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LETTERS

Novel synthesis of hexaaryl[3]radialenes via dibromo[3]dendralenes[†]

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Abstract

We report here an efficient route to the synthesis of highly fluorescent hexaaryl[3]radialenes using the oligomerization of ate-type copper carbenoids, followed by cyclization with hexamethylditin and $Pd(PPh_3)_4$; the structures of the [3]dendralene and hexaaryl[3]radialenes were determined by X-ray crystallographic analysis. © 2000 Elsevier Science Ltd. All rights reserved.

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Radialenes (polymethylenecycloalkanes) have received considerable attention from both theorists and experimentalists,[1] because they display a particular arrangement of π-electrons[2] and because they can serve as electron donors and acceptors.[3] In conjunction with our program to develop methods for transition-metal-catalyzed synthesis of new π-electron systems, we have investigated a one-pot synthesis of radialenes by either cyclooligomerization of cumulenic double bonds[4] or carbenoids.[5,6] Through these investigations, we found that the ate-type copper carbenoids **1** oligomerize to produce dendralenes **2**. We now report here the synthesis of [3]radialenes (**3** and **4**) starting from [3]dendralenes **2** (Scheme 1).

Although the reaction of the ate-type copper carbenoid **1a**, derived from **5** by successive treatment with Bu^nLi (1.1 equiv.) and $CuI{\cdot}PBu^n_3$ (0.5 equiv.) at low temperatures, produced octaphenyl[4]-radialene **7a** with increasing temperature;[6a] tetraphenylbutatriene **8** and the [3]dendralene derivative **9** were obtained by quenching the reaction mixture with CF_3CO_2H at −78°C

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[†] Dedicated to Professor Richard Neidlin on the occasion of his 70th birthday.

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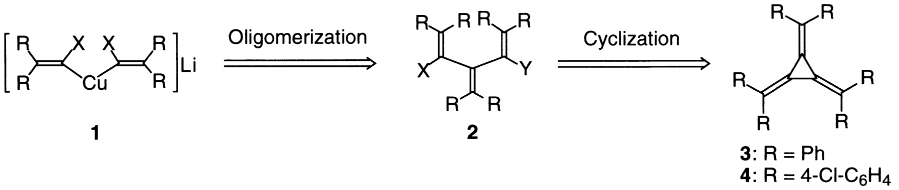
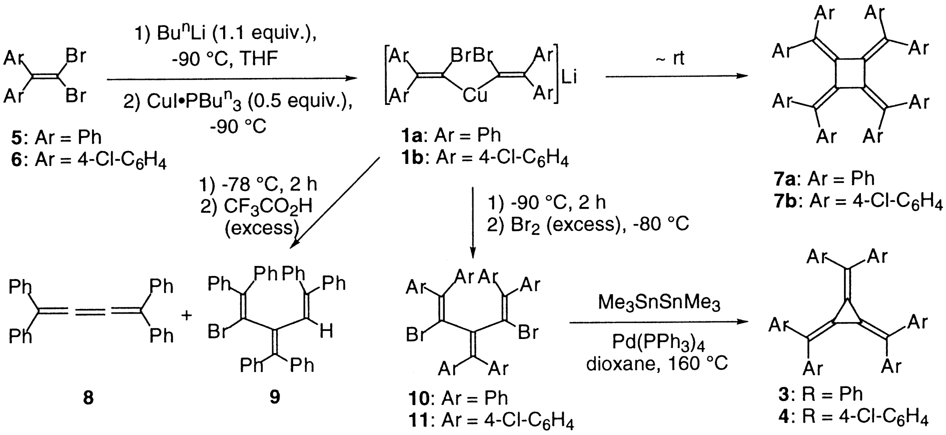


Scheme 1.

(Scheme 2). Since the precursor of **9** was expected as an organocopper species, we quenched the reaction mixture with Br_2 (1.1 equiv.) to form the dibromo[3]dendralene **10** in 27% yield, together with **8** (19%).[7] In a similar manner, successive treatment of **6** with Bu^{n}Li (1.1 equiv.) and CuI·PBu$^n_3$ (0.5 equiv.) at low temperatures, followed by quenching with Br_2 (1.4 equiv.), produced the [3]dendralene **11** in 35% yield.



Scheme 2.

Although it is difficult to determine the structures of **10** and **11** exactly by using complicated ^{1}H NMR spectra due to hindered rotation of aromatic rings, the structure of **10** was determined unambiguously by an X-ray diffraction method (Fig. 1).[8] The [3]dendralene **10** has a stacking structure with approximate C_2 symmetry. In agreement with the temperature-dependent ^{1}H NMR spectra, **10** has crowded phenyl groups, and the two sets of benzene rings are stacked face-to-face with a distance of 3.41 Å, whereas the terminal two are apart from each other. Interestingly, two bromine atoms are oriented in the same direction, and the intramolecular Br···Br distance is 3.95 Å. Therefore, the conformation of **10** is favorable for intramolecular coupling using metal catalysts.

After some unsuccessful attempts for the cyclization of **10**, we found that the reaction of **10** with hexamethylditin (2 equiv.) and $Pd(PPh_3)_4$ (0.3 equiv.)[9] in dioxane at 160°C for 24 h resulted in the formation of hexaphenyl[3]radialene **3** (28%; 34% based on the consumed **10**), together with the recovered **10** (14%; Scheme 2). In a similar manner, the reaction of **11** with hexamethylditin (2 equiv.) and $Pd(PPh_3)_4$ (0.3 equiv.) in dioxane at 160°C for 24 h led to hexa(4-chlorophenyl)[3]radialene **4** in 35% yield. As has been reported previously,[2c] aryl-substituted [3]radialenes show redox properties. The reduction potentials of **3** and **4** measured by cyclic voltammetry (V versus Fc/Fc$^+$, 0.1 M Bu$^n_4$NClO$_4$, *o*-dichlorobenzene, rt) revealed two reversible

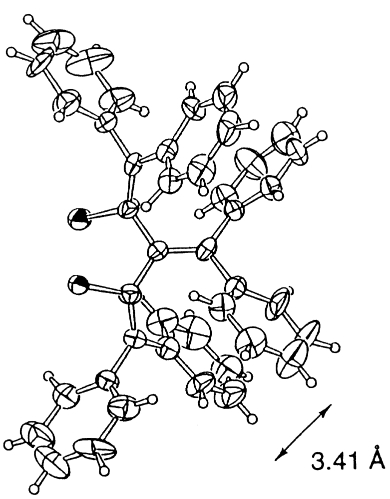


Figure 1. ORTEP diagram of **10**

one-electron redox steps (**3**: –1.08 and –1.53 V; **4**: –0.82 and –1.31 V). Although **3** and **4** show similar electronic spectra, crystals of **3** and **4** have orange–yellow and red color, respectively.

The crystal structures of **3** and **4** were determined by X-ray analysis (Fig. 2).[10] As shown in Fig. 2a, **3** has an approximate C_3 symmetry, and the six phenyl groups are arranged to form a screw-shaped geometry. The radialene ring shows a high coplanarity, and the maximum atomic deviations from the least-squares planes of the three-membered ring and radialene framework are 0.006 and 0.02 Å, respectively. The three exocyclic double bonds reveal a slight torsion (8–13°), and the three sets of approximately parallel phenyl groups are located at angles of 33–47° to the

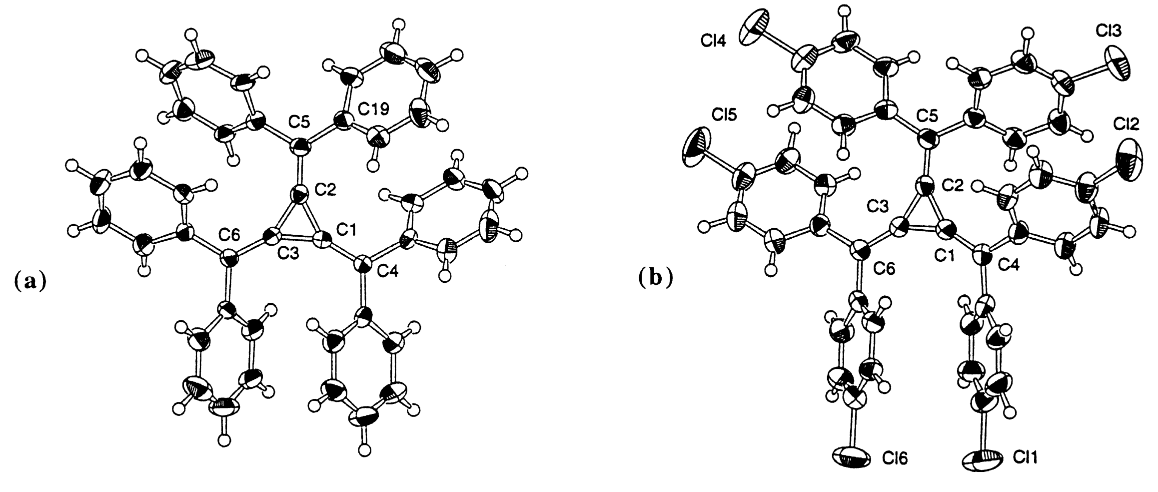


Figure 2. (a) ORTEP diagram of **3**. Selected bond lengths (Å) and angles (°): C1–C2 1.450(10), C2–C3 1.430 (10), C3–C1 1.430(10), C1–C4 1.35(1), C2–C5 1.359(10), C3–C6 1.37(1), C2–C1–C3 59.6(4), C1–C2–C3 59.5(4), C1–C3–C2 60.9(4), C1–C2–C5 152.0(6), and C2–C5–C19 122.2(6). (b) ORTEP diagram of **4**. Selected bond lengths (Å) and angles (°): C1–C2 1.429(5), C2–C3 1.423 (6), C3–C1 1.436 (5), C1–C4 1.349(5), C2–C1–C3 59.6(3), C1–C2–C5 147.7(4), and C2–C5–C19 118.4(4)

plane of the radialene ring. Although the substitution of chlorine sometimes causes a structural deformation, the crystal structure of **4** is very similar to that of **3** (Fig. 2b).

As shown in Fig. 3, hexaaryl[3]radialenes **3** and **4** are fluorescent. The fluorescence quantum yield ($\Phi_F = 0.18$) of **4** is three times larger than that of **3** ($\Phi_F = 0.064$). The introduction of a heavy atom such as chlorine is often observed to enhance intersystem crossing and decrease fluorescence intensity drastically,[11] while this is not the case for **3** and **4**. Both **3** and **4** exhibit rather large shifts between the absorption and fluorescence maxima ($\Delta\nu$), in accord with their having intramolecular charge transfer character in the lowest excited singlet states as predicted by CNDO/S3 and AM1 MO calculations. The zero–zero band energies (E_{0-0}) are similar, while the fluorescence lifetime ($\tau = 6.6$ ns) of **4** is three times longer than that (2.6 ns) of **3** (Fig. 3 and Table 1).

The lower fluorescence quantum yield of **3** than **4** is mainly due to the larger non-radiative rate constant (k_{nr}), while the radiative rate constants (k_r) are very similar (Table 1). The lack of a heavy atom effect suggests that the intersystem crossing makes a small contribution to the non-radiative process in radialenes. Detailed study on this point is now in progress.

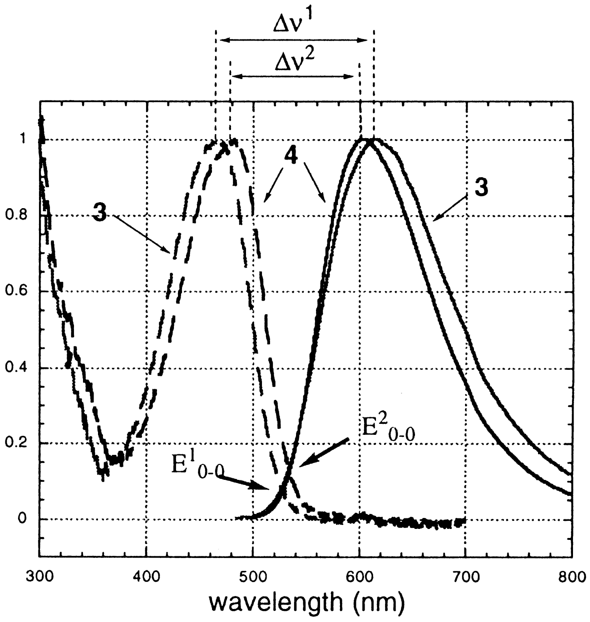


Figure 3. Electronic and fluorescence spectra of **3** and **4** in benzene

Table 1
Absorption spectra and fluorescence data of **3** and **4**[a)]

	Absorption		Fluorescence[c)]			$\Delta\nu$	E_{0-0}	k_r	k_{nr}
	λ_{max} (nm)	ε (10^3)[b)]	λ_{max} (nm)	Φ_F (10^{-2})	τ (ns)	(10^3 cm^{-1})	(10^4 cm^{-1})	(10^7 s^{-1})	(10^8 s^{-1})
3	468	37	617	6.4	2.6	5.2	1.90	2.5	3.6
4	483	48	606	18	6.6	4.2	1.87	2.7	1.2

a) In benzene. b) M^{-1}cm^{-1}. c) Fluorescence quantum yields (Φ_F) were determined by comparison with 4-amino-fluorenone in benzene ($\Phi_F = 0.074$).[12]

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7. All compounds gave satisfactory analytical and spectral data. For example, compound **10**: pale orange prisms, mp 174.5–175.8°C (decomp.); MS m/z 696, 694, 692 (M^+); ^1H NMR ($CDCl_3$) δ 7.01–7.31 (m, 30H); ^{13}C NMR ($CDCl_3$) δ 109.86, 126.49, 127.60, 127.86, 127.94, 128.21, 128.26, 128.31, 128.34, 128.37, 128.57, 128.61, 128.77, 128.81, 128.85, 128.87, 129.55, 129.58, 129.72, 130.10, 130.11, 131.54, 134.83, 136.99, 141.24, 141.32, 141.48, 142.99, 143.33, 143.36, 145.29, 145.59, 146.75, 147.19, 148.81, 149.02, 150.02, 152.55; UV (CH_2Cl_2): λ_{max} (log ε) 308 (4.30), 360sh (3.94) nm; HRMS calcd for $C_{42}H_{30}{}^{79}Br^{81}Br$: 694.0693. Found: 694.0677. Compound **11**: pale yellow crystals, mp 260.4–264.2°C (decomp.); FAB-MS m/z 901, 899, 897 (M^++1); ^1H NMR ($CDCl_3$) δ 6.92–7.05 (m, 18H), 7.28–7.31 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 125.22, 126.30, 127.92, 127.97, 128.52, 128.57, 128.61, 129.96, 130.15, 130.21, 130.33, 130.35, 130.37, 133.57, 133.65, 133.95, 134.00, 134.05, 134.39, 134.51, 134.64, 136.62, 138.09, 138.20, 138.40, 139.61, 139.92, 139.96, 141.54, 141.83, 144.19, 144.58, 144.89, 145.23, 149.93. Compound **3**: yellow prisms, mp 334.7–336.8°C (decomp.); MS m/z 534 (M^+); ^1H NMR ($CDCl_3$) δ 6.76 (t, J = 7.4 Hz, 12H), 6.81 (dd, J = 8.2 and 1.2, 12H), 7.09 (tt, J = 7.4 and 1.2, 6H); ^{13}C NMR ($CDCl_3$) δ 118.24, 123.82, 126.58, 126.87, 130.26, 141.25; UV (CH_2Cl_2): λ_{max} (log ε) 277 (4.43), 467 (4.47) nm; UV (benzene): λ_{max} (log ε) 468 (4.57) nm. Compound **4**: reddish orange needles, mp 353.5–355.2°C (decomp.); MS m/z 738 (M^+); ^1H NMR ($CDCl_3$) δ 6.72 (d, J = 8.5 Hz, 12H), 6.85 (d, J = 8.5, 12H); ^{13}C NMR ($CDCl_3$) δ 117.99, 122.08, 127.14, 131.29, 134.31, 138.75; UV (CH_2Cl_2): λ_{max} (log ε) 285 (4.76), 339sh (4.08), 482 (4.77) nm; UV (benzene): λ_{max} (log ε) 483 (4.68) nm; HRMS calcd for $C_{42}H_{34}Cl_6$: 738.0009. Found: 737.9964.

8. Crystal data for **10**: $C_{42}H_{30}Br_2$, *Mw* = 694.51, monoclinic, space group *P2*$_1$*/c* (No. 14), *a* = 12.25(1), *b* = 15.755(8), *c* = 18.000(8) Å, *β* = 99.86(5)°, *V* = 3423(3) Å^3, *Z* = 4, *D*c = 1.347 g cm^{-3}, *R* = 0.069, *R*w = 0.071, GOF = 4.23 for 3372 reflections with $I > 3.00\sigma(I)$.
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10. Crystal data for **3**: $C_{42}H_{30}$, *Mw* = 534.70, triclinic, space group *P-1* (No. 2), *a* = 12.374(7), *b* = 13.685(6), *c* = 10.635(3) Å, *α* = 100.46(3)°, *β* = 106.57(3)°, *γ* = 115.49(4)°, *V* = 1458(1) Å^3, *Z* = 2, *D*c = 1.217 g cm^{-3}, *R* = 0.056, *R*w = 0.069, GOF = 1.18 for 1384 reflections with $I > 3.00\sigma(I)$. Crystal data for **4**: $C_{42}H_{24}Cl_6$, *Mw* = 741.37, monoclinic, space group *P2*$_1$ (No. 4), *a* = 14.307(2), *b* = 9.517(2), *c* = 14.715(2) Å, *β* = 117.25(1)°, *V* = 1781.2(6) Å^3, *Z* = 2, *D*c = 1.382 g cm^{-3}, *R* = 0.037, *R*w = 0.049, GOF = 1.20 for 2595 reflections with $I > 3.00\sigma(I)$.
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