Angewandte
International Edition Chemie

DOI: 10.1002/anie.201203266

Kekulene

Septulene: The Heptagonal Homologue of Kekulene[**]

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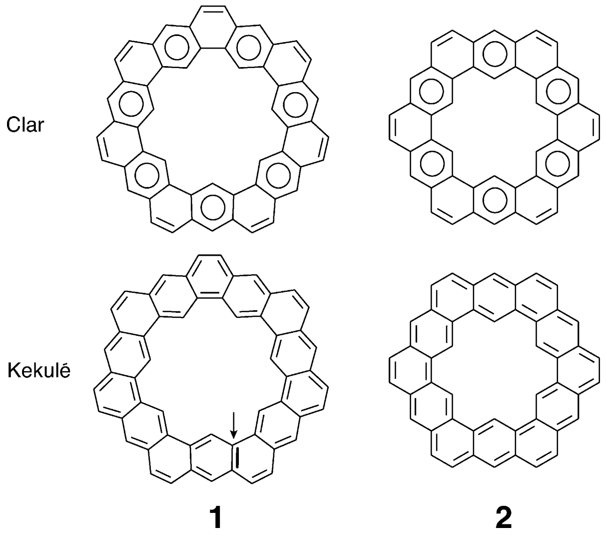
Dedicated to Professor Robert G. Bergman on the occasion of his 70th birthday

Staab and Diederich defined cycloarenes as comprising annelated benzene rings that form a macrocycle with inward-pointing C–H bonds.[1] Their synthesis and characterization of kekulene, the prototypical cycloarene,[1–4] answered a long-standing and fundamental question about arenes and the nature of aromaticity: do π electrons move throughout the entire system, as hypothesized by Pauling,[5] or do they remain localized in rings, as predicted by McWheeny[6] and described phenomenologically by Clar.[7] The chemical shift of the inner protons of **2** gave the answer. Pauling's model suggested that kekulene **2** should behave as concentric annulenes (Scheme 1 bottom right), and that the inner protons ought to be strongly shielded, as in [18]annulene.[8] The localized model, as embodied by Clar's aromatic sextets, suggests that the ring currents arise from localized rings (Figure 1 top right), and that the inner protons should be deshielded, as in benzene. Experiments showed that the inner protons are deshielded and resonate at $\delta > 7$ ppm. This deshielding demonstrates that electrons do not move freely about the entire molecule, but are instead localized into individual rings, just as in benzene.

We report the synthesis and properties of kekulene's seven-sided cousin septulene (**1**), and find that its properties reinforce the conclusions above and open some new questions.



Scheme 1. Septulene **1** and kekulene **2**. The unique radial double bond in the Kekulé structure of **1** is indicated.

The properties of **1** are strikingly similar to those of **2**, even though their Kekulé structures (Scheme 1 bottom) are fundamentally different. This difference arises from the odd number of C atoms in both the inner and outer annuli of **1**, which necessitates a radial double bond in the Kekulé structure. It also follows that **1** is non-alternant. The remarkable similarity between **1** and **2**, despite their fundamentally different Kekulé structures, dispels the notion that a consideration of a few Kekulé structures provides much insight into the chemistry of condensed arenes.[9]

The only previously known cycloarenes were **2** and its hexaaza analogue.[10] Some computational[11] and synthetic studies[12] towards **1** have appeared in dissertations, but otherwise **1** appears to have escaped attention.

The scarcity of known cycloarenes is offset by the abundance of schemes for their nomenclature. The current schemes either assume a graphene lattice, which excludes **1**, or fail to convey the structure of the molecule. We agree with the assertion by Staab and Diederich that, "The naming of (**2**) as a polycyclic system according to the IUPAC rules on nomenclature leads to an extraordinarily complicated name which does not give any direct information about the structure and symmetry of the molecule".[1] We propose the following solution: To handle the general case of cycloarenes, we adopt the corannulene nomenclature developed by Agranat et al.,[13] in which the name for kekulene (**2**) is

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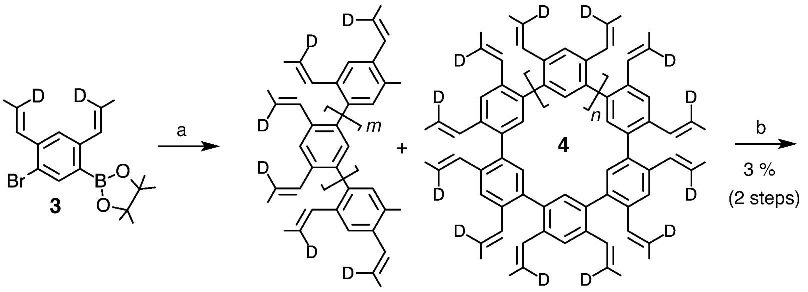
[**] This work was supported by the US-NSF (CHE-0957702). We thank Dr. S. M. Spain and Dr. J. L. Dallas (NSF DBI-0722538) for assistance with spectroscopy, and Profs. A. D. Schlüter, K. K. Baldridge, and H. B. Bürgi for useful suggestions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201203266.

corannulene [6^2,6^1,6^2,6^1,6^2,6^1,6^2,6^1,6^2,6^1,6^2,6^1], where the superscript numbers designate the number of carbon atoms of the small ring that are on the periphery of the molecule and are not shared by any other small rings. In this case, all the small rings are six-membered, hence the twelve sixes. The numbering of the small rings begins with the ring that contains the carbon atom that is designated C1 when the molecule is drawn in standard orientation.[14] Although not given by Agranat et al., the trivial systematic name for **2** may be abbreviated as "corannulene[(6^2,6^1)$_6$]", where the subscript six clearly indicates the sixfold repeat unit. Thus, **1** becomes "corannulene[(6^2,6^1)$_7$]", with the sevenfold repeat unit clearly indicated.

The key to our synthesis of **1** was to introduce seven olefinic phenanthrene bridges onto the cyclohepta-*m*-phenylene framework (Scheme 2) by ring-closing metathesis (RCM) of pendant olefins.[15–17] The cyclohepta-*m*-phenylene was produced in low yield as a by-product in the polymerization of monomer **3**, which was designed to have two features that would simplify the analysis and handling: 1) Methyl groups help suppress the spontaneous vinylic polymerization and cross-linking that plagued the simple vinyl system, and 2) deuterium provided a spectroscopic handle for the RCM reaction: the disappearance of the C–D stretch in the infrared spectrum enabled the course of the RCM to be monitored in the complicated mixture.



Scheme 2. a) [Pd{P(*p*-tol)$_3$}$_3$], K_2CO_3,THF/H_2O, b) Grubbs 2nd generation catalyst, 1,2,4-trichlorobenzene, toluene, 70 °C (**4**, $n = 2$).

Monomer **3** was synthesized in five steps on 25 g scale (see the Supporting Information). Deuterium was introduced at the β-vinyl positions using the Wittig reagent derived from the deuterated salt $CH_3CD_2PPh_3Br$, which was easily prepared at low cost.[18]

The polymerization of **3** under standard Suzuki conditions[19–21] gave a mixture of polymers typically having about 100 repeat units and a polydispersity index (PDI) of 1.98, as determined by gel-permeation chromatography versus polystyrene standards. MALDI-TOF analysis suggested that some macrocycles were also present. By performing the polymerization under dilute conditions, we were able to increase the fraction of macrocycles formed. Although the cyclohexameric precursor to kekulene (**2**) could be detected by mass spectrometry, the cycloheptameric precursor (**4**) to septulene was the dominant product. The reason for the preferential formation of heptamer **4** over the hexamer is unclear.

Simple purification through silica gel gave a mixture of open-chain polymers and cyclic oligomers. This unfractionated polycondensation product[22] was treated with the metathesis catalyst. By monitoring the disappearance of the C–D stretch in the IR spectrum, we optimized the RCM reaction to push it to near completion.[23] Septulene (**1**) crystallized from THF during workup and was purified by HPLC.

Similar to **2**, **1** is also insoluble in common organic solvents. It dissolves slightly in 1,2-dichlorobenzene and 1,2,4-trichlorobenzene (ca. 1 mg/20 mL at 100 °C). The melting point of **1** is >500 °C. This behavior is similar to that of **2**. Septulene (**1**) is stable, and no decomposition was observed when stored at room temperature under air for several months. Septulene (**1**) crystallizes from 1,2-dichlorobenzene and 1,2,4-trichlorobenzene as yellow crystals having a light-green fluorescence.

The optical absorbance spectrum of **1** is similar to that of **2**,[4] with the same three transitions (λ_{max} 339 nm, log ε 4.90; 365 (sh), 4.45; 396, 4.04; Figure 1) just slightly red-shifted from those of **2** (λ_{max} 326 nm, log ε 4.93; 347 (sh), 4.74; 388, 4.22).[3] The fluorescence spectrum of **1** shows bands at 453, 466, 486, and 517 nm, which are remarkably similar to those observed for **2** at 453, 468, 483, and 513 nm (± 5 nm).[4]

The NMR spectroscopic properties of **1** and **2** are also similar. The ^{1}H NMR spectrum of **1** in [D$_4$]1,2-dichlorobenzene (referenced to tetramethylsilane) showed three singlets at 7.86, 8.36, and 10.19 ppm in the ratio 2:1:1 (Figure 2). The chemical shifts of **2** are 7.94, 8.37, and

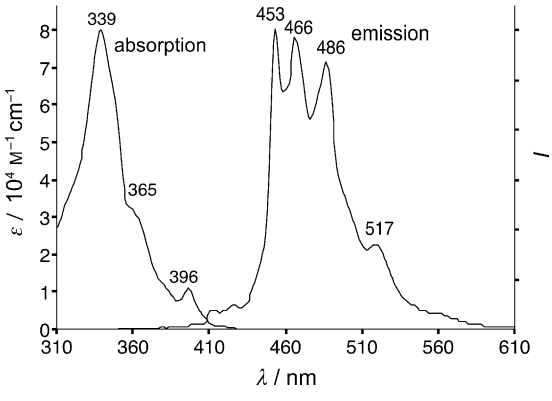


Figure 1. UV/Vis absorption and fluorescence spectrum of **1**.

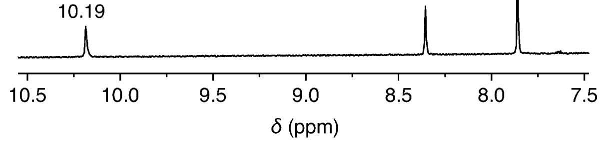


Figure 2. ^{1}H NMR spectrum of **1**.

10.45 ppm, also in a 2:1:1 ratio. The chemical shifts of **1** and **2** cannot be directly compared because the spectrum of **1** was measured in [D$_4$]1,2-dichlorobenzene and that of **2** was measured in [D$_3$]1,2,4-trichlorobenzene. To support the assertion that the chemical shifts of **1** and **2** are quite similar, and to aid in the assignment, we calculated the chemical shifts of **1** (the saddle-shaped minimum, averaged over apparent D_{7h} symmetry) as 8.37 (outer vinyl), 8.5 (outer aryl), and 10.31 (inner). For **2**, we calculated similar chemical shifts of 8.37, 8.79, and 10.05 ppm; thus the calculated NMR spectra of **1** and **2** are essentially the same.

In 1978, Staab and Diederich described the acquisition of the ^{1}H NMR spectrum of **2** as "extraordinarily difficult."[3] Their high standard compelled us to record the ^{13}C NMR spectrum of **1**, an experiment that required 14 h on a high-field NMR spectrometer (800 MHz for ^{1}H, 200 MHz for ^{13}C) equipped with a cryoprobe. [D]Bromoform was used to avoid interfering solvent resonances. Five signals were evident at $\delta = 131.7$, 130.4, 129.8, 128.2, and 118.0 ppm, which are in reasonable agreement with the calculated (B3LYP/6-31G(d)) values of $\delta = 134.0$, 133.4, 131.3, 129.7, and 122.3.

Nucleus independent chemicals shifts (NICS-1)[24] are widely used to quantify ring currents. The NICS-1 values for the benzenoid rings of **1** and **2** (−11.3 and −11.5 ppm) match those of the benzenoid rings of phenanthrene (−11.0) and benzene (−10.5). The NICS-1 values for the olefinic ring in **1** and **2** (−5.8 and −6.3 ppm) indicate ring currents smaller than that of the olefinic ring of phenanthrene (−8.1 ppm). These NICS values are in full accordance with Clar's picture of aromatic sextets, and suggest that the olefinic bonds in **1** and **2** are even more pronounced than in phenanthrene.

X-ray diffraction analysis established the structure of **1** (Figure 3).[25] We were surprised that **1** is not saddle-shaped in the crystal, as predicted by gas-phase density functional theory (DFT) calculations (see below), but rather has a chair-type conformation.[26] Nonetheless, it is not flat: the root-mean-square deviation (RMS) of carbon atoms of **1** from the least-squares plane passing through all 56 carbon atoms is 0.285 Å (Figure 3). As in kekulene, the bond lengths are in full agreement with Clar's representation, and six unique types of bonds can be identified. Indeed, the average bond lengths in **1** and **2** are essentially identical (Figure 4).

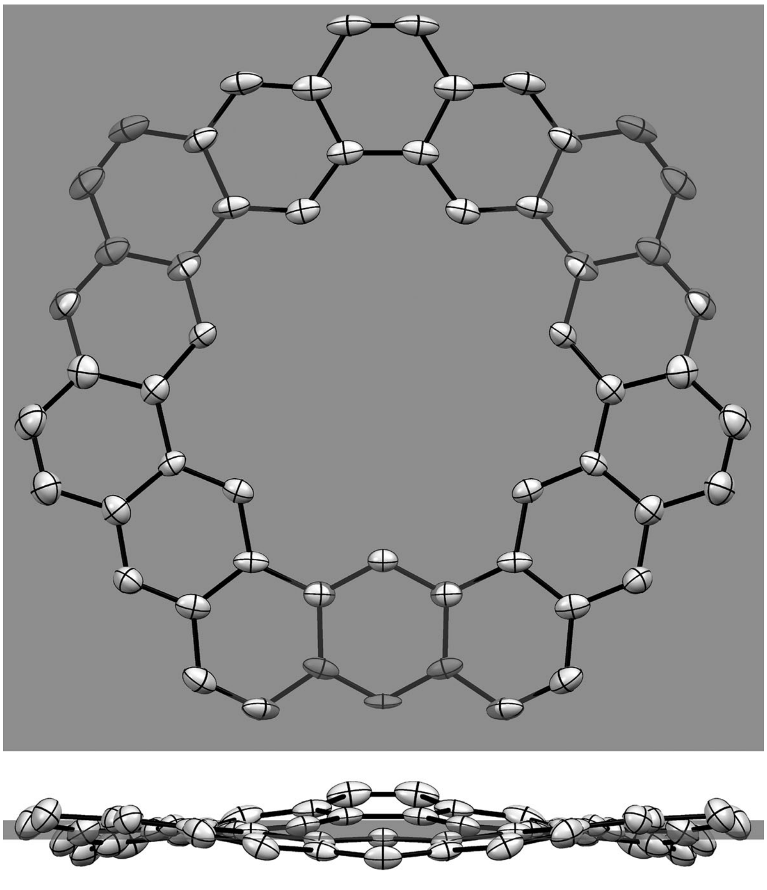


Figure 3. The conformation of **1** in the solid state viewed from the top and the side. The least-squares molecular plane is shown in translucent gray, and thus atoms behind this plane appear gray. Atomic displacement parameters are drawn at 50% probability and H atoms are omitted.

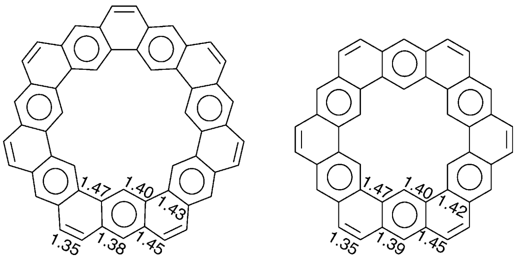


Figure 4. Unique C–C bonds lengths of **1** and **2**.

The similarity between **1** and **2** even extends to their crystal packing. Both **1** and **2** form slipped stacks arranged in a herringbone pattern. The side-by-side comparison (Figure 5) of the packing diagrams of **1** with those reported for **2** compels us to discuss the packing of **1** in the same terms used to describe the packing of **2**.[2] The average molecular plane forms an angle of 27.3° with the stacking axis, which is parallel to the *b* axis. Stacked molecules are slipped by 5.86 Å, and the interplanar spacing is 3.19 Å. The herringbone angle—the inclination of molecules in adjacent stacks—is 54.5°.[27] For **2**, molecules form an angle 42.9° with the stacking axis, adjacent stacks are slipped by 3.12 Å, the interplanar spacing is 3.35 Å, and the herringbone angle is 86°.

Gas-phase DFT calculations usually predict the correct crystallographic conformation of distorted polyaromatic hydrocarbons (PAHs), but they fail for **1**. The solid-state chair conformation of **1** could not be located in unconstrained gas-phase calculations, but we could model the chair conformation by fixing the distance from the mean molecular plane for seven atoms. We also considered the planar D_{7h}, saddle C_s, and saddle C_2 conformations. The energies calculated by several DFT methods (Table 1) are in agree-

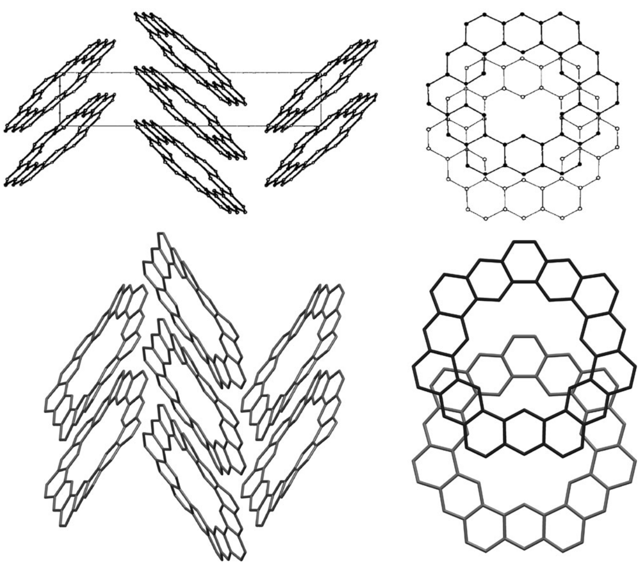


Figure 5. The crystal packing of **1** (bottom) and **2** (top).[28]

Table 1: Energies (kcal mol^{-1}) of various conformations of **1**.[30]

	B3LYP 6-31G(d)	B3LYP 6-311G (2d,p)	B3LYP 6-311G (2df,2pd)	B97D 6-31G(d)	M06-2X 6-31G(d)
chair	5.4	5.6	5.5	5.8	5.8
D_{7h}	4.5	4.9	4.8	5.3	5.2
C_s	0.1	nd[a]	nd	0.1	0.1
C_2	0	0	0	0	0

[a] nd = not determined.

ment, and show that the saddle structures are lowest in energy and the planar D_{7h} and chair-shaped structures are about 5–6 kcal mol^{-1} higher in energy. So why does septulene adopt a chair conformation in the solid state instead of its lower-energy saddle conformation?

The answer to this question is evident from lattice-energy calculations using force fields.[29] If one replaces the chair conformation in the experimental crystal structure by a saddle conformation and optimizes the lattice with fixed molecular geometry, the lattice is drastically distorted. The resulting packing has a lower density and an unfavorable lattice energy (see the Supporting Information). Similar to DFT methods, the force-field methods used favor a saddle conformation in the gas phase. However, a full optimization from the saddle conformation in the crystal packing leads back to the experimental structure with molecules in a chair conformation. These calculations demonstrate that the preference in the crystal for the chair conformation is a packing effect.

To investigate whether a saddle-type molecule can crystallize with a different molecular arrangement we performed a global crystal structure prediction with molecules in C_s and C_2 conformations.[31] The calculations were carried out with fixed molecular geometries in various space groups with free lattice parameters, starting from more than 300 000 random crystal packing arrangements (details are given in the Supporting Information). The energetically best resulting structures were compared with the experimental structure optimized under the same conditions. All the hypothetical structures with molecules in C_s and C_2 conformations have less favorable packing arrangements. Their density is at least 4.6 % (C_s conformation) or 5.5 % (C_2 conformation) lower than the density of the optimized experimental structure. The intermolecular energy is worse by at least 4.3 kcal mol^{-1}, which is on the same order as the difference in the intramolecular energies calculated by DFT. While we could not rule out the existence of another polymorph that favors the saddle conformer, the saddle geometry does not allow for good, dense packing with low lattice energy.

The curvature of **1** invites a discussion of strain. Assuming that **1**, similar to **2**,[32–34] does not enjoy any unusual aromatic stabilization, we can define the strain energy of **1** by the simple homodesmotic reaction 7(**2**)→6(**1**), which gives a strain energy of only 9.8 kcal mol^{-1} (B3LYP/6-31G(d)) for the gas-phase C_2 structure. This amounts to only about 0.2 kcal mol^{-1} C atom^{-1}—about the same intrinsic strain as in the gauche conformation of butane. This strain is incorporated in the RCM steps of the synthesis. Homodesmotic reactions (B3LYP/6-31G(d)) based on the lowest energy conformations[35] of the various intermediates and 2,2′-dipropenylbiphenyl show that the first three RCM steps reduce strain by about 9 kcal mol^{-1} and the last four steps increase strain by about 14 kcal mol^{-1}. The energy released in creation of an aromatic ring (ca. 28 kcal mol^{-1})[15] in each RCM step more than compensates for the strain built up in any step.

The undulating structure of **1** gives rise to vibrations similar to the "Mexican wave" cheer in sport stadiums,[36] where spectators stand and sit in response to their neighbor, thereby generating a wave that rotates around a stadium. For the chair conformation of **1**, this motion is a pseudorotation[37] that occurs on a flat potential energy surface. The C_s and C_2 gas-phase minima (B3LYP/6-31G(d)) lie on the pseudorotation coordinate and, because of the fourteen-fold symmetry of the potential energy surface (sevenfold rotation and a twofold reflection), are interconverted by a motion of less than 13° along the pseudorotation coordinate. These minima are isoenergetic within 0.1 kcal mol^{-1}.[38] The proximity of these minima on the pseudorotation coordinate and their energetic similarity hints at a low energy barrier.

The "Mexican wave" vibrational modes are remarkably low in energy (2 cm^{-1} for the C_2 minimum and 4 cm^{-1} for the C_s minimum). These frequencies are comparable to the uncertainty of the calculations. We therefore attempted to locate a transition state for the pseudorotation. Geometrical interpolation between the superimposed C_2 and C_s conformations provided a set of structures that lie on the pseudorotation trajectory. DFT calculations at points along this trajectory reveal that the surface is flat (the calculated barrier was 0.05 kcal mol^{-1}). The energy barrier to psuedorotation is less than the uncertainty of the calculations. Similar to cyclopentane,[39] **1** is a free pseudorotor. Not surprisingly, a closely related pseudorotation is manifest in [7]circulene.[40]

In conclusion, septulene was prepared by a sevenfold RCM reaction. Its conformational behavior is unusual: Two saddle-shaped conformers were identified by gas-phase calculations, and a chair-type conformer was observed in the crystal structure. The two saddle-shaped conformers interconvert through a vanishingly small energy barrier, thus making **1** a free pseudorotor. The chair conformation that is observed in the crystal structure is not a gas-phase minimum, but exists as a result of packing forces.

The electronic and structural properties of **1** are essentially the same as those of **2**. This similarity follows from their Clar structures. The similarity does not—and indeed cannot—follow from their Kekulé structures, which fundamentally differ, by virtue of their inner and outer annuli having an odd or even number of atoms. Septulene (**1**) unequivocally demonstrates that Clar structures, not Kekulé structures, should be used to represent bonding in polycyclic aromatic molecules.

The conclusion that Clar structures are the correct way to represent bonding in PAHs has not permeated popular chemical thinking. Most textbook authors avoid circles in aromatic rings altogether, an expedient work-around that deprives the student of this simple and useful model. Indeed, Carey and Sundberg draw kekulene **2** as concentric annulenes,[41] even though the main lesson from kekulene was that the concentric annulene model was wrong. In other textbooks, circles are drawn willy-nilly, simply to indicate that a ring is "aromatic" in some ill-defined sense, thus compounding the suffering student's confusion. We recommend that chemists treat circles in rings with the same respect and care that they give to doubly barbed, curly arrows.

To close, we note the irony that molecules named in honor of August Kekulé have diminished the utility of a bonding model also named in his honor.

Received: April 27, 2012
Revised: September 9, 2012
Published online: October 12, 2012

Keywords: aromaticity · fused-ring systems · kekulenes · macrocycles · metathesis

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[28] The top figure (copyright 1983 Wiley) is used with permission.
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