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Synthesis, Structure, and Properties of Hexaaryl[3]radialenes[1]

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A number of hexaphenyl[3]radialene derivatives were synthesized in modest to good yields by the reaction of tetrachlorocyclopropene with diarylmethyl anion followed by oxidation with oxygen. That the acidity of diarylmethane is higher than that of diphenylmethane is found to be an important factor for the successful synthesis. Lithiation and protonation of hexa(4-iodophenyl)[3]radialene thus obtained leads to the first synthesis of hexaphenyl[3]radialene. These hexaaryl[3]radialenes are stable, orange to red, crystalline substances. An X-ray crystallographic analysis of hexa(4-cyanophenyl)[3]radialene reveals a double three-bladed propeller conformation. The effects of substituents in the phenyl groups on their properties are most clearly seen in their electrochemical reduction potentials; among hexaphenyl[3]radialenes here obtained, hexa (4-nitrophenyl)[3]radialene (${}^{1}E_{\mathrm{red}} = -0.30$ V, ${}^{2}E_{\mathrm{red}} = -0.45$ V) is found to be a good electron acceptor stronger than *p*-benzoquinone.

[3]Radialene (trimethylenecyclopropane) is the smallest member of [*n*]radialenes (all *exo*-methylenecycloalkanes) and has received considerable attention from both theoretical and experimental points of view owing to its unique structure and electronic properties.[2,3] Although several tris(dibenzoarylidene)cyclopropanes (**2**) have been synthesized,[4] 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 novel extended π-electron systems incorporating [3]radialene framework(s). We here report the synthesis, structure, and properties of **1a** and its derivatives **1b**—**h**.[1]

Early attempts to synthesize **1a** through dehydration or dehydrobromination of the precursor alcohols or bromides similar to the synthesis of the parent compound were reported to be unsuccessful.[5] More recently, cyclo-oligomerization of copper and nickel carbenoids generated from 1,1-dihaloalkenes was found to be a simple and effective method for the synthesis of [3] to [6]-radialenes.[4c—e,6a,b] Application of the cyclo-oligomerization method to 1,1-dihalogeno-2,2-diphenylethenes, however, has yielded octaphenyl[4]radialene and tetraphenylbutatriene without formation of **1a**.[6a,b] Another effective way to [3]radialenes is Fukunaga's synthesis of the dianions of hexacyano- and hexakis(methoxycarbonyl)[3]radialene, (**3a**) and (**3b**),[7] by the reaction of tetrachlorocyclopropene with the anions of malononitrile and dimethyl malonate. This method was recently applied to the synthesis of a hexaethynyl[3]radialene derivative **4** though the yield was only modest.[3] We also attempted to apply this method to the synthesis of **1a** using diphenylmethyl anion, but in vain. The question then is what are the governing factors for the successful application of Fukunaga's method. Dialkyl malonate and malononitrile are typical active methylene compounds with considerable acidity (pK_a = 13.4 and 11.4, respectively).[8,9] The methylene protons of diethynylmethanes (1,4-pentadiynes) would be somewhat more acidic, though no data is available, than diphenylmethane **5a** (pK_a = 32.3),[8] because an ethynyl group (sp carbons) should be more electron-withdrawing than a phenyl group (sp^2 carbons). This consideration led us to suppose that acidity of active methylene compounds, in other words stability of their conjugate bases, could be an important factor. We therefore examined the reaction of tetrachlorocyclopropene with the carbanions of substituted diphenylmethanes and found that diarylmethanes having higher acidity than **5a** do afford hexaaryl[3]radialenes in modest to good yields (Chart 1).

Results and Discussion

Synthesis. For a typical synthesis, the reaction of tetrachlorocyclopropene with six equivalents of di(4-bromophenyl)methyllithium (pK_a of the conjugate acid **5b** = 29.7; Table 1) in a mixed solvent of THF-DMSO (1/1 v/v) at 0 °C to room temperature for 1 h, followed by oxidation with oxygen, afforded hexa (4-bromophenyl)[3]radialene (**1b**) as yellow-orange crystals in 25—35% yield. We assume the intermediacy of dianion **6b** as in the case of Fukunaga's synthesis of **3a** and **3b**. The use of three molar amounts of **5b** and six molar amounts of sodium hydride in THF or DME after Fukunaga's procedure resulted in much poorer yields of **1b**. The co-solvent DMSO, which has weaker acidity (pK_a = 35)[8] than **5b**, did not interfere with the reaction and played a favorable role for giving the reaction mixture a higher homogeneity. THF was added also to keep homogeneity of the reaction mixture under the use of commercial hexane solution of *n*-BuLi for the lithiation. In similar ways, hexa (4-iodophenyl)-, hexa (4-carbomethoxyphenyl)-, hexa (4-cyanophenyl)-, and hexa(4-nitrophenyl)[3]radialenes, (**1c**)—(**1f**), were obtained from the corresponding diarylmethanes **5c**—**5f** (pK_a = 15.8—29.4; Table 1). This procedure was also applicable

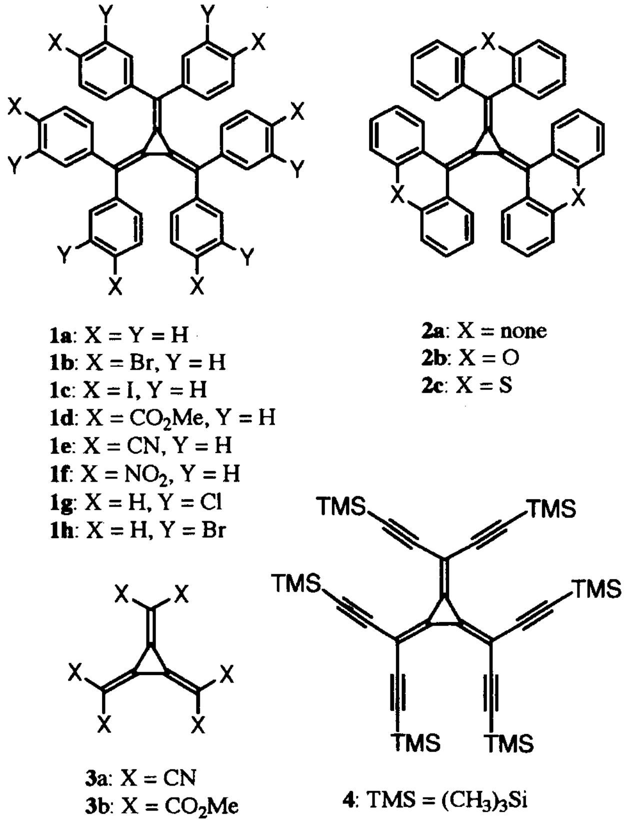


Chart 1.

to the synthesis of *meta*-substituted hexaphenyl[3]radialenes such as hexa(3-chlorophenyl)- and hexa(3-bromophenyl)-[3]radialene, (**1g**) and (**1h**), in moderate yields, Scheme 1. Fluorene too afforded **2a** in 14% yield. The use of diphenylmethane under similar conditions again practically failed to give hexaphenyl[3]radialene (**1a**) itself, although thin layer chromatographic analysis suggested its formation in a trace amount.

The synthesis of **1a** was attained in 36% yield by careful lithiation of hexaiodide **1c** with *t*-BuLi at −100 °C, followed by protonation with 2-propanol. Use of *n*-BuLi or lithiation at higher temperatures resulted in greater decomposition of **1c** and hence poorer yield of **1a**, Scheme 2.

Table 1. Acidity (pK_a) of Diphenylmethanes **5a**—**5h** and Related Compounds[a)]

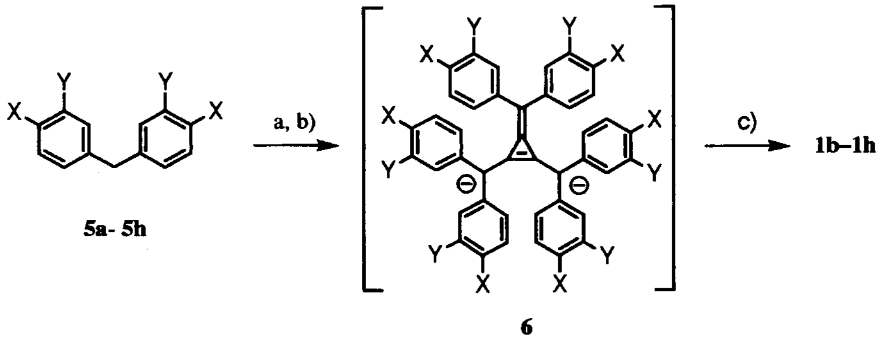
Compound	pK_a value	Remark
Diphenylmethane **5a**	32.3	Ref. 8
4,4′-Dibromo- **5b**	29.7	This work
4,4′-Diiodo- **5c**	29.4	This work
4,4′-Bis(methoxycarbonyl)- **5d**	27.3	This work
4,4′-Dicyano- **5e**	23.0	Ref. 16
4,4′-Dinitro- **5f**	15.8	Ref. 17
3,3′-Dichloro- **5g**	28.8	This work
3,3′-Dibromo- **5h**	29.8	This work
Fluorene	22.6	Ref. 10
Triphenylmethane[b)]	30.6	Ref. 10
Hexamethyldisilazane[b)]	25.8	Ref. 11

a) See the experimental section for details of measurements.
b) Used as standard compounds.

pK_a Measurements of Some Substituted Diphenylmethanes. Since the number of diarylmethanes whose acidity were reported is limited, the acidity of the substituted diphenylmethanes, here used, of unknown acidity was determined by NMR spectroscopic measurement of the equilibrium constant between the anion of a substrate and a standard compound such as triphenylmethane (pK_a = 30.6)[10] or hexamethyldisilazane (pK_a = 25.8).[11] *n*-BuLi in hexane was used for the anion formation, AcOD for quenching after the equilibration, and ^{1}H NMR for measuring the degree of deuterium incorporation into the recovered mixture. The pK_a values thus obtained are listed in Table 1 together with known values of related compounds.

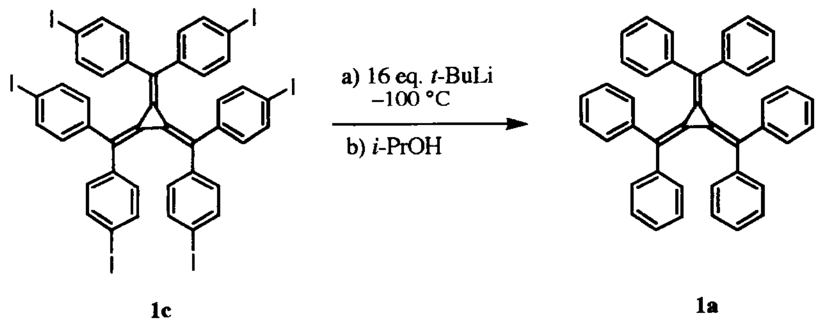
Properties of Hexaaryl[3]radialenes 1a—1h. Hexaaryl[3]radialenes **1a**—**1h** except for the nitro-substituted compound **1f** are stable, orange to red, crystalline substances. Although **1f** was obtained in reasonably pure form for spectroscopic analyses, it tended to decompose somewhat during recrystallization, preventing the preparation of samples pure enough for the elemental analysis. These radialenes, in particular the unsubstituted one **1a**, have rather low solubility in organic solvents.

Table 2 summarizes UV-vis and NMR spectral data of **1a**—**1h**. Radialenes **1a**—**1h** show strong absorptions in the



Reagents and conditions: a) 1 eq. *n*-BuLi/THF–DMSO (1/1 v/v), 0 °C; b) 1/6 eq. tetrachlorocyclopropene (neat); c) Bubbling of O_2, 0 °C.

Scheme 1.



Scheme 2.

visible region of about 460—500 nm responsible for their deep coloration. Hexaphenyl[3]radialene (**1a**) shows the strong longest absorption at λ_{max} = 467 nm (log ε = 4.42), which is appreciably shorter than those of **4** (567 nm)[3] and **2a** (615 nm).[4a] The effects of the *para*-substituents on the UV-vis spectra are not so significant; the largest bathochromic shift is only 27 nm for hexanitro compound **1f** (494 nm). A reason for the rather small substituent effects may be noncoplanarity of the molecules due to steric crowding between the aryl groups. The high field appearance of aromatic protons of **1a**—**1h** (δ = 6.1—7.0) conforms to the noncoplanarity of the molecules around the hexaaryl groups. A similar high field shift of aromatic protons have also been observed for octaphenyl[4]radialene[6a].In accord with the small substituent effects on UV-vis spectra, the ^{13}C NMR chemical shifts of cyclopropane carbons of **1a**—**1h** are observed in a narrow range of δ = 122.34 to 124.37. No clear trend is observed in terms of the electronic nature of the substituents. These chemical shifts are slightly higher than those of **2a** (δ = 124.45)[4a] and **4** (δ = 126.7).[3]

The substituent effects are, however, more significant on the electrochemical properties (Table 3). Upon cyclic voltammetry (CV) in DMF, radialenes **1b**, **1d**, **1e**, **1f**, **1g**, and **1h** exhibited two reversible reduction waves between −0.30 V and −1.50 V (V vs. Ag/AgCl) probably corresponding to the formation of anion radicals and dianions. On the other hand, no oxidation waves were observed up to +1.5 V in acetonitrile. The poor solubility of **1a** made the measurement of its redox potenitals difficult. The reduction potentials are lower (less negative) in the order of **1f** < **1e** < **1d** < **1b** with a relatively wide range of 0.63 V for the first reduction potentials (similar difference for the second reduction potentials, too) in line with the electron-withdrawing properties of the *para*-substituents. In particular, the first reduction potential of hexanitro compound **1f** (−0.30 V) is 0.06 V lower than that of **2a** ($^1E_{red}$ = −0.36 V) which is in turn 0.04 V lower than *p*-benzoquinone ($^1E_{red}$ = −0.40, $^2E_{red}$ = −1.25 V under the same conditions). The second reduction po-

Table 2. NMR and UV-vis Spectral Data of Hexaaryl[3]radialenes **1a**—**1h**

Compound	^{1}H NMR/δ[a)]	^{13}C NMR/δ[b,c)]	UV-vis/λ_{max} nm (log ε)[d)]
1a	6.76 (t, *J* = 7.4 Hz, 12H, *meta*),[e)] 6.81 (dd, *J* = 1.3, 7.4 Hz,12H, *ortho*), 7.08 (tt, *J* =1.3, 7.4 Hz, 6H, *para*)	118.24, 123.85, 126.60, 126.86, 130.26, 141.26	236 (4.53), 245 (4.50), 275 (4.53), 467 (4.42)
1b	6.64 (d, *J* = 8.6 Hz, 12 H), 7.01 (d, *J* = 8.6 Hz, 12 H)	117.92, 122.34, 122.55, 130.21, 131.64, 139.14	287 (4.71), 354 sh (4.09), 485 (4.64)
1c	6.49 (d, *J* = 8.3 Hz, 12H), 7.21 (d, *J* = 8.3 Hz, 12H)	94.09, 117.84, 122.64, 136.24, 139.69	282 (4.90), 304 sh (4.82), 361 sh (4.51), 492 (4.73)
1d	3.89 (s, 18H), 6.83 (d, *J* = 8.6 Hz, 12H), 7.45 (d, *J* = 8.6 Hz, 12H)	52.01, 120.02, 124.37, 128.25, 129.61, 129.85, 144.39, 166.38	246 sh (4.75), 305 (4.98), 488 (4.70)
1e[f)]	6.10 (d, *J* = 8.3 Hz, 12H), 6.53 (d, *J* = 8.3 Hz, 12H)	110.69 (CN), 118.24, 120.61, 123.24; 130.51, 130.89, 143.43	302 (4.94), 488 (4.65)
1f[f)]	6.26 (d, *J* = 8.9 Hz, 12H), 6.93 (d, *J* = 8.9 Hz, 12H)	121.57, 122.18, 123.15, 130.95, 145.25, 147.08	257 (4.70), 320 (4.75), 494 (4.59)
1g	6.73 (m, 6H), 6.81 (m, 6H), 6.88 (t, *J* = 7.9 Hz, 6H), 7.16 (ddd, *J* = 1.3, 2.0, 7.9 Hz, 6H)	118.48, 122.99, 128.14, 128.43, 128.51, 130.68, 133.83, 142.15	280 (4.62), 471 (4.63)
1h	6.78 (m, 12H), 6.96 (m, 6H), 7.18 (m, 6H)	118.83, 121.99, 122.75, 128.71, 130.99, 133.44, 142.19	281 (4.53), 474 (4.53)

a) Measured at 270 MHz in $CDCl_3$ unless otherwise noted. b) At 67.8 MHz in $CDCl_3$ unless otherwise noted. c) The values underlined are assigned to the cyclopropane carbons. d) In CH_2Cl_2. e) At 600 MHz. f) In $(CD_3)_2SO$.

Table 3. Reduction Potentials of Hexaaryl[3]radialenes and Related Compounds[a)]

Compound	$^1E_{red}$/V	$^2E_{red}$/V	$\Delta E(^1E_{red} - ^2E_{red})$/V
1b	−0.93	−1.41	0.48
1d	−0.67	−0.97	0.30
1e	−0.50	−0.75	0.25
1f	−0.30	−0.45	0.15
4	−0.36	−0.83	0.47
BQ[b)]	−0.40	−1.25	0.85

a) Measured by cyclic voltammetry, V vs. Ag/AgCl in 0.1 M Bu_4NClO_4/DMF (F_c/F_c^+ = +0.52 V), sweep rate 100 mV s^{-1}, 20 °C. b) *p*-Benzoquinone.

tentials of these radialenes are markedly lower than that of *p*-benzoquinone, indicating a decrease of electronic repulsion in the dianions owing to the extended π-systems, regardless of non-coplanarity of the molecules. Radialene **1f** is thus the strongest electron acceptor among the hexaaryl[3]radialenes so far known, including **2a**—**2c**.

Hexacyano compound **1e** formed a good single crystal from dichloromethane with inclusion of one mole equivalent of the solvent, and its structure was confirmed by X-ray crystallographic analysis (Figure 1, Tables 4 and 5).[12] The notable structural features are : (i) the [3]radialene framework is nearly planar 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 1.42 Å on average, similar to the values observed for **4**; (iii) the two 4-cyanophenyl groups on each methylene carbon are twisted by 40—44° from the [3]radialene plane in the opposite direction, which places the *ortho* and *meta* protons of one 4-cyanophenyl group in the magnetically shielding region of the other to cause high field shift of the aromatic protons, as observed in the ^{1}H NMR spectra and reduces the electronic effects of the *para*-substituents to the radialene moiety; and (iv) the three sets of two neighboring 4-cyanophenyl groups on the adjacent methylene carbons face each other with a separation of 3.6—4.0 Å, the six aryl groups as a whole thus taking the conformation of a double three-bladed propeller.

Conclusion

The present findings related to the importance of acidity of methylene compounds in the synthesis of [3]radialene derivatives from tetrachlorocyclopropene would expand the applicability of Fukunaga's radialene synthesis, promising the synthesis of good number of hexaaryl[3]radialenes other than those here reported. Except for hexanitro compound **1f**, the hexaaryl[3]radialenes are fairly stable and hence could be subjected to functional group transformation. In particular, in view of recent development of transition-metal mediated coupling or functionalization of halobenzenes, halogen-substituted hexaphenyl[3]radialenes would open ways to a good variety of novel hexaaryl[3]radialenes whose direct syntheses from tetrachlorocyclopropene are difficult.

Experimental

Table 4. Crystal Data for Hexa(4-cyanophenyl)[3]radialene

Chemical formula	$C_{49}H_{24}Cl_2N_6$
Molecular weight	767.67
Crystal size/mm	0.2 × 0.2 × 0.4
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	15.326(9)
b/Å	46.529(6)
c/Å	11.401(6)
V/Å^3	8129(6)
Z	8
D_{calcd}/g cm^{-3}	1.254
μ(Mo $K\alpha$)/cm^{-1}	2.02
2θ range/degree	5 < θ < 50.0
Scan width/degree	(0.94 + 0.30 tan θ)
Scan mode	ω–2θ
Scan rate/degree min^{-1}	16.0
No. of reflection measured	7365
No. of independent reflection observed	1668
No. of parameters	514
R	0.067
R_w	0.074

The melting points were measured on a hot-stage apparatus and are uncorrected. Mass spectra were recorded with a JEOL JMS-SX 102 spectrometer by EI or FAB method. IR spectra were measured on a Perkin Elmer 1650 spectrophotometer in KBr disks and only significant absorption bands are reported. UV-vis spectra were taken in CH_2Cl_2 solution on a Hitachi U-3400 spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ solution on a JEOL EX-270 (270 MHz) or JEOL GCX-400 (400 MHz) spectrometer, and were recorded in δ-value from TMS as an internal standard. Cyclic voltammetry was performed in DMF on a Yanaco Model P-1100 voltammetric analyzer using Et_4NClO_4 as an electrolyte. Tetrachlorocyclopropene, [13] di(4-cyanophenyl)-methane **5e**,[14] and di(4-nitrophenyl)methane **5f**[15] were prepared according to literature.

Standard Procedure for Acidity Measurements : In a 50 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar, rubber septum, and Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, triphenylmethane (733 mg, 3.00 mmol) or hexamethyldisilazane (484 mg, 3.00 mmol) and THF (10 mL) were placed at 0 °C. A hexane solution (1.671 M, titrated by Gilman method) (1 M = 1 mol dm^{-3}) of butyllithium (1.80 mL, 3.00 mmol) was added dropwise via syringe. After 30 min, well-dried diarylmethane (3.00 mmol) was added quickly and the resulting mixture was stirred for 1 h at 0 °C. Acetic acid-d_1 (0.4 mL, 4.0 mmol) was added in one portion via syringe under vigorous stirring. After 1 h, the mixture was poured into water (30 mL) and extracted with benzene (30 mL×2). The organic layer was washed with water and brine, and dried over $MgSO_4$. The solvent was evaporated and the residue was passed through a short column packed with silica gel (10 g) eluted with benzene. The mixture of recovered triphenylmethane and diarylmethane was dried in vacuo. Molar ratio of deuterium incorporation and then equilibrium constant (K_{eq}), were calculated from the integral ratio of methylene (diarylmethane) and methyne (e.g. triphenylmethane) proton signal in the ^{1}H NMR spectra (270 MHz). Duplicate runs showed an error in deuterium-incorporation to be less than 3%.

Standard Procedure for Hexaaryl[3]radialenes 1b—1h : A 50 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar, rubber septum, and Y-shaped adaptor for nitrogen inlet

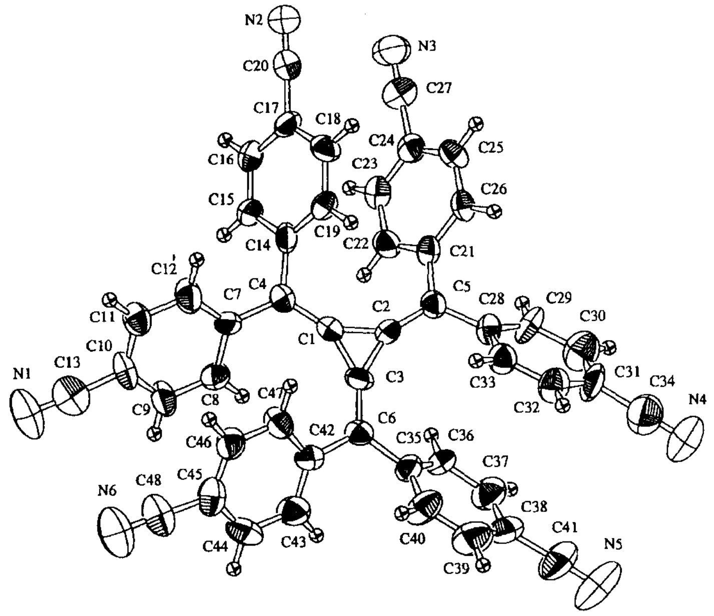


Fig. 1. ORTEP drawing of **1e** with thermal ellipsoids at 50% probabilities (solvent molecules are omitted for simplicity).

and outlet attached to a bubbler was charged with anhydrous THF (10 mL) and dry DMSO (10 mL) under nitrogen atmosphere. A hexane solution (1.6 M) of butyllithium (3.75 mL, 6.0 mmol) was added dropwise at 0 °C (ice bath). After stirring for 30 min, well-dried diarylmethane (6.0 mmol) was added and the mixture was stirred for 30 min. Into the deep colored reaction mixture, tetrachlorocyclopropene (0.12 mL, 1.0 mmol) was added dropwise via syringe. The mixture was stirred at 0 °C for 30 min, then at room temperature for an additional 30 min, and again cooled to 0 °C. Oxygen gas was bubbled into the reaction mixture for 30 min at 0 °C and then for 1 h at room temperature. Water (50 mL) was added and the mixture was extracted with benzene or ethyl acetate. The organic phase was washed with water and then brine, and dried over $MgSO_4$. The solvent was removed by evaporation and the residue was chromatographed at first on alumina (30 g) eluted with benzene or ethyl acetate. The mixture of crude products from the deep colored fraction was again chromatographed, this time on silica gel (30 g), and eluted with appropriate solvent (TLC analysis for the choice of solvent) capable of separation of the corresponding [3]-radialene from the recovered diarylmethane. The colored fraction was collected and the solvent was removed. Benzene (2 mL) and then hexane were added to the solid residue, and the precipitates were collected by filtration. The products thus obtained were fairly pure and for further purification they were recrystallized from benzene, chlorobenzene, or ethyl acetate.

1b : Yield 25—35%; yellow orange needles; mp > 340 °C (decomp) ; MS (FAB) m/z = 1008 (M^+); IR 1589, 1517, 1345, 852 cm^{-1}. Found : C, 49.98; H, 2.40%. Calcd for $C_{42}H_{24}Br_6$: C, 50.04; H, 2.40%.

1c : Yield 30%; yellow orange needles; mp > 360 °C (decomp); MS (FAB) m/z = 1290 (M^+). Found : C, 39.27; H, 1.91%. Calcd for $C_{42}H_{24}I_6$: C, 39.10; H, 1.88%.

1d : Yield 21%; yellow brown needles; mp 301—302 °C ; MS (FAB) m/z = 882 (M^+); IR 2952, 1724 (CO), 1279, 1112, 854 cm^{-1}. Found : C, 73.27; H, 4.73%. Calcd for $C_{54}H_{42}O_{12}$: C, 73.46; H, 4.80%.

1e : Yield 73%; reddish orange needles; mp > 400 °C (decomp); MS (FAB) m/z = 685 ($[M+H]^+$); IR 3063, 2225 (CN),

Table 5. Selected Structural Parameters of **1e** Determined by X-Ray Analysis

Bond distances (Å)		Bond angles (°)		Torsion angles (°)	
C(1)–C(2)	1.42(2)	C(2)–C(1)–C(3)	60.2(8)	C(2)–C(3)–C(1)–C(4)	−178(2)
C(1)–C(3)	1.42(2)	C(1)–C(2)–C(3)	59.8(8)	C(1)–C(3)–C(2)–C(5)	179(2)
C(2)–C(3)	1.43(2)	C(1)–C(3)–C(2)	59.9(8)	C(1)–C(2)–C(3)–C(6)	174(2)
C(1)–C(4)	1.37(1)	C(2)–C(1)–C(4)	148(1)	C(4)–C(1)–C(3)–C(6)	6(4)
C(2)–C(5)	1.35(1)	C(3)–C(1)–C(4)	150(1)	C(4)–C(1)–C(2)–C(5)	−1(3)
C(3)–C(6)	1.35(1)	C(1)–C(3)–C(6)	150(1)	C(5)–C(2)–C(3)–C(6)	−5(4)
C(4)–C(7)	1.47(1)	C(2)–C(3)–C(6)	149(1)	C(1)–C(2)–C(5)–C(21)	−11(2)
C(7)–C(8)	1.38(1)	C(2)–C(3)–C(6)	154(1)	C(2)–C(3)–C(6)–C(35)	−6(2)
C(7)–C(12)	1.41(1)	C(1)–C(2)–C(5)	146(1)	C(3)–C(1)–C(4)–C(7)	−11(3)
C(8)–C(9)	1.38(1)	C(1)–C(4)–C(7)	122(1)	C(1)–C(4)–C(7)–C(12)	−39(1)
C(9)–C(10)	1.37(2)	C(1)–C(4)–C(14)	118(1)	C(1)–C(4)–C(14)–C(15)	−42(1)
C(10)–C(11)	1.38(2)	C(7)–C(4)–C(14)	118(1)	C(2)–C(5)–C(21)–C(26)	−40(1)
C(11)–C(12)	1.38(1)	C(4)–C(14)–C(15)	121(1)	C(2)–C(5)–C(28)–C(29)	−38(1)
C(10)–C(13)	1.44(2)	C(9)–C(10)–C(13)	119(1)	C(3)–C(6)–C(35)–C(40)	−36(1)
N(1)–C(13)	1.14(2)			C(3)–C(6)–C(42)–C(43)	−35(1)

1602, 1496, 844 cm^{-1}. Found: C, 83.90; H, 3.42; N, 12.25%. Calcd for $C_{48}H_{24}N_6$: C, 84.19; H, 3.53; N, 12.27%.

1f : Yield 40 %; deep red needles; mp > 150 °C (decomp); IR 3065, 1589, 1517 (NO_2), 1345 (NO_2), 852 cm^{-1}. FAB mass spectra did not show any peaks around or higher than the molecular weight of this compound.

1g : Yield 24%; orange fine needles; mp 258—260 °C; MS (FAB) m/z 740 (M^{+}; 4^{35}Cl·2^{37}Cl) with M^{+} pattern that matched with the calculated one ; IR 3059, 1541, 1471, 1078, 780, 692 cm^{-1}. Found: C, 67.79; H, 3.24%. Calcd for $C_{42}H_{24}Cl_6$: C, 68.04; H, 3.26%.

1h : Yield 48%; orange fine needles; mp 267—268 °C; MS (FAB) m/z 1008 (M^{+}; 3^{79}Br·3^{81}Br); IR 3060, 1583, 1469, 1072, 785, 694 cm^{-1}. Found: C,49.69; H, 2.40%. Calcd for $C_{42}H_{24}Br_6$: C, 50.04; H, 2.40%.

Hexaphenyl[3]radialene 1a : In a 50 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar, rubber septum, and Y-shaped adaptor for nitrogen inlet and outlet attached to a bubbler, hexa (4-iodophenyl)[3]radialene **1c** (258 mg, 0.2 mmol) and anhydrous THF (20 mL) were placed under nitrogen atmosphere. The mixture was cooled at −100 °C and a pentane solution (1.6 M) of *t*-butyllithium (2.0 mL, 3.2 mmol) was added dropwise. After stirring for 30 min, 2-propanol (0.3 mL) was added via syringe; the mixture was stirred for 30 min, then poured into water (30 mL), and extracted with benzene (20 mL×2). The organic layer was washed with water and brine, and dried over $MgSO_4$. The solvent was evaporated and the residue was chromatographed on silica gel (15 g) eluted with hexane/benzene (1 : 1 v/v) to give **1a** (38 mg, 36% yield): orange needles; mp 329—330 °C (decomp); MS (FAB) m/z = 534 (M^{+}); IR 3048, 1538, 1486,768, 755, 692 cm^{-1}. Found: C, 94.17; H, 5.60%. Calcd for $C_{42}H_{30}$: C, 94.35; H, 5.66%.

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