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Hexaaryl[3]radialenes

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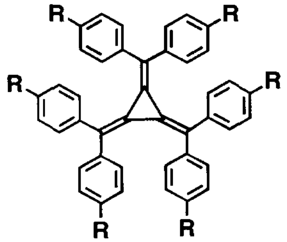
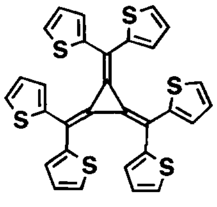
Abstract: Reactions of diarylmethyl anions whose conjugate acids are more acidic than diphenylmethane with tetrachlorocyclopropene are found to afford hexaaryl-[3]radialenes in modest to good yields, thus leading to the first synthesis of hexaphenyl[3]radialene itself too; X-ray crystalographic analysis of hexakis(*p*-cyanophenyl)[3]radialene reveals a double three-bladed conformation.

[3]Radialenes have received considerable attention because of the unique structures and physicochemical properties.[1,2] Although several tris(dibenzoarylidene)cyclopropanes are known,[3] neither hexaphenyl[3]radialene (**1a**) nor its simple derivatives have been reported. In addition to the interest in their own structures and properties, functionalized hexaaryl[3]radialenes could be useful synthons for extended novel π-systems incorporating [3]radialene frameworks. We wish here to report the first synthesis, structure and properties of **1a**, its derivatives **1b-e**, and hexakis(2-thienyl)[3]radialene **2**.

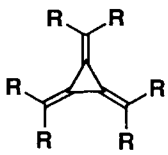


1a: R = H
1b: R = Br
1c: R = I
1d: R = CO_2Me
1e: R = CN

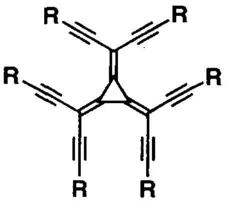


2

The carbenoid cycloaddition or cyclooligomerization, which has been successful for the synthesis of several [3]radialenes including tris(dibenzoarylidene)cyclopropanes, has failed to give **1a**.[3,4] Fukunaga's method[5] used for the synthesis of the dianions of hexacyano- and hexacarbomethoxy[3]radialene, (**3a**) and (**3b**), namely the reaction of tetrachlorocyclopropene with the carbanions of the corresponding active methylene compounds could not be applied to the synthesis of **1a** using diphenylmethyl anion.[6] However, this method was the effective way for the synthesis of a hexaethynyl[3]radialene derivative **4**, although the yield was modest.[2] What are governing factors for successful application of Fukunaga's method ? We supposed that acidity of active methylene compounds could be an important factor and have found that diarylmethanes which are more acidic than diphenylmethane **5a** (p*K*a = 32.3[7]) furnish hexaaryl[3]radialenes in modest to good yields.



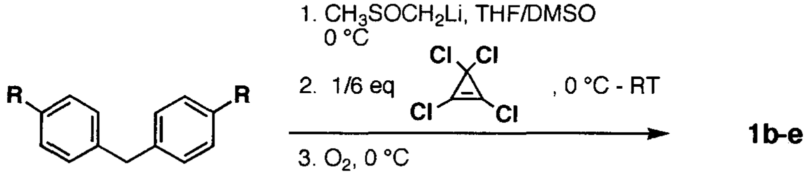
3a: R = CN
3b: R = CO_2Me



4: R = Me_3Si

The reaction of tetrachlorocyclopropene with 6 equiv of the lithio carbanion of bis(4-bromophenyl)methane (**5b**) (p*K*a = 29.7[8]) in a mixed solvent of THF-DMSO (1/1 v/v) at 0 °C followed by oxidation with oxygen afforded hexakis(4-bromophenyl)[3]radialene (**1b**) as yellow-orange crystals in 25-35% yield. In similar ways, bis(4-iodophenyl)-, bis(4-carbomethoxyphenyl)-, and bis(4-cyanophenyl)methane, **5c** (p*K*a =29.4[8]), **5d** (27.3[8]), and **5e** (23.0[9]), respectively, yielded the corresponding hexaaryl[3]radialenes, **1c** (30%), **1d** (21%), and **1e** (73%). Bis(2-thienyl)methane (p*K*a = 28.9[8]) also yielded radialene **2** (14%) as the first example of hexaheteroaryl[3]radialene. Among these diarylmethanes, dicyanodiphenylmethane **5e** has so far given the highest yield of 73%. The use of 3 equiv of **5b** and 6 equiv of sodium hydride in THF or DME after Fukunaga's procedure resulted in much poorer yields of **1b**.

The synthesis of hexaphenyl[3]radialene **1a** itself was attained by the careful reductive transformation of hexaiodide **1c**: the lithiation of **1c** with 16 equiv of *t*-BuLi at -90 °C for 30 min followed by protonation with *i*-PrOH furnished **1a** in 36% yield.



5a: R = H; **5b**: R = Br; **5c**: R = I
5d: R = CO_2Me; **5e**: R = CN

$$\mathbf{1c} \xrightarrow[2.\ i\text{-PrOH}]{1.\ 16\ \text{eq.}\ t\text{-BuLi, THF, -90 °C}} \mathbf{1a}$$

Radialenes **1a-e** and **2** are stable, crystalline substances. While **1a-e** are deep yellow to orange red in solutions (λ_{max} 467-488 nm; Table 1), **2** has a reddish purple color with the longest absorption at 545 nm, thus 2-thienyl group showing greater conjugative effect. ^1H NMR spectra of **1a-e** show their aromatic ring protons at relatively high field (e.g. δ 6.76-7.08 for **1a**; Table 1) due to the congestion of the six aryl groups. Similar high field shifts have also been observed for octaphenyl[4]radialene.[11,12] While the carbon chemical shifts of the cyclopropane ring are only slightly affected by the *para*-substituents of **1b-e** (δ 122.34-124.37), that of **2** is at considerably higher field (δ 117.30) probably reflecting the electron-donating nature of 2-thienyl group. Clear substituent effects are observed on the electrochemical reduction potentials of two reversible waves (CV); the reduction potentials are lower in the order of **1e** < **1d** < **1b** < **2** in correlation with the electronic nature of the aryl groups (Table 2). Hexacyanide **1e** is thus the strongest electron acceptor among **1a-e**; however, **1e** is a little weaker in electron accepting ability than trifluorenylidenecyclopropane ($^1E_{red}$ = -0.27, $^2E_{red}$ = -0.75 V vs. Ag/AgCl in DMF)[11] and comparable to **4** (-0.40 and -0.95 V in CH_2Cl_2[2]).

Table 1. Physical and spectral data of hexaaryl[3]radialenes[a,b]

1a: orange needles; mp 329-330 °C (dec.); MS (FAB) m/z = 534 (M^+); ^{1}H-NMR: δ = 6.78 (m, 24H), 7.08 (tt, J = 7.3, 1.7 Hz, 6H); ^{13}C-NMR: δ = 118.24, $\underline{123.85}$, 126.60, 126.86, 130.26, 141.26; UV-Vis: λmax [nm] (log ε) 236 (4.53), 245 (4.50), 275 (4.53), 467 (4.42).

1b: yellow orange needles; mp 341-342 °C (dec.); MS (FAB) m/z = 1008 (M^+); ^{1}H-NMR: δ = 6.64 (d, J = 8.6 Hz, 12 H), 7.01 (d, J = 8.6 Hz, 12 H); ^{13}C-NMR: δ = 117.92, $\underline{122.34}$, 122.55, 130.21, 131.64, 139.14; UV-Vis: λmax [nm] (log ε) 287 (4.71), 354 sh (4.09), 485 (4.64).

1c: yellow orange needles; mp 363-364 °C (dec.); MS (FAB) m/z = 1290 (M^+); ^{1}H-NMR: δ = 6.49 (d, J = 8.3 Hz, 12H), 7.21 (d, J = 8.3 Hz, 12H); ^{13}C-NMR: δ = 94.09, 117.84, $\underline{122.64}$, 136.24, 139.69; UV-Vis: λmax [nm] (log ε) 282 (4.90), 304 sh (4.82), 361 sh (4.51), 492 (4.73).

1d: yellow brown needles; mp 301-302 °C ; MS (FAB) m/z = 882 (M^+); ^{1}H-NMR: δ = 3.89 (s, 18H), 6.83 (d, J = 8.6 Hz, 12H), 7.45 (d, J = 8.6 Hz, 12H); ^{13}C-NMR: δ = 52.01, 120.02, $\underline{124.37}$, 128.25, 129.61, 129.85, 144.39, 166.38; IR (KBr) ν [cm^{-1}] 1724 (C=O); UV-Vis: λmax [nm] (log ε) 246 sh (4.75), 305 (4.98), 488 (4.70).

1e: reddish orange needles; mp 400-402 °C (dec.); MS (FAB) m/z = 685 ($[M+H]^+$); ^{1}H-NMR (DMSO-d_6): δ = 6.10 (d, J = 8.3 Hz, 12H), 6.53 (d, J = 8.3 Hz, 12H), 6.10; ^{13}C-NMR (DMSO-d_6): δ = 110.69 (CN), 118.24, 120.61, $\underline{123.24}$, 130.51, 130.89, 143.43; IR (KBr) ν [cm^{-1}] 2225 (CN); UV-Vis: λmax [nm] (log ε) 302 (4.94), 488 (4.65).

2: reddish brown needles; mp 295-296 °C; MS (FAB) m/z = 570 (M^+) ^{1}H-NMR: δ = 6.53 (dd, J = 3.6, 1.0 Hz, 6H), 6.63 (dd, J = 4.9, 3.6 Hz, 6H), 7.22 (dd, J = 4.9, 1.0 Hz, 6H); ^{13}C-NMR: δ = 109.29 $\underline{117.30}$, 126.49, 126.79, 129.49, 144.95; UV-Vis: λmax [nm] (log ε) 230 (4.57), 310 (4.43), 395 (3.93), 545 (4.68).

[a] ^{1}H and ^{13}C-NMR spectra were taken at 270 MHz and 67.8 MHz, respectively, in $CDCl_3$ unless otherwise noted, and UV-Vis spectra in CH_2Cl_2. [b] Underlines indicate the chemical shifts of cyclopropane carbons.

Table 2. Reduction potentials of hexaaryl[3]-radialenes by cyclic voltammetry[a,b]

Compound	$^1E_{red}$	$^2E_{red}$
1b	-0.93	-1.41
1d	-0.67	-0.97
1e	-0.50	-0.75
2	-1.12	-1.58

[a] V vs Ag/AgCl, 0.1 M nBu_4NClO_4 in DMF, sweep rate 100 mV/s. [b] **1a** could not be measured because of poor solubility.

Hexacyanide **1e** formed a good single crystal with inclusion of 1 mol equiv of dichloromethane and its structure was confirmed by X-ray structure analysis (Fig. 1).[13] The notable structural features are; (i) the [3]radialene carbons are nearly coplanar with a maximum deviation of 0.14 Å out of the best plane, (ii) the C-C bond lengths in the three-membered ring are about 1.42 Å similar to the values observed for **4**, (iii) the two phenyl groups on each methylene carbon are twisted by 40-44° from the [3]radialene plane in the

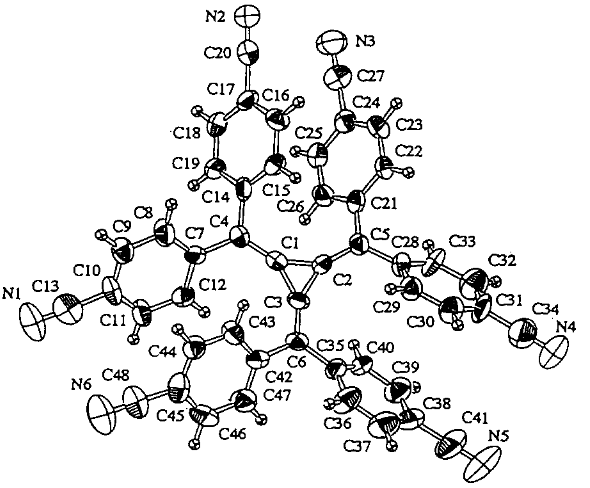


Fig. 1. Molecular structure of **1e**. Selected bond lengths [Å] and angles [°] (standard deviation in parentheses; the acuracy is lowered due to inclusion of CH_2Cl_2): C1-C2, 1.42(2); C1-C3, 1.42(2); C2-C3, 1.43(2); C1-C4, 1.37(1); C2-C5, 1.35(1); C3-C6, 1.35(1); C2-C1-C3, 60.2(8); C1-C2-C3, 59.8(8); C1-C3-C2, 59.9(8); C1-C2-C5, 146(1); C2-C3-C6, 149(1); C3-C1-C4, 150(1); C1-C4-C7, 122(1); C2-C5-C21, 120(1); C3-C6-C35, 119(1); C7-C4-C14, 118(1); C21-C5-C28, 119(1); C35-C6-C42, 119(1); C1-C4-C7-C8, 140(1); C1-C4-C14-C15, -43(1); C2-C5-C21-C22, 136(1); C2-C5-C28-C29, -38(1); C3-C6-C35-C36, 143(1); C3-C6-C42-C43, -35(1).

opposite direction, thus placing the ortho and meta protons of one phenyl group in the shielding region of the other and thus reducing the electronic effects of the *para*-substituents to the radialene moiety, and (iv) the three sets of two neighboring phenyl groups on the adjacent methylene carbons face each other with distance of 3.6-4.0 Å; hence, the six phenyl groups as a whole take a conformation of double three-bladed propeller.

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8. The acidity (p*K*a) of these compounds was determined in THF-hexane (5:1) by measuring equilibrium (AcOD quenching and measurement of deuterium incorporation by ^{1}H-NMR) using triphenylmethane (p*K*a = 30.6[10]) and 1,1,1,3,3,3-hexamethyldisilazane (p*K*a = 25.8[14]) as standards.
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12. ^{1}H-NMR (600 MHz, 30 °C): δ = 6.74 (somewhat br. d due to dynamic process, J = 8.6 Hz, 16H), 6.82 (somewhat br. t, J = 8.6 Hz, 16H), 6.92 (somewhat br. t, J = 8.6 Hz, 8H).
13. Crystal data for $\mathbf{1e{\bullet}CH_2Cl_2}$:$C_{49}H_{24}N_6Cl_2$, crystallized from benzene-dichloromethane, approximate dimension: 0.20 x 0.20 x 0.40 mm; M = 767.67, orthorhombic, space group *Pbca* (#61), a = 15.326(9), b = 46.529(6), c = 11.401(6) Å, V = 8129(6) Å^3, Z = 8, ρ_{calcd} = 1.254 g cm^{-3}, Mo$K\alpha$ radiation, $2\theta \leq 50°$, 6578 unique reflections, T = 296 K. The structure was solved by direct methods (SHELXS-86) and refined with the TEXSAN crystallographic software package of Molecular Structure Corporation. All the non-hydrogen atoms were refined anisotropically. Final R = 0.067, Rw = 0.074 for 514 variables and 1668 observed reflections with $F > 5\sigma$. Further details of the crystal structure investigations may be obtained from the director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation.
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