate effect and closed-shell structure. Although substitutions of heteroatom have a stabilizing effect on  $C_{20}$ ,  $C_{18}B_xN_y$  isomers are still antiaromatic because the parent molecule is too antiaromatic. The twelve pentagons must be responsible for it. So we predict that  $C_{20}$  and  $C_{18}B_xN_y$  are difficult to isolate.  $C_{20}$  and  $C_{18}B_xN_y$  isomers have great tendencies as electron acceptors because they are electron deficient compounds. Adding one or two electrons are not enough to stabilize to it. With the increasing of obtained electrons, their anions get more aromaticity. If the isomers have 26  $\pi$ -electrons, they achieve closed-shell structures and get the highest aromaticity.

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