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Expanded Kekulenes

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ABSTRACT: The synthesis of kekulene and its higher homologues is a challenging task in organic chemistry. The first successful synthesis and characterization of the parent kekulene were reported by Diederich and Staab in 1978. Herein, we report the facile preparation of a series of edge-extended kekulenes by bismuth(III) triflate-catalyzed cyclization of vinyl ethers from the properly designed macrocyclic precursors. Their molecular structures were confirmed by X-ray crystallographic analysis and NMR spectroscopy. Their size- and symmetry-dependent electronic structures (frontier molecular orbitals, aromaticity) and physical properties (optical and electrochemical) were investigated by various spectroscopic measurements, assisted by theoretical calculations. Particularly, the acene-like units along each zigzag edge demonstrate a dominant local aromatic character. Our studies provide an easy synthetic strategy toward various fully fused carbon nanostructures and give some insights into the electronic properties of cycloarenes.



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INTRODUCTION

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According to Staab and Diederich, "cycloarenes" were defined as "polycyclic aromatic compounds in which, by a combination of angular and linear annellations of benzene units, fully annelated macrocyclic systems are present enclosing a cavity into which carbon-hydrogen bonds point".¹ A typical example of this family is a D_{6h} symmetry cycloarene molecule, which was named as "kekulene" in homage to Kekulé (Figure 1).²



Figure 1. From kekulene to core-expanded kekulenes ([m,n]-cycloarenes).

The early interest in cycloarenes was focused on their electronic structure, that is, whether the π -electrons are globally delocalized through the entire molecular skeleton or only delocalized into individual benzene-type rings.³ This question provoked experimental synthesis of cycloarenes, particularly the D_{6h} symmetric kekulene, which turned out to be a very challenging task.⁴ In 1978, Diederich and Staab reported the successful synthesis and structural character-

ization of the parent kekulene.⁵ This work was considered as a milestone in cycloarene chemistry because it not only provided a general synthetic strategy for cycloarenes but also answered the question regarding their electronic structure. X-ray crystallographic analysis and NMR measurements revealed a local aromatic character for the kekulene, which was further confirmed by modern on-surface synthesis and a scanning probe microscopy technique.⁶ In 1986, a contracted cycloarene was synthesized by a similar strategy.⁷ The original synthetic protocol for kekulene involved multistep tedious procedures, and the final product has poor solubility, both limiting the further development of expanded kekulenes. Therefore, chemists started to look for new synthetic methods for cycloarenes.⁸ In 2012, King et al. reported the synthesis of a heptagonal homologue of kekulene, septulene, by intramolecular alkene metathesis.⁹ The molecule shows a similar electronic structure to kekulene, with low solubility. In 2016, Stepień et al. developed a fold-in synthetic strategy and obtained alkoxy chain-substituted kekulene and octulene; both are soluble in common organic solvents.¹⁰ Meanwhile, other related structures such as extended coronoids have been synthesized either in solution or on the surface, which show different electronic properties from the single-chain cycloarenes.¹¹ In 2020, our group developed an efficient synthetic method for aryl-substituted kekulene and octulene through a

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Scheme 1. (a) Synthetic Strategy toward Expanded Kekulenes; (b) Synthesis of the Key Building Blocks; and (c) Synthesis of the Derivatives of Expanded Kekulenes^a



^{*a*}Reagents and conditions: (a) $Pd(PPh_3)_{4^{\prime}}$ K₂CO₃, toluene/ethanol/H₂O, 90 °C; (b) $Pd(OAc)_{2^{\prime}}$ K₂CO₃, DMF/H₂O, 100 °C; (c) B₂pin_{2^{\prime}} [Ir(OMe)cod]_{2^{\prime}} dtbpy, cyclohexane, 80 °C; (d) $Pd_2(dba)_{3^{\prime}}$ DPEphos, K₃PO₄, toluene, reflux; (e) B₂pin₂, Pd(dppf)Cl₂, KOAc, dioxane, 110 °C; (f) $Pd_2(dba)_{3^{\prime}}$ [(^tBu)₃PH]BF₄, NaHCO₃, THF/H₂O, 80 °C; (g) Bi(OTf)₃, 1,2-dichloroethane, 90 °C.

bismuth(III) triflate-catalyzed cyclization of vinyl ethers.¹² The macrocyclic precursors can be easily synthesized, and the $Bi(OTf)_3$ -mediated cyclization is very efficient, which was also demonstrated by other related systems.¹³ We expected that this method could be a suitable approach toward a series of

edge-extended kekulenes (Figure 1), which were only theoretically discussed in the literature but experimentally not available.¹⁴ Different from septulene and octulene, the core-expanded kekulenes discussed here have six zigzag edges like kekulene, but the number of linearly annelated benzenoid



Figure 2. X-ray crystallographic structures of [3,4]CA-1. (a, b) Top view of the whole molecule and side view of the backbone; (c, d) overlap and close contacts of two neighboring molecules and 3D packing structures; (e) selected bond lengths (in Å) from the X-ray structures.

rings increases. According to the nomenclature proposed by Bergan et al.,¹⁵ they can be called [m,n] cycloarenes, where m and n represent the number of annelated benzenoid rings on the two types of zigzag edges, respectively (Figure 1). In this article, we will report the synthesis and structural characterization of their derivatives. Their size- and symmetry-dependent electronic structures and physical properties will also be discussed.

RESULTS AND DISCUSSION

Synthesis. The general synthetic strategy toward these core-expanded kekulenes is shown in Scheme 1a. The macrocyclic precursors (F) with different size arene units and six vinyl ether groups can be synthesized by a Suzuki coupling reaction between the building blocks A/B carrying two bromine or triflate (OTf) groups and the building blocks C/D/E carrying two pinacol borate (Bpin) groups. Then, Bi(OTf)₃-catalyzed cyclization of vinyl ethers is supposed to give the desired cycloarenes (G) with either 3- or 6-fold symmetry. The building blocks A and C were prepared through a similar synthetic route previously reported by us (Scheme 1b).¹² Building block B, which contains a naphthalene unit, was synthesized by Suzuki coupling between 1^{16} and 2 (Scheme 1b). The second naphthalene-based building block D was prepared by Suzuki coupling reaction between 3 and 4, followed by Ir-catalyzed regioselective C-H borylation. Similarly, the anthracene-based building block E was obtained by Suzuki coupling between 6 and 7 followed by regioselective Ir-catalyzed C-H borylation. The structure of E was unambiguously confirmed by X-ray crystallographic analysis.¹⁷ Then, three types of macrocyclic oligo(m-arylene)intermediates were synthesized by combinational Suzuki

coupling reactions between these building blocks under a catalytic condition involving $Pd_2(dba)_{3}$, $[(t-Bu)_3PH]BF_4$, and aqueous NaHCO₃ (Scheme 1c). In the initial test, the expanded [3,4]cycloarene derivatives [3,4]CA-1 and [3,4]CA-2 with either 4-*tert*-butyphenyl or mesityl substituents at different positions were prepared. Reactions between A and D gave the intermediate 10 in 30% isolated yield, and subsequent Bi(OTf)₃-catalyzed cyclization in 1,2-dichloroethane at 90 °C afforded [3,4]CA-1 as a yellow solid in 53% yield. On the other hand, Suzuki couplings between B and C (in 15% yield) followed by Bi(OTf)₃-catalyzed cyclization (in 35% yield) gave [3,4]CA-2. Next, the further expanded [4,4]cycloarene derivative [4,4]CA was synthesized as an orange solid by a similar strategy starting from building blocks **B** and **D** in an overall 10.2% (15% \times 68%) yield. The cycloarenes [3,5]CA and [4,5]CA, containing five linearly annelated benzenoid rings, were obtained starting from building blocks A/E and B/E in an overall 5.8% and 3.8% yield, respectively. It is worth noting that in both cases the reactions at the second step should be conducted in the dark since the final products are light sensitive (vide infra).

Ground-State Geometry. Single crystals of [3,4]CA-1 were grown by slow diffusion of methanol into its solution in tetrahydrofuran (THF).¹⁷ X-ray crystallographic analysis reveals a slightly distorted backbone in the solid state (Figure 2a,b), which could be due to the strain induced by the repulsion between the two neighboring aryl substituents. The molecules are packed into a slipped 1D chain with regular dislocation between the adjacent molecules due to intermolecular steric repulsion between the aryl substituents (Figure 2c,d). Close $\pi-\pi$ contacts with distances of 3.31 and 3.25 Å are found. Bond length analysis shows that the bond lengths of



Figure 3. Selected bond lengths (in Å) from the optimized structures, calculated NICS(1)_{zz} values (the numbers in blue and pink color): (a) [3,3]CA, (b) [3,4]CA-1, (c) [3,4]CA-2, (d) [4,4]CA, (e) [3,5]CA, (f) [4,5]CA. All substituents are omitted for clarity.

the six nearly equivalent bonds *a* along the outer periphery are around 1.32-1.34 Å, close to that for typical olefins (~1.35 Å) (Figure 2e). The CC bonds *b*, *k* linking these "double bonds" are much longer (1.44–1.46 Å), implying a typical C(sp²)– C(sp²) single-bond character. Additionally, the CC bonds *c*, *d*, *e*, *f*, *g*, *h* along ring A and the neighboring ring B had typical bond lengths (1.37–1.44 Å) similar to that of an aromatic naphthalene ring, whereas the bond lengths in ring C (1.38– 1.43 Å) are close to that of an aromatic benzene ring. In addition, the bonds *i* and *l* linking these benzenoid rings (1.46–1.47 Å) also exhibit typical C(sp²)–C(sp²) single-bond character. All these suggest that [**3**,**4**]CA-**1** has a dominant local aromatic character with electrons on the backbone mainly delocalized in three benzene rings and three naphthalene rings.

The geometries of all five molecules were optimized by density functional theory (DFT) at the B3LYP/6-31G(d,p) level of theory and compared with [3,3]CA (Figure 3 and Figure S32 in the Supporting Information (SI)). The calculations indicate that [3,4]CA-2, [3,5]CA, and [4,5]CA possess an almost planar backbone, while [3,4]CA-1 and [4,4]CA have a slightly distorted backbone due to the steric repulsion between the two neighoring 4-tert-butylphenyl substituents. The calculated bond lengths show that all the fused CC bonds from the vinyl ethers are close to 1.36 Å and similar to the typical olefins, and the bond lengths of center benzene/naphthalene/anthracene units along each zigzag edge resemble that of the respective aromatic rings. Therefore, the π -electrons are mainly delocalized into the central individual benzene, naphthalene, and anthracene rings rather than globally delocalized.

Electronic Structure and Aromaticity. The ¹H NMR spectra show that both the inner- and outer-rim protons of the five cycloarenes are deshielded and their resonances appear in the low field (Figure 4a). All the NMR peaks were assigned by 2D ROESY and NOESY NMR techniques and gaugeindependent atomic orbital (GIAO) calculations (see Supporting Information). The ¹H NMR spectra of [3,4]CA-1 and [3,4]CA-2 that share the same backbone are similar to each other. The inner protons of these two molecules are further shifted to low field compared to those of [3,3]CA, presumably owing to the additional deshielding effect from the naphthalene ring which has one extra benzenoid ring. The further expanded kekulene [4,4]CA can be regarded as a super-kekulene. It exhibits certain aggregation in common organic solvents, and its ¹H NMR signals in CDCl₂CDCl₂ are broadened at room temperature, while heating leads to sharpening of the peaks (Figures S5 and S6 in SI). The resonances are also slightly shifted to higher field when the concentration is increased (Figure S7 in SI). When the sample was heated to 363 K, the resonances for the inner-rim protons a and b split into two peaks (Figure 4a). However, all of the respective protons from [4,4]CA appear at higher field as compared to [3,3]CA, [3,4]CA-1, and [3,4]CA-2. As to [3,5]CA, the constitutional isomer of [4,4]CA, the inner-rim protons (a-c) are deshielded into lower field, indicating a different π -conjugation throughout the backbone. For [4,5]CA, whose edges possess one extra benzenoid ring as compared to [3,5]CA, the inner-rim protons (a-c) are less deshielded.



.0 11.8 11.6 11.4 11.2 11.0 10.8 10.6 10.4 10.2 10.0 9.8 9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 chemical shift (ppm)



Figure 4. (a) ¹H NMR spectra (aromatic region) of the five cycloarenes ([3,4]CA-1 in CD_2Cl_2 , others in $CDCl_2CDCl_2$). The resonance assignment refers to the structure and labeling in Scheme 1. Calculated ACID plots of (b) [3,4]CA-1, (c) [4,4]CA, (d) [3,5]CA, and (e) [4,5]CA with an isovalue of 0.02; the arrows indicate the ring current flow.



Figure 5. (a) Calculated 2D ICSS_{zz} (top) and 3D ICSS (bottom) maps: (a and e) for [3,4]CA-1; (b and f) for [4,4]CA; (c and g) for [3,5]CA; (d and h) for [4,5]CA. The isovalue of 3D ICSS is 4.

In order to further understand the electronic structures and magnetic shielding response of these cycloarenes, nucleusindependent chemical shift (NICS) (Figure 3), anisotropy of the induced current density (ACID) (Figure 4b–e), and 2D/ 3D isochemical shielding surface (ICSS) calculations (Figure 5 and Figure S48 in SI) were conducted. Generally, the calculated $NICS(1)_{zz}$ values (the numbers in pink color) for the hexagons fused from vinyl ethers are much less negative compared to those for the benzenoid rings between them (numbers in blue color), indicating that they are only weakly

aromatic. ACID maps also show clockwise (diatropic) ring current circuits for those aromatic units. Nevertheless, weak ring current flow over the CC double bonds at each corner is also observed in all cases (see additional ACID maps with different isovalues in Figures S43–S47 in SI), implying that the π -electrons are also globally delocalized along the periphery to some extent. The calculated 2D ICSS maps show a magnetically deshielded chemical environment (negative values) in the inner cavity and outside the periphery (Figure 5a). Three-dimensional ICSS maps reveal that the shielding spheres mainly locate on the backbone of these expanded kekulenes (Figure 5b). All these computational results together with the experimental data suggest a dominant local aromatic character, with π -electrons mainly confined in the individual benzene/naphthalene/anthracene rings.

It is also found that the π -electron delocalization and aromatic character vary slightly depending on the size and symmetry, which is reflected by the different calculated magnetic shielding tensor quantities and the experimentally observed NMR chemical shifts. For example, the $NICS(1)_{zz}$ value for the fused rings from vinyl ethers in [4,4]CA (-5.3 ppm) is less negative in comparison to [3,4]CA-1/[3,4]CA-2 (ca. -8 ppm) and [3,3]CA (-14 ppm) (Figure 3), indicating a weaker π -conjugation between the neighboring arms. Twodimensional ICSS maps also clearly reveal a less deshielded cavity in [4,4]CA than that of [3,4]CA-1/[3,4]CA-2 (Figure 5a), which well explains the observed high-field shift of the resonances for the inner-rim protons in the NMR spectrum of [4,4]CA (Figure 4a). Moving on to the [4,5]CA, the coupling becomes even weaker, as indicated by the near-zero $NICS(1)_{zz}$ values (ca. -2.5 ppm) for the bridging hexagons (Figure 3f) and nearly broken ring current flow across the CC double bond at the corner (Figure 4e). The π -electron delocalization in [3,5]CA lies in between [3,4]CA-1/[3,4]CA-2 and [4,5]CA as inferred from the calculated NICS(1)₇₇ values (ca. -7.0 ppm) of the bridging hexagons and the magnetic shielding response in the cavity. As a consequence, the chemical shifts for the inner-rim protons also locate in between (Figure 4a). The trend observed in this series of expanded kekulenes is consistent with the calculated NMR data (Figures S49-S54 in SI).

Optical and Electrochemical Properties. All these expanded kekulene compounds together with the kekulene derivative [3,3]CA display well-resolved absorption spectra in solution (Figure 6a, and the data are collected in Table 1). The absorption maxima (λ_{abs}) of [3,4]CA-1 and [3,4]CA-2 are redshifted to 352 and 349 nm, respectively, compared with that of [3,3]CA (λ_{abs} = 327 nm), which can be explained by the extended π -conjugation. In addition, several weak shoulder peaks at the 400-500 nm region are found for both, which can be assigned to a combination of multiple HOMO- $n \rightarrow$ LUMO+m (n,m = 0-2) electronic transitions according to the time-dependent (TD) DFT calculations (see SI). It is worth noting that these peaks are much stronger than the corresponding peaks in [3,3]CA. Such change can be explained by the decreased symmetry in the D_{3h} symmetric [3,4] cycloarene backbone in comparison to the D_{6h} symmetry kekulene. Calculations also show that the frontier HOMO and LUMO coefficients of [3,4]CA-1 and [3,4]CA-2 are primarily distributed along the edges with four annelated benzenoid rings somewhat similar to the tetracene, while the HOMO and LUMO in [3,3]CA are delocalized along the whole backbone (Figure 7a,b). The absorption maximum of [4,4]CA was



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Figure 6. (a) UV-vis absorption and (b) normalized fluorescence spectra of [3,3]CA and the five cycloarenes measured in THF (1 × 10^{-5} M) (except that [4,4]CA was measured in tetrachloroethane) at room temperature. Inset in (a) shows the magnified spectra at the long-wavelength region, and that in (b) displays the photos of five cycloarenes under UV lamp irradiation (from left to right: [3,4]CA-1, [3,4]CA-2, [4,4]CA, [3,5]CA, and [4,5]CA).

further shifted to 390 nm. The spectral structure resembles that of [3,3]CA due to a similar 6-fold symmetry of the backbone, with very weak shoulder bands beyond 500 nm. It shows two nearly degenerated HOMOs and LUMOs, with coefficients distributed at half of the molecule (Figure 7c). [3,5]CA shares the same number of benzenoid rings in the backbone as [4,4]CA but shows a quite different absorption spectrum (Figure 7a). In addition to the major absorption at 375 nm, several vibrational peaks are clearly observed in the 450-600 nm region, with maxima at 482, 517, and 553 nm. The band structure at this fingerprint region resembles the absorption spectrum of pentacene.¹⁸ [3,5]CA also shows two nearly degenerated HOMOs and LUMOs, with coefficients distributed at half of the molecule. The profile at each edge with five fused benzenoid rings is similar to that of the pentacene (Figure 7d), which is consistent with the observed pentacene-like band structure at the low-energy edge.¹⁹ According to TD-DFT calculations, this weak band is originated from the HOMO/HOMO-1 \rightarrow LUMO/LUMO +1 electronic transitions (see SI). Compound [3,5]CA in THF was much more stable when kept in the dark, but it slowly decomposed under the ambient light irradiation in air with a half-life of around 8 h, as monitored by the UV-vis spectrometry (Figures S17, S18, S21, and S22 in SI). Compound [4,5]CA exhibits a maximum absorption at 408 nm and a long tail with two weak shoulder peaks at 495 and 519 nm. The HOMO and LUMO coefficients are mainly distributed among the three pentacene-like arms (Figure 7e).

	$\lambda_{abs} [nm]^a$	$\lambda_{\text{onset}} [\text{nm}]^{b}$	$E_{g}^{opt}[eV]^{b}$	$\lambda_{\rm em} [{\rm nm}]^a$	LUMO [eV] ^c	HOMO [eV] ^c	$E_{\rm g}^{\rm \ cal} [{\rm eV}]^c$	$\Phi_{\rm F}$	$\tau_{\rm F}({\rm ns})^d$
[3,3]CA	327	406	3.05	460	-1.68	-5.18	3.50	4.6%	23
[3,4]CA-1	352	496	2.50	554	-2.16	-4.68	2.52	11%	17
[3,4]CA-2	349	484	2.56	538	-2.25	-4.84	2.59	8%	20.5
[4,4]CA ^b	390	480	2.58	534	-1.94	-4.92	2.98	5.5%	29.1
[3,5]CA	375	568	2.18	561/619	-2.41	-4.68	2.27	5.5%	9.0
[4,5]CA	408	524	2.37	559	-2.40	-4.70	2.30	4.0%	16.5

Table 1. Photophysical Properties and Energy Levels of the Cycloarenes

 ${}^{a}\lambda_{abs}$ and λ_{em} were measured in THF (1.0 × 10⁻⁵ M); [4,4]CA in tetrachloroethane (1.0 × 10⁻⁵ M). ^bObtained from the edge of the absorption spectra according to $E_{g}^{opt} = (1240/\lambda_{onset})$. ^cCalculated at the B3LYP/6-31G(d,p) level. ^dFluorescence lifetimes of [3,3]CA ($\lambda_{exc} = 340$ nm, $\lambda_{probe} = 460$ nm) and the five cycloarenes ($\lambda_{exc} = 365$ nm, $\lambda_{probe} = 553$, 554, 534, 561, and 559 nm, respectively).



Figure 7. (a) Calculated frontier molecular orbital profiles of the cycloarenes: (a) [3,3]CA, (b) [3,4]CA-1, (c) [4,4]CA, (d) [3,5]CA, and (e) [4,5]CA.

The weak long-wavelength absorption band is originated from a combination of HOMO- $n \rightarrow LUMO+m$ (n,m = 0, 1, 2) electronic transitions according to the TD-DFT calculations (see SI). Compound [4,5]CA in THF was also stable in the dark, and it underwent slow decomposition under the ambient air and light conditions, with a half-life of about 30 h (Figures S19–S21 and S23 in SI). From the mass spectra (Figures S25 and S26 in SI), photochemical oxygenation reactions occur when solutions of [3,5]CA and [4,5]CA were exposed to air and ambient light over the time and followed the first-order kinetic reaction process (Figures S22 and S23).²⁰ Among all six compounds, [3,5]CA has the lowest optical energy gap (2.18 eV) as roughly estimated from the onset of the lowest energy absorption, which is also in agreement with the calculated HOMO-LUMO energy gaps (Table 1).

The fluorescence (FL) spectra of the five cycloarenes are all red-shifted compared to that of [3,3]CA, attributed to their extended conjugated structures (Figure 6b). [3,4]CA-1 and [3,4]CA-2 show the maximum emission (λ_{em}) peaks at 554 and 538 nm, respectively. [3,3]CA and [4,4]CA display similar well-resolved emission spectra, probably originating from their similar symmetry. Due to extended π -conjugation, the emission maximum of [4,4]CA is red-shifted to 534 nm as compared to [3,3]CA (λ_{em} = 460 nm). [3,5]CA exhibits two major emission peaks at 561 and 619 nm, while [4,5]CA displays an emission maximum at 559 nm. The absolute fluorescence quantum yields of [3,3]CA, [3,4]CA-1, [3,4]CA-2, [4,4]CA, [3,5]CA, and [4,5]CA in solution were determined to be 4.6%, 11.0%, 8.0%, 5.5%, 5.5%, and 4.0%, respectively, by using the integrating sphere technique (Table 1). The relatively low quantum yields may be related to their generally weak absorption in the lower energy region. In addition, their corresponding fluorescence lifetimes (τ) were measured as

23.0, 17.0, 20.5, 29.1, 9.0, and 16.5 ns, respectively (Table 1, Figure S24 in SI). Cyclic voltammetry measurements of the five expanded kekulenes in chlorobenzene generally revealed multiple irreversible redox waves (Figures S27–S31 in SI), which can be distinguished by differential pulse voltammetry. [3,4]CA-1 and [3,4]CA-2 exhibit three similar oxidation peaks with half-wave potentials ($E_{1/2}^{\text{ox}}$) at 1.0/1.28/1.76 V and 1.04/ 1.27/1.78 V (vs Fc⁺/Fc), respectively. [4,4]CA shows just one apparent oxidation wave with $E_{1/2}^{\text{ox}}$ at around 0.9 V due to the aggregation in solution. [3,5]CA also shows three oxidation peaks with $E_{1/2}^{\text{ox}}$ at around 0.83, 0.99, and 1.33 V, whereas [4,5]CA displays only one broad oxidation peak with $E_{1/2}^{\text{ox}}$ at around 0.98 V owing to its low solubility.

CONCLUSION

In summary, five expanded kekulene molecules were synthesized by a facile strategy involving macrocyclization by the Suzuki coupling reaction followed by $Bi(OTf)_3$ -catalyzed cyclization of vinyl ethers. Similar to the kekulene, the π -electrons in these skeletons are mainly delocalized into the individual benzene/naphthalene/anthracene units at the center of each arm. They display size- and symmetry-dependent electronic properties, which are reflected from their electronic absorption spectra, fluorescence spectra, and NMR chemical shift. With extension of the zigzag edges, the molecules show an acene-like electronic structure and become more reactive, implying the challenge to synthesize even more extended kekulenes. The method could be applicable for the synthesis of other belt-shaped molecules or large-size hexagonal nano-graphenes, and related works are ongoing in our group.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c06757.

Synthetic procedures and characterization data, additional spectra, X-ray crystallographic data, and DFT calculations details (PDF)

Accession Codes

CCDC 2081432–2081433 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Staab, H. A.; Diederich, F. Cycloarenes, A New Class of Aromatic Compounds, I. Synthesis of Kekulene. *Chem. Ber.* **1983**, *116*, 3487. (b) Staab, H. A.; Diederich, F.; Krieger, C.; Schweitzer, D. Cycloarenes, a New Class of Aromatic Compounds, II. Molecular Structure and Spectroscopic Properties of Kekulene. *Chem. Ber.* **1983**, *116*, 3504.

(2) Staab, H. A. Plenary Lecture at the Annual Meeting, Gesellschaft Deutscher Chemiker (Kekulé Centennial) in Bonn on 14.9.1965

(3) McWeeny, R. The Diamagnetic Anisotropy of Large Aromatic Systems: III Structures with Hexagonal Symmetry. R. *Proc. Phys. Soc., London, Sect. A* **1951**, *64*, 921.

(4) Vögtle, F.; Staab, H. A. Zur Konjugation in makrocyclischen Bindungssystemen, XII. Versuche zur Darstellung des Cyclo-[*d.e.d.e.d.e.d.e.d.e.*]dodecakisbenzens. Eine neue Synthese von 1.2;7.8-Dibenzo-anthracenen. *Chem. Ber.* **1968**, *101*, 2709. (5) Diederich, F.; Staab, H. A. Benzenoid *versus* Annulenoid Aromaticity: Synthesis and Properties of Kekulene. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 372.

(6) (a) Pozo, I.; Majzik, Z.; Pavliček, N.; Melle-Franco, M.; Guitián, E.; Peña, D.; Gross, L.; Pérez, D. Revisiting Kekulene: Synthesis and Single-Molecule Imaging. J. Am. Chem. Soc. 2019, 141, 15488.
(b) Haags, A.; Reichmann, A.; Fan, Q.; Egger, L.; Kirschner, H.; Naumann, T.; Werner, S.; Vollgraff, T.; Sundermeyer, J.; Eschmann, L.; Yang, X.; Brandstetter, D.; Bocquet, F. C.; Koller, G.; Gottwald, A.; Richter, M.; Ramsey, M. G.; Rohlfing, M.; Puschnig, P.; Gottfried, J. M.; Soubatch, S.; Tautz, F. S. Kekulene: On-Surface Synthesis, Orbital Structure, and Aromatic Stabilization. ACS Nano 2020, 14, 15766.

(7) Funhoff, D. J. H.; Staab, A. Cyclo[*d.e.d.e.e.d.e.e.*]-decakisbenzene, a New Cycloarene. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 742.

(8) (a) Buttrick, J. C.; King, B. T. Kekulenes, Cycloarenes, and Heterocycloarenes: Addressing Electronic Structure and Aromaticity Through Experiments and Calculations. *Chem. Soc. Rev.* 2017, 46, 7.
(b) Majewski, M. A.; Stępień, M. Bowls, Hoops, and Saddles: Synthetic Approaches to Curved Aromatic Molecules. *Angew. Chem., Int. Ed.* 2019, 58, 86.

(9) Kumar, B.; Viboh, R. L.; Bonifacio, M. C.; Thompson, W. B.; Buttrick, J. C.; Westlake, B. C.; Kim, M.; Zoellner, R. W.; Varganov, S. A.; Mörschel, P.; Teteruk, J.; Schmidt, M. U.; King, B. T. Septulene: The Heptagonal Homologue of Kekulene. *Angew. Chem., Int. Ed.* **2012**, *51*, 12795.

(10) Majewski, M. A.; Hong, Y.; Lis, T.; Gregoliński, J.; Chmielewski, P. J.; Cybińska, J.; Kim, D.; Stępień, M. Octulene: A Hyperbolic Molecular Belt that Binds Chloride Anions. *Angew. Chem., Int. Ed.* **2016**, *55*, 14072.

(11) (a) Beser, U.; Kastler, M.; Maghsoumi, A.; Wagner, M.; Castiglioni, C.; Tommasini, M.; Narita, A.; Feng, X.; Müllen, K. A C216-Nanographene Molecule with Defined Cavity as Extended Coronoid. J. Am. Chem. Soc. 2016, 138, 4322. (b) Hou, I. C.; Sun, Q.; Eimre, K.; Giovannantonio, M. D.; Urgel, J. I.; Ruffieux, P.; Narita, A.; Fasel, R.; Müllen, K. On-Surface Synthesis of Unsaturated Carbon Nanostructures with Regularly Fused Pentagon-Heptagon Pairs. J. Am. Chem. Soc. 2020, 142, 10291. (c) Giovannantonio, M. D.; Yao, X.; Eimre, K.; Urgel, J. I.; Ruffieux, P.; Pignedoli, C. A.; Müllen, K.; Fasel, R.; Narita, A. Large-Cavity Coronoids with Different Inner and Outer Edge Structures. J. Am. Chem. Soc. 2020, 142, 12046. (d) Fan, Q.; Martin-Jimenez, D.; Werner, S.; Ebeling, D.; Koehler, T.; Vollgraff, T.; Sundermeyer, J.; Hieringer, W.; Schirmeisen, A.; Gottfried, J. M. On-Surface Synthesis and Characterization of a Cycloarene: C108 Graphene Ring. J. Am. Chem. Soc. 2020, 142, 894. (e) Hou, H.; Zhao, X.; Tang, C.; Ju, Y.; Deng, Z.; Wang, X.; Feng, L.; Lin, D.; Hou, X.; Narita, A.; Müllen, K.; Tan, Y. Synthesis and assembly of extended quintulene. Nat. Commun. 2020, 11, 3976.

(12) Fan, W.; Han, Y.; Dong, S.; Li, G.; Lu, X.; Wu, J. Facile Synthesis of Aryl-Substituted Cycloarenes via Bismuth(III) Triflate-Catalyzed Cyclization of Vinyl Ethers. *CCS Chem.* **2021**, *2*, 1445.

(13) (a) Yang, L.; Zhang, N.; Han, Y.; Zou, Y.; Qiao, Y.; Chang, D.; Zhao, Y.; Lu, X.; Wu, J.; Liu, Y. A sulfur-containing hetero-octulene: synthesis, host-guest properties, and transistor applications. *Chem. Commun.* **2020**, *56*, 9990. (b) Su, J.; Fan, W.; Mutombo, P.; Peng, X.; Song, S.; Ondráček, M.; Golub, P.; Brabec, J.; Veis, L.; Telychko, M.; Jelínek, P.; Wu, J.; Lu, J. On-Surface Synthesis and Characterization of [7]Triangulene Quantum Ring. *Nano Lett.* **2021**, *21*, 861.

(14) (a) Aihara, J.; Makino, M. Constrained Clar Formulas of Coronoid Hydrocarbons. J. Phys. Chem. A 2014, 118, 1258.
(b) Aihara, J.; Makino, M.; Ishida, T.; Dias, J. R. Analytical Study of Superaromaticity in Cycloarenes and Related Coronoid Hydrocarbons. J. Phys. Chem. A 2013, 117, 4688. (c) Miyoshi, H.; Nobusue, S.; Shimizu, A.; Tobe, Y. Non-alternant non-benzenoid kekulenes: the birth of a new kekulene family. Chem. Soc. Rev. 2015, 44, 6560.

(15) Bergan, J. L.; Cyvin, S. J.; Cyvini, B. N. Number of kekulé structures of single-chain corona-condensed benzenoids (cyclo-arenes). *Chem. Phys. Lett.* **1986**, *125*, 218.

(16) Hindenberg, P.; Busch, M.; Paul, A.; Bernhardt, M.; Gemessy, P.; Rominger, F.; Romero-Nieto, C. Diphosphahexaarenes as Highly Fluorescent and Stable Materials. *Angew. Chem., Int. Ed.* **2018**, *57*, 15157.

(17) Crystallographic data with CCDC number 2081432 (for E) and 2081433 (for [3,4]CA-1) are deposited in the Cambridge Crystallographic Data Center.

(18) (a) Kawanaka, Y.; Shimizu, A.; Shinada, T.; Tanaka, R.; Teki, Y. Using Stable Radicals To Protect Pentacene Derivatives from Photodegradation. Angew. Chem., Int. Ed. 2013, 52, 6643.
(b) Holec, J.; Cogliati, B.; Lawrence, J.; Berdonces-Layunta, A.; Herrero, P.; Nagata, Y.; Banasiewicz, M.; Kozankiewicz, B.; Corso, M.; Oteyza, de D. G.; Jancarik, A.; Gourdon, A. A Large Starphene Comprising Pentacene Branches. Angew. Chem., Int. Ed. 2021, 60, 7752.

(19) Lijina, M. P.; Benny, A.; Ramakrishnan, R.; Nair, N. G.; Hairharan, M. Exciton Isolation in Cross-Pentacene Architecture. J. Am. Chem. Soc. **2020**, 142, 17393.

(20) (a) Omoto, K.; Tashiro, S.; Shionoya, M. Phase-Dependent Reactivity and Host-Guest Behaviors of a Metallo-Macrocycle in Liquid and Solid-State Photosensitized Oxygenation Reactions. J. Am. Chem. Soc. 2021, 143, 5406. (b) Bedi, A.; Manor, A.; Gidron, O. Effect of Twisting on the Capture and Release of Singlet Oxygen by Tethered Twisted Acenes. Org. Lett. 2020, 22, 7809.