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Theoretical Studies on Graphyne Substructures: Geometry, Aromaticity, and Electronic Properties of the Multiply Fused Dehydrobenzo[12]annulenes

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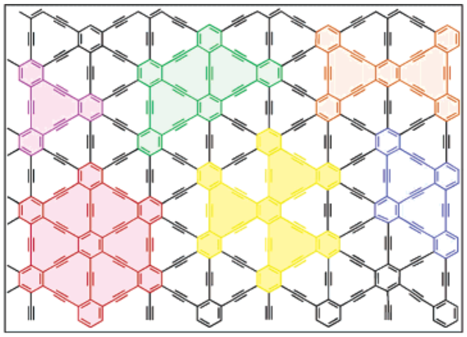
Received November 3, 2006



The geometries of multiply fused dehydrobenzo[12]annulenes [12]DBAs **2**−**7** with various topologies, which are considered as graphyne fragments, have been optimized at the B3LYP/6-31G* level of theory. Most of the optimized geometries of fused DBAs have planar structures excluding a boomerang-shaped bisDBA **4**, a trefoil-shaped trisDBA **6**, and a wheel-shaped DBA **7**. For the boomerang-shaped bisDBA **4** and the trefoil-shaped trisDBA **6**, distortions originate from the steric repulsion between hydrogen atoms attached to adjacent benzene rings. The harmonic oscillator model of aromaticity (HOMA) values at the central benzene ring of multiply fused DBAs decrease as the number of fused 12-membered rings increases except for the closely related structures **4** and **5** and **6** and **7**, because of bond length elongation due to conjugation with the phenylethynyl groups. Nucleus-independent chemical shifts (NICS) were computed at the individual ring centers of the fused DBAs. The fusion of the antiaromatic 12-membered rings results in increasing (more positive) NICS values at the central benzene ring, indicating the decrease of diatropic ring currents. Furthermore, HOMO-LUMO gaps of the DBAs **2**−**7** are strongly influenced by the molecular topology. The para-conjugation pathway of the bis(phenylethynyl)benzene unit plays a more important role in the determination of the electronic properties of multiply fused DBAs than the meta- and ortho-conjugation pathways.

Introduction

Among the various forms of carbon allotropes,[1] graphyne has been the subject of interest among structural, theoretical, and synthetic scientists due to its unknown electronic, optical, and mechanical properties,[2,3] and its structure and aromaticity.[4]

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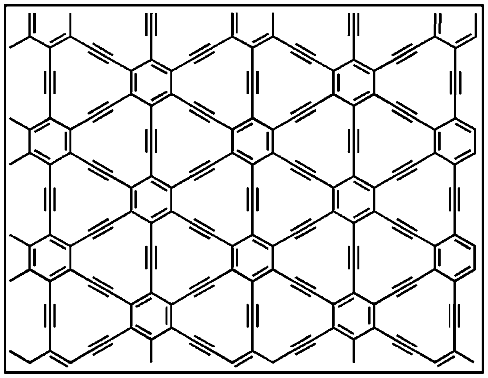
10.1021/jo0622781 CCC: $37.00

CHART 1. Chemical Structure of Graphyne



Graphyne consists of aromatic 6-membered rings and weakly antiaromatic 12-membered rings[5] comprised of alternating triple bonds and conjugated double bonds, the latter being shared by the 6-membered rings (Chart 1). As benzene is considered to be the smallest unit of graphite, dehydrobenzo[12]annulene (**1**, DBA)[6] can be regarded as the smallest unit of graphyne (Figure 1a). It is therefore of interest to explore how the topological differences of fused DBAs change their electronic properties and how many DBA units are needed to confer the semiconductive graphyne-like character. In this respect, doubly[7] and triply fused[8] DBAs **2**, **3**, and **6** have been synthesized by us and some other groups (Figure 1, parts b, c, and f, respectively). However, it is difficult to fully answer these questions due to the lack of experimental information.

Another aspect of interest in multiply fused DBAs is their aromaticity, especially as it is influenced by fusion of the weakly antiaromatic 12-membered rings to the benzene ring. The effect of annulating antiaromatic rings to benzene has been studied intensively by both theory and experiment.[9−11] For example, the annulation of small cyclobutadineno rings (4π electron system) induces severe bond length alternations and decreased diatropicity in the benzene ring because of the bond angle strain and the paratropic character of the cyclobutadiene ring.[9,10] Similarly, the annulation of a cyclooctatetraene ring to the benzene ring reduces the aromatic character of the benzene ring.[12] Consequently, it is expected that annulation of the antiaromatic 12-membered rings onto the benzene ring would change its geometry, aromaticity, and electronic properties.

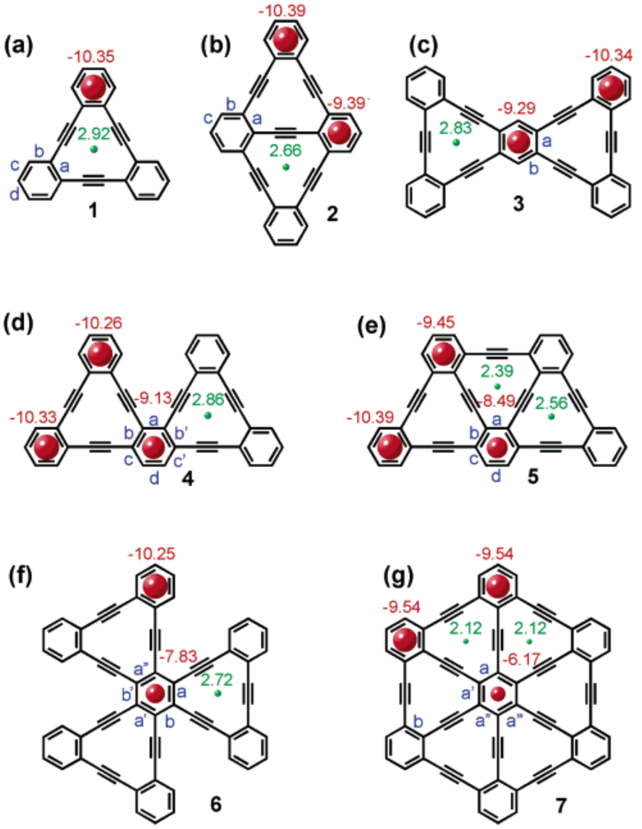


FIGURE 1. Chemical structures, NICS values (GIAO-HF/6-31G*//B3LYP/6-31G*) and bond labeling of dehydrobenzo[12]annulenes: (a) dehydrobenzo[12]annulene (DBA) **1**; (b) rhombic-shaped bis(dehydrobenzo[12]annulene) (bisDBA) **2**; (c) bow-tie-shaped bisDBA **3**; (d) boomerang-shaped bisDBA **4**; (e) trapezoid-shaped tris(dehydrobenzo-[12]annulene) (trisDBA) **5**; (f) trefoil-shaped trisDBA **6**; and (g) wheel-shaped hexakis(dehydrobenzo[12]annulene) (hexakisDBA) **7**. The NICS values calculated at each ring center are shown in red and green solid circles. The size of the circles in the 6- and 12-membered rings represents the relative magnitudes of the NICS values in the benzene rings (red) and the 12-membered rings (green). The prime notated bonds are chemically equivalent to the parent bonds.

For the series of fused DBAs **2**−**7** (Figure 1) and the parent molecule **1**, we calculated the geometries, electronic properties (HOMO-LUMO gaps), and aromatic character (nucleus-independent chemical shift, NICS[13]) using the B3LYP/6-31G* method. In contrast with previous theoretical studies which focused on the electronic and mechanical properties of graphyne and some fused DBAs or the aromaticity of the parent DBA **1**,[4] our study highlights the influence of the type of annulation on the local aromaticity and electronic properties of fused DBAs **2**−**7**. These properties are discussed in terms of the topology of the π-orbitals and the conjugation pathway.

Methods

Optimized geometries, vibrational frequencies, and NICS were calculated with the Gaussian 03 package.[14] The structures of DBAs **1**−**7**, **9**, and **10** are shown in Figures 1 and 3. There are a number

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of literature reports discussing the method and basis set dependency of the degree of bond length alternation (BLA) in conjugated π-systems: BLA is exaggerated with the HF method, whereas DFT methods tend to overly favor more delocalized structures with less BLA.[15] However, it has been demonstrated that optimization of various condensed aromatic compounds, including octadehydro-[14]annulenes, using the B3LYP/6-31G* method provides results in excellent agreement with experimental data.[16] For the parent DBA, the B3LYP/6-31G* optimized structure virtually reproduces the experimental geometry.[4,17] The molecules **1**−**7**, **9**, and **10** were optimized at B3LYP/6-31G* under D_{3h} symmetry for **1**, D_{2h} symmetry for **2**, D_{2h} symmetry for **3**, C_2 symmetry for **4**, C_{2v} symmetry for **5**, D_3 symmetry for **6**, D_{3d} symmetry for **7**, C_{2v} symmetry for **9**, and D_{3h} symmetry for **10**. All geometries were confirmed as minima by frequency analysis. Both B3LYP/6-31G* and HF/6-31G* NICS values were computed (GIAO approach) at the center of each 6- and 12-membered ring in the fused DBAs **1**−**7** on the B3LYP/6-31G* optimized geometries.[18] The orbital energies were calculated at the B3LYP/6-31G* level of theory with use of the B3LYP/6-31G* optimized geometries. The frontier orbitals of trefoil-shaped trisDBA **6** and D_{3d} wheel-shaped hexakisDBA **7** exhibit 2-fold degeneracy. Important molecular orbitals are shown in the Supporting Information.

HOMA values were calculated from the DFT optimized geometries with eq 1,[19]

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum(R_{\mathrm{opt}} - R_{\mathrm{i}})^2 \qquad (1)$$

where n is the number of bonds taken into the summation and α is an empirical constant ($\alpha = 257.7$) chosen to give HOMA = 0 for the hypothetical Kekulé structures of aromatic system and HOMA = 1 for the system with all bonds equal to the optimal value R_{opt} ($R_{\mathrm{opt}} = 1.388$). R_{i} is the individual bond length.

The harmonic oscillator model of aromaticity (HOMA) values can be separated into two terms describing different contributions to decrease aromaticity: (i) due to the bond elongation (the term called EN) and (ii) due to the bond length alternation (the term called GEO).[20] These two values are defined by eq 2.

$$\begin{aligned}\mathrm{HOMA} &= 1 - \frac{\alpha}{n}\sum(R_{\mathrm{opt}} - R_{\mathrm{i}})^2 \\ &= 1 - \left[\alpha(R_{\mathrm{opt}} - R_{\mathrm{av}})^2 + \frac{\alpha}{n}\sum(R_{\mathrm{av}} - R_{\mathrm{i}})^2\right] \\ &= 1 - \mathrm{EN} - \mathrm{GEO} \qquad (2)\end{aligned}$$

Results and Discussion

Geometries. Optimized geometries of the parent DBA **1**, the rhombic-shaped bisDBA **2**, and the bow-tie-shaped bisDBA **3** are planar. On the other hand, the boomerang-shaped bisDBA **4** has a C_2 symmetric structure, in which the two 12-membered rings twist presumably because of steric repulsion of the hydrogen atoms attached to the peripheral benzene rings (Figure 2a). The distance between the two closest hydrogen atoms of the peripheral benzenes is 2.33 Å. The dihedral angle between the peripheral triple bond and the bond shared by the 12-membered ring of the central benzene ring is 2.7°. Additionally, the central benzene ring does not adopt a planar conformation with the dihedral angles ranging from 0.131° to 1.655° between two bonds in the benzene ring (dihedral angles through bonds $b-a-b' = 1.655°$, $a-b-c = 1.063°$, $b-c-d = 0.131°$, and $c-d-c' = 0.736°$). The trapezoid-shaped trisDBA **5** possesses a planar structure of C_{2v} symmetry.

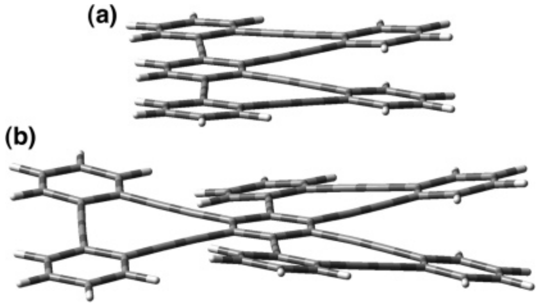

FIGURE 2. Side views of stick models of the optimized structures of **4** (a) and **6** (b).

The trefoil-shaped trisDBA **6** possesses a D_3 symmetric propeller-like structure in which the 12-membered rings are slightly twisted (Figure 2b). The dihedral angle between the peripheral triple bond and the bond shared by the 12-membered ring of the central benzene ring (7.5°) is larger than that of the boomerang-shaped bisDBA **4** (2.7°). The distance between the closest two hydrogen atoms attached to the peripheral benzenes is 2.35 Å. The dihedral angles between C−C bonds at the central benzene ring indicates a very shallow chair conformation with dihedral angles of 0.8° (dihedral angles $a-b-a' = 0.838°$ and $b-a'-b' = 0.840°$).

Surprisingly, the B3LYP/6-31G* optimized geometry of the wheel-shaped DBA **7** has D_{3d} symmetry (but is almost planar). The expected planar D_{6h} conformation proved to be a transition structure (1 imaginary frequency). The central benzene ring of the D_{3d} species adopts a shallow chair conformation. Both dihedral angles $a-a'-a''$ and $a'-a''-a'''$ are 1.865°. One possible rationalization for the unexpected nonplanarity of DBA **7** is the difference in bond lengths of the central ($a = 1.419$ Å) and the peripheral benzene rings ($b = 1.423$ Å) which are shared by the 12-membered ring. The bond lengths of each DBA are discussed in the next section.

Bond Lengths. BLA is one of the traditional criteria for the aromaticity of conjugated ring systems.[21] For example, annulenes following the Hückel rule ($4N + 2$) have either no or very little alternation, whereas those of $4N$ annulenes exhibit a strong alternation.[22] The C−C bond distances of the triple bonds of all the optimized structures are virtually constant (1.215−1.216 Å), and the same is true for the single bond lengths (1.418−1.423 Å). The notable difference of the bond lengths was observed in the benzene rings. As shown in Table 1, the benzene ring of DBA **1** shows four different bond lengths, $a =$

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TABLE 1. Selected Bond Lengths (Å), Bond Length Alternation (BLA), and HOMA Values at the Central Benzene Rings of DBA 1, Multiply Fused DBAs 2−7, and Hexakis(phenylethynyl)benzene (8)

	bond lengths							
compd	*a*	*b*	*c*	*d*	BLA[a]	HOMA[b]	EN[b]	GEO[b]
1	1.427	1.406	1.392	1.398	0.035	0.904	0.061	0.035
2	1.423	1.406	1.393		0.030	0.865	0.094	0.040
3	1.428	1.402			0.026	0.832	0.129	0.039
4	1.419	1.427	1.405	1.387	0.040	0.806	0.143	0.051
5	1.419	1.424	1.407	1.387	0.037	0.820	0.137	0.043
6	1.417	1.425			0.008	0.715	0.280	0.005
7	1.419				0.000	0.751	0.249	0.000
8	1.421				0.000	0.723	0.277	0.000

[a] The values indicate the difference between the largest and smallest values. [b] Calculated at the central benzene ring.

1.427 Å, $b = 1.406$ Å, $c = 1.392$ Å, and $d = 1.398$ Å. The degree of BLA is 0.035 indicating that the 12-membered ring reduces the aromatic character of the benzene ring. The length of the shared bond between the 12-membered ring and the benzene ring (bond a) is elongated presumably due to weak conjugation between the two alkyne units and the benzene ring via ortho-type conjugation. Indeed, the optimized geometry of *o*-bis(phenylethynyl)benzene computed at the same level of theory shows that the distance between the two *ipso* carbon atoms is 1.426 Å. We abbreviate this bond as a "*shared bond*" hereafter. The shared bonds of the rhombic-shaped DBA **2** (bond $a = 1.423$ Å) are shorter than that of DBA **1**, whereas the lengths of the shared bonds of the bow-tie-shaped bisDBA **3** (bond $a = 1.428$ Å) are similar to that of DBA **1**. Therefore, we consider that the fusion of 12-membered rings, in such a manner that each 12-membered ring shares one triple bond and two benzene rings, makes the shared bonds slightly shorter. This trend also emerges in the boomerang-shaped bisDBA **4** ($a = 1.419$ Å), the trapezoid-shaped trisDBA **5** ($a = 1.419$ Å), the trefoil-shaped trisDBA **6** ($a = 1.417$ Å), and the wheel-shaped hexakisDBA **7** ($a = 1.419$ Å). This structural trend is also observed in the multiply ethynyl substituted benzenes. For example, the C−C bond length of the central benzene ring of hexakis(phenylethynyl)benzene (**8**) calculated at the same level of theory is 1.421 Å, which is shorter than the distance between the *ipso* carbons of bis(phenylethynyl)benzene (1.426 Å).

The HOMA attempts to quantify the degree of BLA.[19] HOMA is defined as 0 for a model nonaromatic system and is 1 for a system assumed to be a fully aromatic system. HOMA values for the central benzene rings of the multiply fused DBAs **2**−**7** are summarized in Table 1. The HOMA value of DBA **1** (0.904) is close to 1, indicating a slight decrease of aromatic character. The HOMA values of the benzene rings of DBAs **2**−**7** gradually decrease with the increasing number of annulating 12-membered rings (Table 1). Even though the BLA values of the trefoil-shaped trisDBA **6** and hexakisDBA **7** are very small, the HOMA values indicate a decrease of antiaromatic character probably as a result of the elongation effects of the conjugated bonds rather than bond alternation effects. This conclusion is supported by the comparison of the EN and GEO values of the two compounds. The GEO values of both compounds are very small (0.005 for **6** and 0.000 for **7**), while the EN values of these compounds are large (0.280 for **6** and 0.249 for **7**). Therefore, in multiply fused DBAs, the decrease of HOMA values depends more significantly on the elongation effect than on the degree of BLA. Next, HOMA values of the hexakis(phenylethynyl)benzene (**8**) were calculated to elucidate the annulation effects of an antiaromatic 12-membered ring. HOMA, EN, and GEO values of **8** are 0.723, 0.277, and 0.000, respectively, and these values are similar to those of hexakisDBA **7**. These results indicate that the HOMA values of **7** reflect the phenylethynyl substitution effect rather than any paratropicity of the [12]annulene. Therefore, from the structural point of view, the large EN values caused by annulation of antiaromatic 12-membered rings on the central benzene ring of multiply fused DBAs is attributed to bond length elongation due to conjugation with the phenylethynyl groups.

Magnetic Properties. In an aromatic ring, a diatropic ring current arises which causes magnetic shielding at the ring center, whereas in an antiaromatic ring a paratropic ring current results in deshielding at the ring center.[23] NICS values proposed by Schleyer et al. provide a convenient and useful measure of the degree of aromaticity/antiaromaticity of each ring in a system.[18,24]

NICS values of DBAs **1**−**7** calculated at the center of each ring (NICS(0)$_{\text{iso}}$) by the use of the GIAO method at the HF/6-31G*//B3LYP/6-31G* level of theory are depicted in Figure 1.[25] We used NICS(0)$_{\text{iso}}$ in this study as we have previously found these NICS values to be reliable indicators of aromaticity in the DBAs.[8,26] Schleyer et al. recently demonstrated that more sophisticated NICS indices correlated better with aromatic stabilization energies (ASEs) for a series of 75 compounds than did NICS(0)$_{\text{iso}}$, but that NICS(0)$_{\text{iso}}$ gave acceptable agreement with these ASEs.[27] It should be pointed out, however, that for the nonplanar pyracylene in which the 5-membered rings are paratropic NICS(0)$_{\text{iso}}$ indicates a larger degree of aromaticity than NICS(1)$_{\text{out}}$, a NICS value at 1 Å above the molecular plane, which better reflects the magnetic effects of these distorted rings.[28]

The NICS values of DBA **1** indicate that it consists of aromatic six-membered rings (NICS = −10.35) and weakly antiaromatic 12-membered rings (NICS = 2.92).[4a] The NICS value of the benzene rings of **1** is less negative than that of benzene (−11.5), indicating the decrease of the diatropic ring current. This tendency is clearly seen for the fused DBA series. The NICS values at the central benzene rings increase with the increasing number of fused 12-membered rings (Figure 1). As a result, hexakisDBA **7** exhibits the least negative NICS value at the central benzene ring (−6.17). This annulation effect should be contrasted with that of the central benzene ring of hexakis(phenylethynyl)benzene (NICS = −9.86) calculated at the same level of theory. Along with the changes in the magnetic environment of the benzene rings, the paratropic ring current of the 12-membered rings is slightly reduced as the number of fused DBA units increases (2.92 for **1** vs 2.12 for **7**). Even

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(25) ^{1}H NMR chemical shifts of *tert*-butyl-substituted DBA and trisDBA qualitatively agree with theoretical values computed at the HF/6-31G*//B3LYP/6-31G* level of theory (see the Supporting Information). Therefore NICS values obtained at the HF/6-31G*//B3LYP/6-31G* level of theory are employed in the discussion of this paper.

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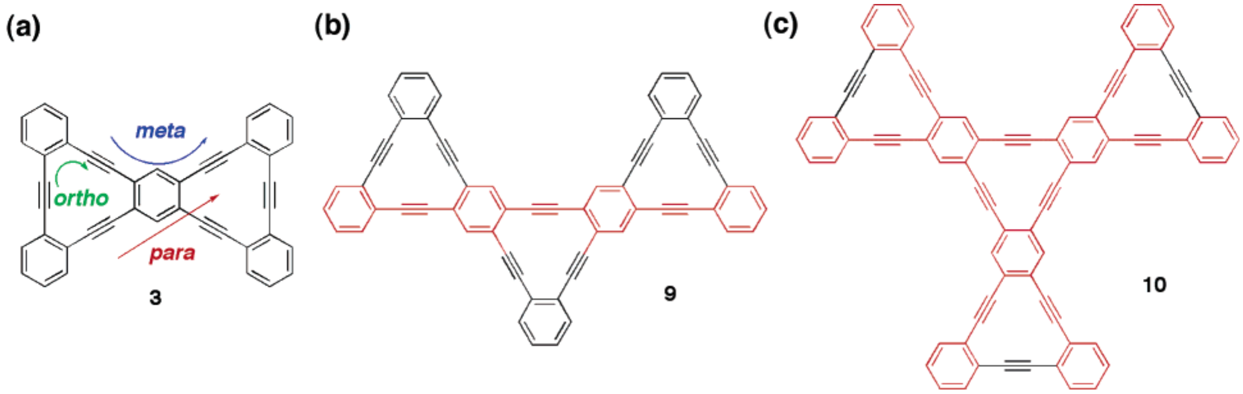

FIGURE 3. (a) Three different conjugation pathways found in bow-tie-shaped **3**. (b) Chemical structures of the linear-shaped trisDBA **9**. (c) Chemical structure of the star-shaped tetrakisDBA **10**. Para-type conjugations are shown in red.

greater changes of ring currents induced by the combination of an aromatic benzene ring and antiaromatic rings have been reported for the cyclobutadienobenzenes and triangular [4]-phenylene,[10,29] in which the diatropic ring current of the central benzene ring is very weak.

We expect that the ring currents in each graphyne substructure would become smaller as the number of accumulated rings increases. Conversely, an opposite tendency was predicted for the magnetic response of polycondensed benzenoids, i.e., graphite substructures: the NICS values of the central benzene ring of large polycondenced benzenoids are known to become more negative with the increasing number of the benzene rings.[30]

HOMO-LUMO Gaps. It has been shown, by consideration of the delocalization index (DI), that electron delocalization between para carbons (rather than ortho or meta) in benzene is most important in determining the aromaticity of the system.[31] Similarly, conjugation in linear phenyleneethynylene systems extends more via the para-substitution mode of a benzene ring than the meta-substitution pattern.[32] Additionally, Haley et al. reported that the ortho-conjugation pathways are less efficient than the para-conjugation pathways in 1,2,4,5-tetrakis(phenylethynyl)benzene derivatives.[33] Moreover, planarization of π-conjugated systems enhances the effectiveness of conjugation.[34] Therefore, it seems reasonable to assume that the electronic properties of multiply fused DBAs **2**−**7** depend on the mode of conjugation. Indeed, the multiply fused DBAs **2**−**7** exhibit different HOMO-LUMO gaps depending on the degree and mode of π-conjugation.

TABLE 2. HOMO-LUMO Gaps (eV) of Multiply Fused DBAs

compd	HOMO-LUMO gaps (eV)
1 ($C_{24}H_{12}$)	3.29
2 ($C_{34}H_{14}$)	3.08
3 ($C_{42}H_{18}$)	2.69
4 ($C_{42}H_{18}$)	2.99
5 ($C_{44}H_{16}$)	3.02
6 ($C_{60}H_{24}$)	2.83
7 ($C_{66}H_{18}$)	2.61
9 ($C_{60}H_{24}$)	2.48
10 ($C_{78}H_{30}$)	2.29
graphyne (MNDO calcn)[a]	1.2

[a] The value reported by Baughman et al. (ref 2a).

The HOMO-LUMO gaps of DBAs **1**−**7** together with those of the larger DBAs **9** and **10** are summarized in Table 2. The HOMO-LUMO gap of the bow-tie-shaped bisDBA **3** (2.69 eV) is notably smaller than those of the rhombic-shaped bisDBA **2** (3.08 eV) and the boomerang-shaped bisDBA **4** (2.99 eV). These values indicate that the conjugation efficiently extends via the *p*-phenyleneethnylene pathway (Figure 3a). The bisDBA **3** has two *p*-bis(phenylethynyl)benzene units and the smallest HOMO-LUMO gap of the three bisDBAs **2**−**4**. Covalent linkage between the two rings of boomerang-shaped bisDBA **4** generates the trapezoid-shaped trisDBA **5**. Both compounds have one bis(phenylethynyl)benzene unit and possess almost the same HOMO-LUMO gap (2.99 eV for **4** and 3.02 eV for **5**). The HOMO-LUMO gap of the trapezoid-shaped trisDBA **5** is larger than that of the bow-tie-shaped bisDBA **3** because of the smaller number of para-conjugation pathways. Surprisingly, the HOMO-LUMO gap of **3** is even smaller than that of the trefoil-shaped trisDBA **6** (2.83 eV) though it comprises three *p*-bis(phenylethynyl)benzene units. This is presumably ascribed to the deviation of the π-system from planarity (vide supra) and the degenerate frontier orbitals of **6** (Figures S3 and S4 in the Supporting Information). Planarization of trefoil-shaped trisDBA **6** by the covalent acetylene linkages generates the wheel-shaped hexakisDBA **7**, which has a relatively small HOMO-LUMO gap (2.61 eV) similar to that of bisDBA **3**. Since the HOMO and LUMO of hexakisDBA **7** is also 2-fold degenerate, we consider that degeneracy plays a significant role in determining the magnitude of the HOMO-LUMO gaps (Figures S3 and S4 in the Supporting Information).

Moreover, by comparison with graphyne (1.2 eV by the semiempirical MNDO method),[2] the HOMO-LUMO gap of the wheel-shaped hexakisDBA **7** (2.6 eV by B3LYP/6-31G* or 6.8

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eV by MNDO for the DFT-optimized structure) still remains large. It is expected that the extension of the multiple DBA systems maximizing the *p*-phenylethnylene conjugation pathways would eventually exhibit a graphyne-like character. Indeed, the HOMO-LUMO gap of the linear-shaped trisDBA **9** having one bis{*p*-(phenylethynyl)phenyl}acetylene unit is considerably reduced (2.48 eV) (Figure 3b). Furthermore, the star-shaped tetrakisDBA **10** with three bis{*p*-(phenylethynyl)phenyl}-acetylene units shows the smallest HOMO-LUMO gap among the DBA series examined (2.29 eV) (Figure 3c). Therefore, it is concluded that the length and the number of *p*-phenylene-ethynylene conjugation in the fused DBA plays the most significant role in determining their electronic properties.

Summary

The geometries of multiply fused DBAs **2**−**7**, **9**, and **10** with various topologies have been optimized at the B3LYP/6-31G* level of theory and the NICS values of **2**−**7** at individual ring centers computed. Due to steric factors, some of these DBAs have nonplanar structures. HOMA analysis at the central benzene ring of multiply fused DBAs **2**−**7** and hexakis-(phenylethynyl)benzene (**8**) showed that an increase in the number of fused 12-annnulene rings causes a decrease in the HOMA values because of the elongation of conjugated bonds. On the basis of structural criteria, it is difficult to elucidate the local aromaticity of these DBAs. NICS calculations reveal that fusion with the antiaromatic 12-membered rings reduces the diatropic ring current at the center of the benzene rings of the multiply fused DBAs. Therefore, from the magnetic criterion, the annelation of the 12-membered rings to benzene clearly reduces the aromatic character of the benzene rings in multiply fused DBAs.

The HOMO-LUMO gaps of the DBAs gradually change depending on the molecular structure. In all geometries, the *p*-phenyleneethynylene conjugation pathways play the most significant role in determining their electronic structure. The present study does not give any direct clue as to the minimum number of DBA units that are required for the molecules to behave as graphyne. The para-type conjugation dominates the electronic properties of multiply fused DBAs rather than meta, ortho, or cyclic conjugation pathways. We consider that these insights are useful to predict the electronic and optical properties of novel graphyne substructures and in the design of organic materials based on these systems.[35]

Acknowledgment. This work was supported by CREST of JST (Japan Science and Technology Agency) and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. K.T. is grateful for a JSPS Research Fellowship for Young Scientists.

Supporting Information Available: Cartesian coordinates of **1**−**10**, HOMA values of all rings of DBAs **1**−**7**, and molecular orbitals and their energies of DBAs **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0622781

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