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Synthesis and solid state structures of increasingly sterically crowded 1,4-diiodo-2,3,5,6-tetraarylbenzenes: a new series of bulky benzenes and aryls

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A series of very bulky 1,4-diiodo-2,3,5,6-tetraarylbenzenes $I_2Ar_4C_6$ (Ar = 4-$^tBuC_6H_4$, **1**; Ar = 3,5-$^tBu_2C_6H_3$, **2**; Ar = 2,4,6-$Me_3C_6H_2$, **3**) have been prepared by a rapid, convenient procedure involving sequential reaction of hexabromobenzene with the appropriate Grignard reagent in excess, followed by addition of excess elemental iodine. The new materials **2** and **3** were isolated in 18 and 28% yields, respectively. The solid state structures of **1–3** have been investigated by single crystal X-ray techniques. Interesting distortions in the structures of these hexasubstituted benzenes are observed upon the increasing steric pressures in **1–3**. For example, while the structures of **1** and **2** contain central planar benzene rings, steric interactions in **3** produce a non-planar central benzene ring. Regardless of these factors, the carbon–iodine bond lengths in **1–3** are essentially constant (2.108–2.118 Å).

Steric hindrance from bulky substituents, especially bulky arenes, is a key design element for the stablization of a multitude of reactive species from carbenes to main group–main group multiple bonds. Introduction of six substituents onto a benzene ring can dramatically increase its steric bulk and significantly alter its fundamental properties and utility. For example, hexaarylatedbenzenes have been used as integral components for charge storage devices and as precursors to graphitic materials.[1–3] Tetraarylatedbenzenes have also been utlized in many ways. For example, 2,3,5,6-tetraphenylphenols have been successfully employed as cyclometalation resistent ligands to metal centers.[4] 2,3,5,6-Tetrarylbenzenes can be thought of as potential difunctional analogues of *meta*-terphenyls (1,3-$Ar_2C_6H_4$), that are being increasingly utilized in main group and transition metal chemistry.[5] Hart and colleagues have reported a novel and remarkably simple synthesis of 2,3,5,6-tetraarylbenzenes and select 1,4-dibromo-2,3,5,6-tetraarylbenzenes.[6] We have thus recently adapted the Hart procedure to prepare 1,4-diiodo-2,3,5,6-tetra(*para-tert*-butylphenyl)benzene (**1**).[7] This material allowed us to construct materials having two low-coordinate phosphorus centers spanned by a single phenylene group. During the course of this work we determined the single crystal structure of **1**. In addition, we examined a variety of related 1,4-diiodo-2,3,5,6-tetraarylbenzenes as possible bridging groups, and have obtained single crystal X-ray structures of two more members of this family of compounds. The structure of **1** and the two other derivatives show how increasingly sterically congested 1,4-diiodo-2,3,5,6-tetrarylbenzenes can be realized by increasing the size of the peripheral aromatic rings. Herein we present the results of the synthesis and structural work on these new materials.

Results and discussion

Synthesis

Compounds **1–3** were prepared by modifying the convenient one pot procedure that Hart and coworkers used to prepare 2,3,4,6-tetraarylbenzenes and 1,4-dibromo-2,3,5,6-tetrarylbenzenes (Scheme 1). Stirring mixtures of hexabromobenzene and the requisite Grignard reagents (overnight), followed by addition of elemental iodine in THF and workup of the resulting mixture led to fair to good yields of **1–3**. The synthesis of **1** in 68% yield has been reported earlier.[7] Our efforts to utilize 2,3,5,6-tetraarylbenzenes as linking groups focused largely on compound **1**, for it was the material that presented the best combination of good yields and easy workup. For compound **2**, while workup of the final reaction mixture was straightforward, the yields tended to be disappointingly low (28%). The synthesis and purification of **3** proved particularly problematic. Pure **3** was most readily obtained by filtration of concentrated solutions of **3** from the initial ether extracts of the reaction mixtures in low yields (18%). Attempts to maximize yields by complete evaporation of ether extracts made isolation of **3** from byproducts difficult. In general, the best means of obtaining **1–3** relatively free of other materials proved to be simple filtration of ether extracts of the crude reaction mixture after reduction of the solution volume. While these other products were not isolated or fully characterized, the presence of multiple ^1H NMR signals in the vinylic region (*ca.* $\delta \sim 6$ ppm) for the materials remaining in the ether filtrate indicated the presence of **1–3** and other products that were probably related to side products reported during synthesis of 2,3,4,6-tetramesitylbenzene.[8] From this reaction the unusual

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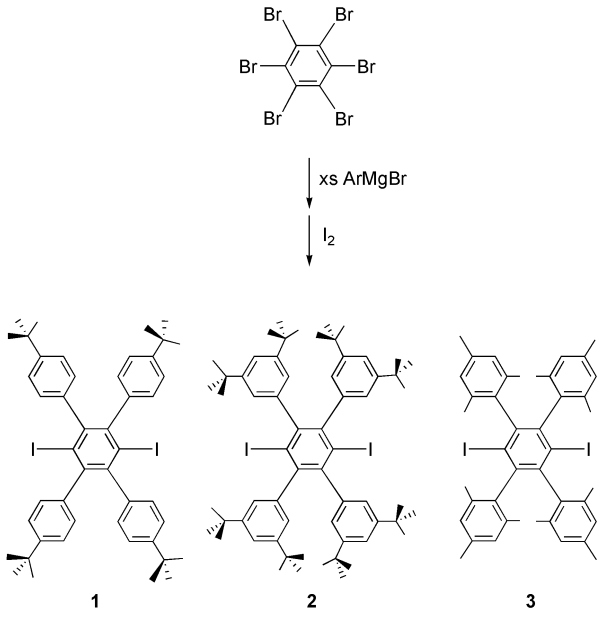


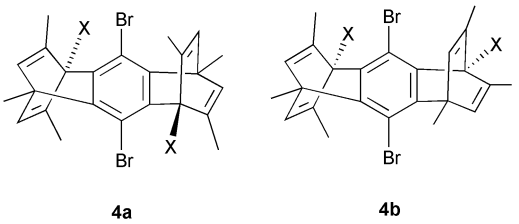
Scheme 1 Synthesis of diiodotetrarylbenzenes.

products of aryne cycloadditions (Chart 1, X = H) were identified and one such species structurally characterized (Chart 1, **4a**). We thus tentively assign the distribution of other products formed along with **3** as **4a** and **4b** with X = I. Initial assays of the reaction of hexabromobenzene and either 2,6-dimethylphenylmagnesium bromide or 2,6-dimethyl-4-*tert*-butylphenylmagnesium bromide by ^{1}H NMR showed the presence of substantial amounts of similar aryne cycloaddition products, and thus these systems were not pursued further.

Solid-state structures of 1–3

Crystals of **1** were grown from toluene and the results of a single crystal X-ray structural analysis are presented in Fig. 1 (top). Selected bond distances and angles are listed in Table 1. The central benzene ring in **1** is quite planar and regular (mean carbon atom deviation is 0.002 Å from the best least-squares plane). The carbon–iodine bond lengths of 2.118(3) Å are normal and nearly identical to the values for **2** and **3**. The four outer aromatic rings are all canted in the same direction about the central ring and are offset from coplanarity with this ring. A dihedral angle (τ) can be used to describe the orientation of the peripheral aromatic rings relative to the benzene ring. Average τ values of 67° and 72° are found for **1**. Compound **1** has been previously used to prepare compounds **5** and **6** (Chart 2).[7] For the section of **5** that contains the tetraarylbenzene, τ values for the peripheral *para*-*tert*-butylphenyl rings relative to the benzene ring are 70° and 78°. Similar τ values for the central section of **6** (68° and 70°) are noted. Overall, no evidence for any significant steric distortions are seen in **1**.

Single crystals of **2**·toluene were grown from toluene. The results of X-ray diffraction studies are also shown in Fig. 1 (middle, disordered toluene molecule omitted for clarity).



4a **4b**

Chart 1

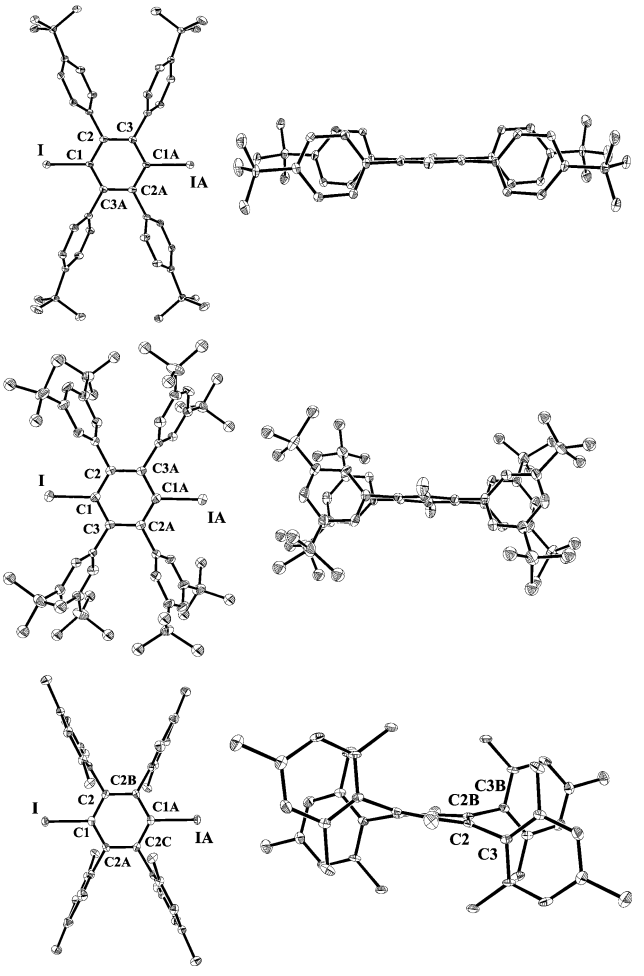


Fig. 1 Two views of **1–3**.

Selected bond distances and angles are listed in Table 1. Like **1**, the central benzene ring in **2** is quite planar and regular (mean carbon atom deviation is 0.002 Å from the best least-squares plane). The attached iodine atoms, however, are not exactly in the plane of the six carbon atoms and are displaced above and below this plane by 0.19 Å. Despite this slight displacement, the carbon–iodine bond lengths are not appreciably elongated (2.116(7) Å). Analysis of the orientation of the 3,5-di-*tert*-butylphenyl groups surrounding the benzene ring in **2** is

Table 1 Selected bond distances (Å) and angles (°) for **1–3**

1	I(1)–C(1)	2.118(3)
	C(1)–C(2)	1.397(3)
	C(1)–C(3A)	1.400(3)
	C(2)–C(3)	1.409(3)
	C(2)–C(1)–C(3A)	121.8(2)
	C(2)–C(1)–I(1)	119.9(2)
	C(3A)–C(1)–I(1)	118.3(2)
2	I(1)–C(1)	2.116(7)
	C(1)–C(2)	1.398(9)
	C(1)–C(3)	1.406(9)
	C(2)–C(1)–C(3)	122.9(6)
	C(2)–C(1)–I(1)	118.2(5)
	C(3)–C(1)–I(1)	118.8(5)
3	I(1)–C(1)	2.108(6)
	C(1)–C(2)	1.392(5)
	C(1)–C(2A)	1.392(5)
	C(2)–C(2B)	1.404(8)
	C(2)–C(1)–C(2A)	123.1(5)
	C(2)–C(1)–I(1)	118.4(3)
	C(2A)–C(1)–I(1)	118.4(3)

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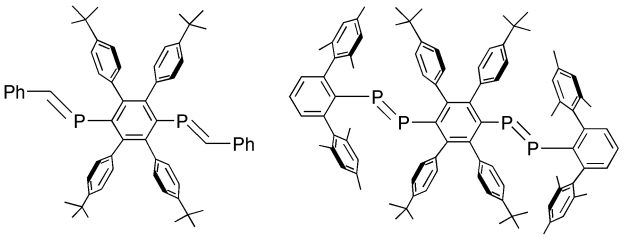

5 6

Chart 2

revealing. All four outer rings are tilted in the same direction, and have τ values of 23°. Each iodine atom is thus nudged in opposite directions by the neighboring aryl groups and results in each iodine atom being offset from the plane of the benzene ring. A similar effect can be discerned for **1**, but to a lesser extent (0.11 Å). Further analysis of the structure of **2** suggests the four aryl rings might adopt this orientation to prevent clashes between *tert*-butyl groups on adjacent aryl rings and to allow a methyl group of the one *tert*-butyl group of each ring to "nest" into the "pocket" located between the two *tert*-butyl groups of the neighboring phenyl ring.

Structural results on a crystal of **3**·0.5 toluene grown from toluene are presented in Fig. 1 (bottom, solvent molecule omitted for clarity). Immediately several features are striking. First, the four mesityl rings are staggered about the rough plane (mean deviation 0.061 Å) of the six carbon atoms of the benzene ring in an up–down–up–down fashion. This result suggests that significant steric interactions between the *ortho*-methyl groups of adjacent mesityl rings are present. Each mesityl ring is nearly orthogonal to the benzene ring (by *ca.* 9°, more rigorous τ values hard to define due to grossly non-planar benzene ring). The mesityl rings flanking each iodine atom lie above and below the plane of the central ring, and act in concert to twist the central benzene ring by 24.5° (as judged by the torsion angle for C3–C2–C2B–C3B). The four carbon atoms bearing mesityl rings are displaced from the mean plane of the six benzene carbon atoms by 0.092 Å, while both the iodine bearing carbons and the iodine atoms themselves fall on the best least-squares plane of the benzene ring. These distortions are not sufficient to significantly disrupt the aromaticity of this ring, as judged by a lack of significant alternating carbon–carbon bond lengths. Finally, the carbon–iodine bond lengths in **3** are quite normal at 2.108(6) Å.

For all three compounds, the internal C–C–C bond angles about the carbon atom attached to the iodine atoms are consistently greater than 120° (121.8–123.1°), and comparable to the angle found of 121.8(5)° in the related terphenyl 2,6-Trip$_2$-C$_6$H$_3$I (Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$).[9] Interestingly, for benzenes attached to very electropositive elements, these angles become less than 120°.[10]

The structures of compounds **1–3** are fairly unique. While many hexaarylbenzenes are known, the most related example of a structurally characterized crowded dihalobenzene is 1,4-di-*tert*-butyl-2,5-diiodobenzene. In this molecule the average C–I distance is 2.116 Å, and no significant distortions are present in the benzene ring (there is a deflection of the iodine atom away from the *tert*-butyl groups, as signaled by a difference of 14° in the I–C$_{ipso}$–C bond angles, however).[11]

In conclusion, we have reported the synthesis and structural characterization of a series of 1,4-diiodo-2,3,5,6-tetraarylbenzenes and shown how modulation of the substituents of the

Table 2 Crystal data and structure refinement for **1–3**

	1	**2**	**3**
Empirical formula	$C_{46}H_{52}I_2$	$C_{69}H_{52}I_2$	$C_{45.5}H_{48}I_2$
Formula weight	858.68	1134.91	844.64
Temperature/K	90(2)	293(2)	293(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2(1)/c$	$P2(1)/c$	$Fddd$
Unit cell dimensions	a = 14.2005(5) Å	a = 16.229(2) Å	a = 8.3261(6) Å
	b = 10.6963(4) Å	b = 16.500(2) Å	b = 31.196(2) Å
	c = 13.9689(5) Å	c = 13.1236(16) Å	c = 31.772(2) Å
	β = 113.4060(10)°	β = 110.941(9)°	
Volume/Å^3	1947.18(12)	3282.0(7)	8252.5(10)
Z	2	2	8
Density (calcd.)/Mg m^{-3}	1.465	1.148	1.366
Absorption coeff./mm^{-1}	1.646	0.992	1.552
F(000)	868	1144	3416
Crystal size/mm	0.10 × 0.09 × 0.08	0.33 × 0.34×0.07	0.18 × 0.16×0.06
Crystal color & shape	colorless cube	colorless plate	colorless block
Diffractometer used	Bruker Smart 100	Seimens P4	Bruker Smart 100
θ range data collection/°	1.56 to 31.52	1.82–24.5	1.83–30.00
Limiting indices	$-20 < h < 18$	$-18 < h < 18$	$-11 < h < 11$
	$-15 < k < 15$	$-1 < k < 19$	$-43 < k < 37$
	$-20 < l < 20$	$-1 < l < 14$	$-44 < l < 40$
Reflections collected	28 187	6622	18 444
Independent reflections	6314 (R_{int} = 0.0659)	5385 (R_{int} = 0.0419)	3005 (R_{int} = 0.0905)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraint/parameters	6313/0/295	5285/0/289	3004/13/118
Goodness-of-fit on F^2	0.899	1.003	1.077
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0336	$R1$ = 0.0721	$R1$ = 0.0567
	$wR2$ = 0.0659	$wR2$ = 0.1791	$wR2$ = 0.1268
R indices (all data)	$R1$ = 0.0663	$R1$ = 0. 1188	$R1$ = 0.0928
	$wR2$ = 0.0758	$wR2$ = 0.2103	$wR2$ = 0.1385

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_W(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

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peripheral aromatic groups can lead to structural distortions of a 1,4-diiodobenzene residue.

Experimental

General considerations

Air sensitive materials were handled in a drybox or using modified Schlenk line techniques under dry nitrogen. Solvents were obtained by distillation from purple Na-benzophenone under nitrogen. Magnesium turnings used in Grignard reagent preparation were activated by heating and stirring overnight under dry N_2. Other reagents were used as obtained from commercial sources. ^{1}H NMR spectra were acquired on a Varian Gemini 300 MHz spectrometer and were referenced to TMS. High resolution mass spectra were taken at the CWRU departmental facility.

2. A solution of 20.0 g (74.3 mmol) 3,5-di-*tert*-butylbromobenzene in 75 mL THF was added to 5.4 g (220 mmol) of activated Mg turnings *via* cannula with stirring. The resultant dark brown mixture was stirred at ambient temperature for 2 hours. This solution was then taken into a drybox, where the solution was decanted into a new flask (leaving excess Mg), and to this solution was added 5.1 g (9.2 mmol) hexabromobenzene as a solid over a period of 20 minutes with rapid stirring, followed by an additional 24 hours of stirring at room temperature. The mixture was then removed from the drybox, quenched with 21 g (82 mol) I_2 and stirred for 15 minutes. Excess I_2 was consumed by addition of aqueous sodium sulfite. The products were extracted from this mixture by portions of ether, and the combined organics were washed twice with water. The solvent was reduced to one-third volume *in vacuo* followed by filtration to afford 2.3 g of pure **2** (28%) as a fine white powder. ^{1}H NMR ($CDCl_3$): δ 1.72 (s, 72 H), 6.90 (d, J_{HH} = 2 Hz, 8 H), 7.10 (t, J_{HH} = 2 Hz, 4 H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.36, 147.40, 144.89, 125.27, 120.26, 109.38, 34.91, 31.68. Anal. Calc. for $C_{62}H_{84}I_2$ C 68.75%, H 7.82%; found: C 66.94%, H 7.56%.

3. A solution of 20.9 g (105 mmol) 2,4,6-trimethylbromobenzene in 120 mL THF was added to 3.8 g (160 mmol) of activated Mg turnings *via* cannula with stirring. The resultant brown mixture was stirred at ambient temperature for 1 hour, and then taken into a drybox, where the solution was decanted from excess Mg. To this solution was added 8.0 g (15 mmol) hexabromobenzene powder over a period of 20 minutes with rapid stirring. Following addition, the reaction was stirred at room temperature for 12 hours. The mixture was then removed from the drybox, quenched with 41.6 g (164 mmol) I_2 and stirred for 15 minutes. Excess I_2 was then consumed by addition of 150 mL 5% aqueous Na_2SO_3, producing a bright yellow solution. The mixture was extracted with three portions of ether, and the combined organics were washed twice with water. The organic layer contained a small amount of white precipitate. The solvent was reduced to one third volume under reduced pressure followed by filtration to yield 2.1 g of pure 3 (18%) as a fine off-white powder. ^{1}H NMR ($CDCl_3$): δ 1.99 (24 H), 2.16 (12 H), 6.67 (8 H). HRMS: found 802.15240, expected 802.15325.

X-Ray crystallography. General details for the data collections and structure solutions are presented in Table 2. Further details may be found in the electronic supplementary information as CCDC reference numbers 198785, 198786 and 199202. See http://www.rsc.org/suppdata/nj/b2/b210577b/ for crystallographic data in CIF or other electronic format.

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