mentary publication no. CCDC-157686 and CCDC-157687. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit @ccdc.cam.ac.uk).

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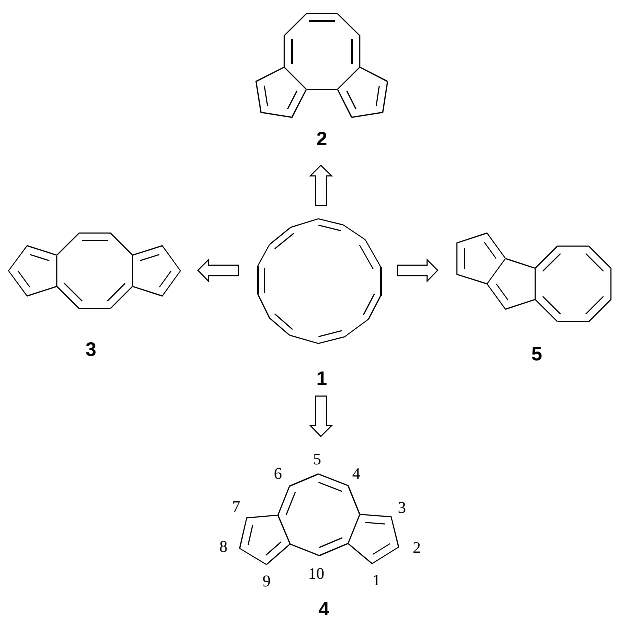
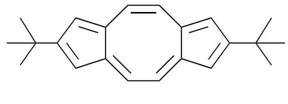
Dicyclopenta[*a*,*d*]cyclooctene: A [14]Annulene Containing Two Zero-Atom Cross-Links[**]

Mitsunori Oda,[*] Yukinari Sakamoto, Takanori Kajioka, Takuya Uchiyama, Ryuta Miyatake, and Shigeyasu Kuroda[*]

The insertion of two zero-atom cross-links between the carbon atoms of the hypothetical all-*cis*-[14]annulene (**1**) provides many types of (benzenoid and non-benzenoid) tricyclic hydrocarbons of the formula $C_{14}H_{10}$, depending on the site of the linkages. With constitutional restriction limited to the production of five- and eight-membered rings, four nonalternant hydrocarbons are formed: dicyclopentacyclooctenes **2**–**4** and cyclooctapentalene (**5**).[1] Compared to alternant benzenoid isomers, such as anthracene and phenanthrene, very little is known about these relatively small parent nonalternant hydrocarbons. Prinzbach and co-workers reported on attempts to synthesize the [*a*,*c*]isomer **2**,[2] and Hafner et al. published the synthesis of the 2,7-di(*tert*-butyl) derivative (**6**) of the [*a*,*e*]isomer **3**.[3] Hydrocarbon **6** has a planar structure and diamagnetic character and, most notably, exhibits the





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[*] Dr. M. Oda, Prof. Dr. S. Kuroda, Y. Sakamoto, Dr. T. Kajioka,
T. Uchiyama, Dr. R. Miyatake
Department of Applied Chemistry, Faculty of Engineering
Toyama University
Gofuku 3190, Toyama 930-8555 (Japan)
Fax: (+81) 76-445-6819
E-mail: oda@eng.toyama-u.ac.jp
kuro@eng.toyama-u.ac.jp

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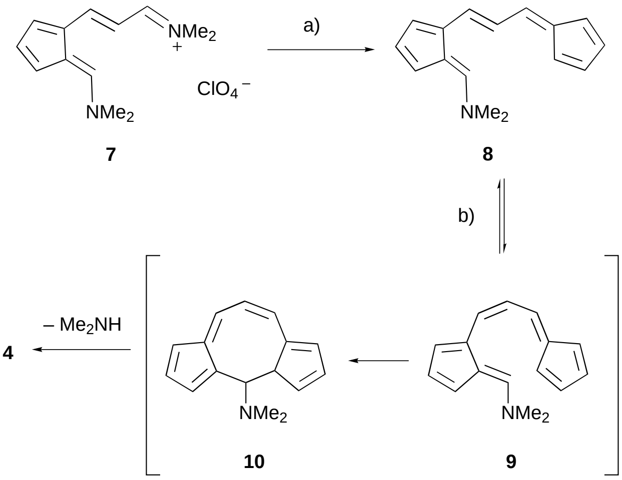
longest wavelength absorption maximum ($\lambda_{max} = 1375$ nm) observed for hydrocarbons with a 14π conjugated system. Here we present the synthesis and spectroscopic properties of the [*a*,*d*]isomer **4**, the first parent of this class of nonalternant hydrocarbons.

Our synthetic strategy for **4** is based on 14π-electrocyclization[4, 5] across the two pentafulvenoid moieties of the precursor 6-dimethylamino-1-{2-(pentafulven-6-yl)ethenyl}-pentafulvene (**8**), with formation of the central eight-membered ring, and subsequent deamination (Scheme 1). This approach is analogous to the azulene synthesis developed by Hafner and Ziegler.[6]



Scheme 1. Synthesis of **4**. a) Sodium cyclopentadienide, THF, 0 °C, 15 min, 63 %; b) reflux in 2,6-lutidine, 90 min, 2 %.

The precursor **8** was prepared by reaction of sodium cyclopentadienide and 6-dimethylamino-1-(3-dimethylimino-1-propenyl)pentafulvene perchlorate (**7**)[7] in 63 % yield. The pentafulvene **8**, isolated as green plates, is stable in the solid state and in solution below 100 °C; decomposition is observed over 150 °C. Thermal electrocyclization of **8** to **4** under reflux in hydrocarbon, alcohol, and ether solvents in a range of 150–250 °C was unsuccessful and gave only gummy dark-colored material, independent of the concentration of **8**.[8] Reactions in DMF or in basic solvents such as pyridine, picoline, and quinoline gave **4** in yields of less than 1 %. The best yield of 2 % was obtained upon reaction in 2,6-lutidine at reflux temperature. Product **4** was isolated as red-purple leaflets after chromatography on silica gel and recrystallization from methanol/water.

The ^{1}H and ^{13}C NMR spectra of **4** (see the Experimental Section) document the double-bond delocalization in the periphery of the ring system and, thus, the diamagnetic property of the compound. Six distinct ^{1}H NMR signals and eight ^{13}C NMR signals indicate the molecular symmetry of **4**, which bears a C_2 axis through C-5 and C-10. The $^3J_{HH}$ coupling constants also confirm the 14π electron delocalization. For example, two triplets for H-2 (or H-8) and H-5 in the ^{1}H NMR spectrum directly evidence two sets of equal coupling constants between ^3J(H-1,H-2)/^3J(H-8,H-9) and ^3J(H-2,H-3)/^3J(H-7,H-8) and between ^3J(H-4,H-5) and ^3J(H-5,H-6). The average ^{1}H chemical shift ($\delta = 7.64$) of **4** is comparable to that of azulene ($\delta = 7.64$)[9] and is larger than that of naphthalene ($\delta = 7.48$),[10] indicating the appreciable diamagnetic nature of **4**.

The UV/Vis spectrum of **4** shows the longest wavelength maximum at 767 nm, which is about 600 nm less than that of **6**. Figure 1 shows correlations of frontier molecular orbitals between [14]annulene (**1**) and dicyclopentacyclooctenes **3** and **4** based on calculations at the MB3LYP/6-31G* level of theory.[11] The annulene **1** has a doubly degenerate HOMO and LUMO; the pair of orbitals forming the HOMO correlate to the HOMO and the HOMO−1 of **3** and **4**, and those forming the LUMO correlate to the LUMO and the LUMO+1 of **3** and **4**. As indicated in Figure 1, **3** has a destabilized HOMO and a stabilized LUMO, whereas **4** has a destabilized HOMO and a slightly destabilized LUMO relative to **1**. Thus **4** should absorb longer wavelength light upon excitation than **1** and much shorter wavelength light than **3**. Although all-*cis*-[14]annulene (**1**) is unknown, its geometrical isomer, dehydro[14]annulenes, and bridged [14]annulenes have been synthesized. Among them, those with a planar structure and without transannular interaction across the bridge[12–16] show the longest wavelength maxima at 558–633 nm in their UV/Vis spectra; these values are indeed lower than that observed for **4**. Since the crystals of **4** obtained so far were not suitable for X-ray crystallographic analysis, we are currently focusing on synthesizing simple derivatives for this purpose.

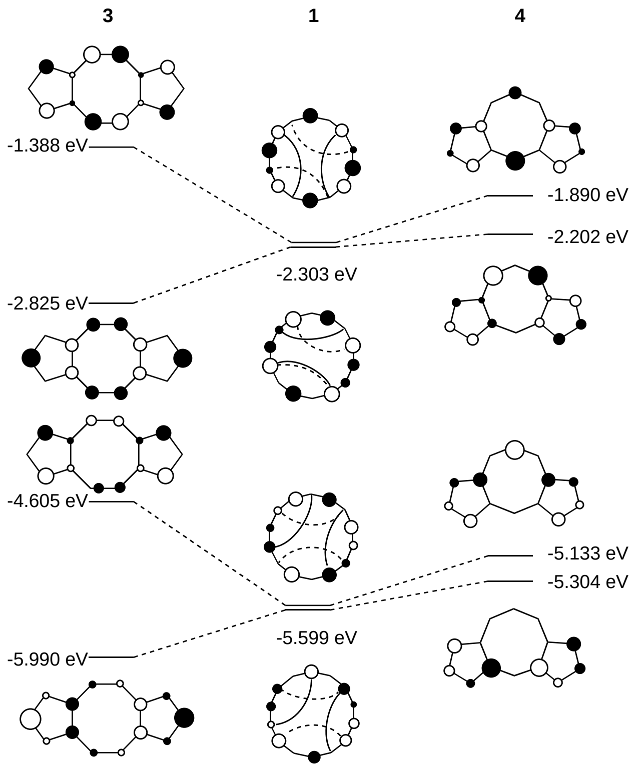


Figure 1. Correlations of frontier molecular orbitals between [14]annulene (**1**) and dicyclopentacyclooctenes **3** and **4** based on calculations at the MB3LYP/6-31G* level of theory. The broken and solid curves in **1** are the cross-links required to form **3** and **4**, respectively.

Experimental Section

8: Compound **7** (30.3 g, 0.1 mol) was added to a stirred solution of sodium cyclopentadienide (0.1 mol) in THF (600 mL) at 0 °C under nitrogen atmosphere. After the mixture was stirred at 0 °C for 15 min, solids were formed and removed by suction filtration through a celite pad. The solids and celite were washed with ethyl acetate/hexane (1/4), and the filtrate was concentrated under vacuum. The residual solids were purified by recrystallization from CH_2Cl_2/hexane (1/2) to give **8** as green plates (14.0 g, 63 % yield). M.p. 145–147 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.29$ (s, 6H; NCH_3), 6.26 (dt, $J = 5.0$, 1.7, 1H), 6.45 (ddm, $J = 5.0$, 3.1 Hz, 1H), 6.54 (ddm, $J = 5.0$, 3.1 Hz, 1H), 6.58 (ddm, $J = 4.6$, 2.9 Hz, 1H), 6.67 (dm, $J = 5.0$ Hz, 1H), 6.73 (dm, $J = 4.6$ Hz, 1H), 6.89 (dm, $J = 2.9$ Hz, 1H), 6.99 (d, $J = 12.4$ Hz, 1H), 7.00 (d, $J = 14.4$ Hz, 1H), 7.19 (dd, $J = 14.4$, 12.4 Hz, 1H), 7.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, −30 °C): $\delta = 40.7$, 48.0, 114.0, 117.7, 118.9, 119.7, 121.4, 124.5, 129.2, 130.9, 131.4, 134.5, 141.2, 142.3, 147.6; IR (KBr): $\tilde{\nu} = 1623$, 1580, 1359, 1055 cm^{-1}; elemental analysis calcd for $C_{16}H_{17}N$: C 86.06, H 7.69, N 6.27; found: C 85.97, H 7.72, N 5.99.

4: A solution of **8** (1.00 g, 4.48 mmol) in 2,6-lutidine (200 mL) was refluxed under nitrogen atmosphere for 90 min. The solvent was removed under vacuum. The dark-colored solids were suspended in hexane (50 mL), and insoluble black solids were removed by filtration. The filtrate was concentrated with an evaporator, and the residue was purified by chromatography on silica gel with hexane as eluent to provide **4** as a dark red solid (16.5 mg, 2 % yield). An analytical sample of **4** as red-purple leaflets was obtained by recrystallization from methanol/water (7/1). M.p. 139–140 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.58$ (d, $J = 11.6$ Hz, 2H; H-4,6), 7.37 (t, $J = 4.0$ Hz, 2H; H-2, 8), 7.59 (dd, $J = 4.0$, 1.6 Hz, 2H; H-3,7), 7.71 (dd, $J = 4.0$, 1.6 Hz, 2H; H-1,9), 7.94 (t, $J = 11.6$ Hz, 1H; H-5), 8.64 (s, 1H; H-10); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 113.7$ (C-5), 128.9 (C-2,8), 129.5 (C-8a, 9a), 133.3 (C-3a, 6a), 138.4 (C-3, 7), 139.4 (C-1, 9), 140.0 (C-4, 6), 141.2 (C-10); IR (KBr): $\tilde{\nu} = 1589$, 1413, 1396, 1192, 774, 749 cm^{-1}; MS (70 eV): m/z (%): 179 ($M^+ + 1$, 15), 178 (M^+, 100), 177 (26), 152 (31), 76 (21); UV/Vis (n-hexane): λ_{max} (ε) = 213 (15100), 218 (15000), 222 (15200), 238 sh (11000), 248 sh (7840), 273 sh (7760), 283 (9770), 290 sh (8320), 329 sh (38900), 344 (112000), 446 (1070), 468 sh (933), 498 sh (812), 531 (851), 608 (186), 631 (186), 649 (194), 663 (224), 677 (257), 692 sh (355), 701 (407), 718 (427), 737 (437), 750 (746), 767 (1290), 800 sh (36), 818 sh nm (12); elemental analysis calcd for $C_{14}H_{10}$: C 94.35, H 5.65; found: C 94.19, H 5.80.

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Nonorthogonal Dilithium-1,3-biborataallenes Containing Planar-Tetracoordinate Carbon Atoms[**]

Yüksel Sahin, Michael Hartmann, Gertraud Geiseler,
Dieter Schweikart, Christian Balzereit,
Gernot Frenking, Werner Massa, and Armin Berndt[*]

Orthogonality ($\Theta = 90°$) of the planes of the terminal atoms of the allene skeleton and their neighbors, here referred to as "terminal planes", is a characteristic feature of allenes. Strong deviation from this orthogonality has been observed up to now only for an allene skeleton as part of a highly strained six-membered ring.[1] Almost orthogonal ($\Theta = 92°$)[2] terminal planes have also been found for the heteroallene **1** of the ion pair $\mathbf{1} \cdot Li \cdot 3\,Et_2O$ (Scheme 1),[2] where **1** contains four sterically demanding aryl substituents. Here we present contaction triples of **2a**, which is isoelectronic with **1**, and of related tetraaryl-1,3-diboratallenes **2b**–**d** and show their planes

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[*] Prof. Dr. A. Berndt, Dr. Y. Sahin, Dr. M. Hartmann, G. Geiseler, Dr. D. Schweikart, Dr. C. Balzereit, Prof. Dr. G. Frenking, Prof. Dr. W. Massa
Fachbereich Chemie der Universität Marburg
35032 Marburg
Fax: (+49) 6421-2828917
E-mail: berndt@chemie.uni-marburg.de

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