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Oxidative C−C Bond Formation (Scholl Reaction) with DDQ as an Efficient and Easily Recyclable Oxidant

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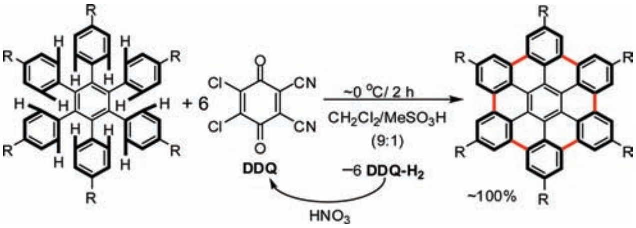
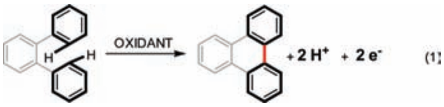
ABSTRACT



DDQ in the presence of an acid is known to oxidize a variety of aromatic donors to the corresponding cation radicals. Herein, we now demonstrate that the DDQ/H$^+$ system can be effectively utilized for the oxidative C−C bond formations or biaryl synthesis. The efficient preparation of a variety of polyaromatic hydrocarbons including graphitic hexa-*peri*-hexabenzocoronenes, ease of isolation of the clean products, and ready regeneration of DDQ from easily recovered reduced DDQ-H$_2$ advances the use of DDQ/H$^+$ for Scholl reactions.

The Scholl reaction[1] is one of the oldest C−C bond forming reactions and has been extensively utilized for intramolecular oxidative cyclodehydrogenation of various polybenzenoid hydrocarbons, e.g., eq 1.



The reaction in eq 1 essentially represents an oxidative C−C bond formation (or biaryl synthesis) that has been especially efficacious for the oxidative cyclodehydrogenation of a variety of (substituted) hexaarylbenzenes and *o*-terphenyls to produce the corresponding planar polyaromatic hydrocarbons (PAH's), i.e., hexa-*peri*-hexabenzocoronenes (HBC's) and triphenylenes, respectively.[2] The Scholl reaction can be accomplished by using a variety of oxidants such as $FeCl_3$,[3] $CuCl_2$ or $Cu(OTf)_2$ and $AlCl_3$,[4] $Tl(O_2CCF_3)_3$ in CF_3CO_2H or $BF_3{-}OEt_2$,[5] $Pb(OAc)_4/BF_3{-}Et_2O$ in MeCN,[5,6] triethyloxonium hexchloroantimonate (Et_3O^+ $SbCl_6^-$),[7] $SbCl_5$,[8] $MoCl_5$,[9] etc. Moreover, the Scholl reaction can also be effected by electrochemical oxidation.[10] The involvement of cation radical intermediates (formed by 1-e$^-$ oxidation) in oxidative C−C bond formations or biaryl syntheses has

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[1] (a) Scholl, R.; Mansfeld, J. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1734–1746. (b) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357–379.

[2] (a) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747–1785. (b) Watson, M. D.; Fechtenkotter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267–1300.

[3] (a) Boden, N.; Bushby, R. J.; Headdock, G.; Lozman, O. R.; Wood, A. *Liq. Cryst.* **2001**, *28*, 139–144. (b) Boden, N.; Bushby, R. J.; Cammidge, A. N.; Duckworth, S.; Headdock, G. *J. Mater. Chem.* **1997**, *7*, 601–605.

[4] (a) Simpson, C. D.; Mattersteig, G.; Martin, K.; Gherghel, L.; Bauer, R. E.; Räder, H. J.; Muellen, K. *J. Am. Chem. Soc.* **2004**, *126*, 3139–3147. (b) Kübel, C.; Eckhardt, K.; Enkelmann, V.; Wegner, G.; Müllen, K. *J. Mater. Chem.* **2000**, *10*, 879–886.

[5] McKillop, A.; Turrell, A. G.; Young, D. W.; Taylor, E. C. *J. Am. Chem. Soc.* **1980**, *102*, 6504–6512.

[6] Aylward, J. B. *J. Chem. Soc. B* **1967**, 1268–1270.

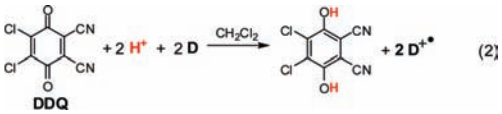
[7] Rathore, R.; Kumar, A. S.; Lindeman, S. V.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 5847–5856.

[8] (a) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321–5322. (b) Yamaguchi, S.; Swager, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 12087–12088. (c) Rose, A.; Tovar, J. D.; Yamaguchi, S.; Nesterov, E. E.; Zhu, Z.; Swager, T. M. *Philos. Trans. R. Soc. London, Ser. A* **2007**, *365*, 1589–1606, and references cited therein.

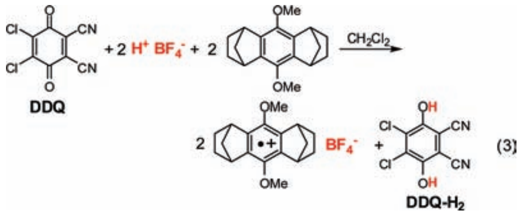
10.1021/ol901331p CCC: $40.75

been carefully probed by Parker and co-workers.[11]

We[12] and others[13] have recently shown that dichlorodicyano-*p*-benzoquinone (DDQ, $E_{\text{red}} = +0.60$ V vs. SCE), in the presence of an acid, readily oxidizes a variety of aromatic donors (**D**), such as naphthalene, anthracene, hexaalkylbenzenes, 1,4-dialkoxybenzenes, biphenyl, etc., with oxidation potentials as high as ~1.7 V vs. SCE, to the corresponding cation radicals according to the stoichiometry shown in eq 2.



It is important to emphasize that in the absence of an added acid, DDQ forms vividly colored electron donor−acceptor (EDA) complexes with various aromatic donors,[14] and the highly *endothermic electron transfer* reaction in eq 2 is only possible in the presence of an acid.[12,13] The electron-transfer stoichiometry in eq 2 was further verified by a quantitative isolation of a stable hydroquinone ether cation radical according to eq 3.[12a,15]



Herein, we will show that the DDQ/acid system (which readily oxidizes aromatic donors to the corresponding cation radicals) can be employed for Scholl reactions (or biaryl synthesis) as demonstrated by the preparation of a number of substituted triphenylenes and hexa-*peri*-hexabenzocoronenes under mild conditions. The usage of DDQ, instead of commonly utilized ferric chloride ($FeCl_3$), as an oxidant in Scholl reactions is advanced owing to the following reasons: (i) Generally a large excess of $FeCl_3$ is needed for the completion of Scholl reactions and in many cases the resulting products are contaminated with chlorinated compounds.[16,17] A need for a large excess of $FeCl_3$ can be avoided by usage of only 1 equiv of DDQ per C−C bond formation for the completion of Scholl reactions. (ii) The isolation of cyclized products and the recovery of the reduced DDQ-H_2, which can be readily recycled into DDQ by oxidation with nitric acid, are easy.[18]

A variety of Scholl precursors (Figure 1) employed in this study were synthesized by using standard synthetic procedures, and the experimental details and the spectral data for **1a**−**n** are compiled in the Supporting Information.

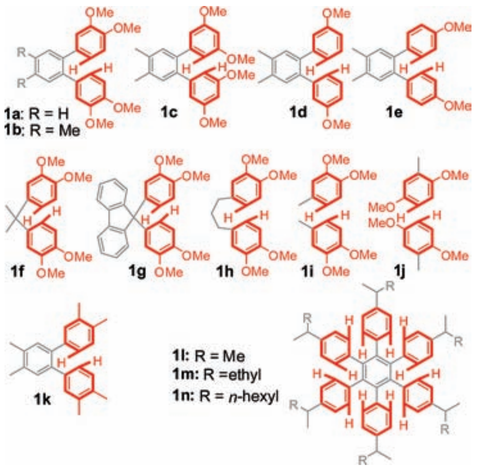
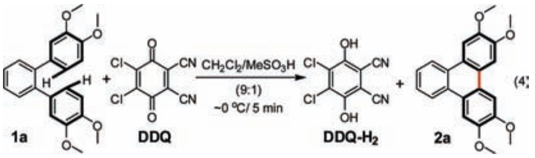


Figure 1. Structure and numbering scheme for various Scholl precursors used in this study.

Thus, when a 0.01 to 0.1 M solution of *o*-terphenyl **1a** in a mixture of dichloromethane and methanesulfonic acid (10%, v/v) was treated with 1 equiv of DDQ under an argon atmosphere at ~0 °C, the solution immediately turned dark green.[19] Upon stirring for 5 min at 0 °C, the reaction mixture took on a brown coloration. The reaction was then quenched by an addition of a saturated aqueous solution of sodium bicarbonate (20 mL). The dichloromethane layer was separated and washed with aqueous sodium bicarbonate (2 × 10 mL) and dried over anhydrous $MgSO_4$, then the solvent was evaporated to afford the corresponding triphenylene **2a** in quantitative yield (i.e., eq 4).



It is important to note that the reduced hydroquinone (DDQ-H_2) in eq 4 readily dissolves into the aqueous sodium

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(9) (a) Kramer, B.; Fröhlich, R.; Waldvogel, S. R. *Eur. J. Org. Chem.* **2003**, *354*, 9–3554. (b) Waldvogel, S. R.; Aits, E.; Holst, C.; Fröhlich, R. *Chem. Commun.* **2002**, 1278–1279. (c) Kovacic, P.; Lange, R. M. *J. Org. Chem.* **1963**, *28*, 968–972.

(10) (a) Ronlan, A.; Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* **1973**, *95*, 7132–7138. (b) Ronlan, A.; Parker, V. D. *J. Org. Chem.* **1974**, *39*, 1014–1016. (c) Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1995**, *60*, 7479–7490.

(11) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55–189, and references cited therein.

(12) (a) Rathore, R.; Kochi, J. K. *Acta Chem. Scand.* **1998**, *52*, 114–130. (b) Rathore, R.; Zhu, C.-J.; Lindeman, S. V.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1837–1840.

(13) (a) Handoo, K. L.; Gadru, K. *Curr. Sci.* **1986**, *55*, 920–922, and references cited therein. (b) Also see: Eberson, L.; Hartshorn, M. P.; Persson, O. *J. Chem. Soc., Perkin Trans. 2* **1997**, 195–201.

(14) Rathore, R.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 9393–9404, and references cited therein.

(15) Rathore, R.; Burns, C. L.; Deselnicu, M. I. *Org. Synth.* **2005**, *82*, 1–6.

(16) Rempala, P.; Kroulik, J.; King, B. T. *J. Am. Chem. Soc.* **2004**, *126*, 15002–15003, and references cited therein.

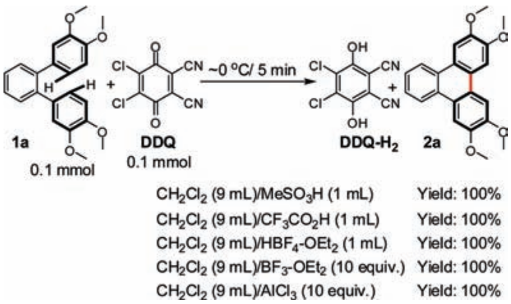
(17) Zhou, Y.; Liu, W.-J.; Zhang, W.; Cao, X.-Y.; Zhou, Q.-F.; Ma, Y.; Pei, J. *J. Org. Chem.* **2006**, *71*, 6822–6828, and references cited therein.

(18) (a) Brook, A. G. *J. Chem. Soc.* **1952**, 5040–5041. (b) Newman, M. S.; Khanna, V. K. *Org. Prep. Proced. Int.* **1985**, *17*, 422–423. (c) Scott, J. W.; Parrish, D. R.; Bizzarro, F. T. *Org. Prep. Proced. Int.* **1977**, *9*, 91–94.

bicarbonate layer and can be recovered quantitatively by acidification (using aqueous hydrochloric acid, 10%) followed by extraction with diethyl ether. The identity of the recovered DDQ-H_2 was confirmed by comparison of the ^{13}C NMR spectrum and melting point with an authentic sample.[20] Furthermore, DDQ can be regenerated from DDQ-H_2 by a simple oxidation by using either concentrated nitric acid or N_2O_4.[18]

As summarized in Scheme 1, the oxidative cyclodehydrogenation of *o*-terphenyl **1a** can be accomplished, using DDQ as an oxidant, in quantitative yield, irrespective of the use of either a protic acid (such as methanesulfonic acid, trifluoroacetic acid, or tetrafluoroboric acid) or a Lewis acid (such as $AlCl_3$ or BF_3-OEt_2). It is further emphasized that DDQ or a protic acid or a Lewis acid alone is not sufficient to carry out the transformation in Scheme 1 (eq 4).[21]

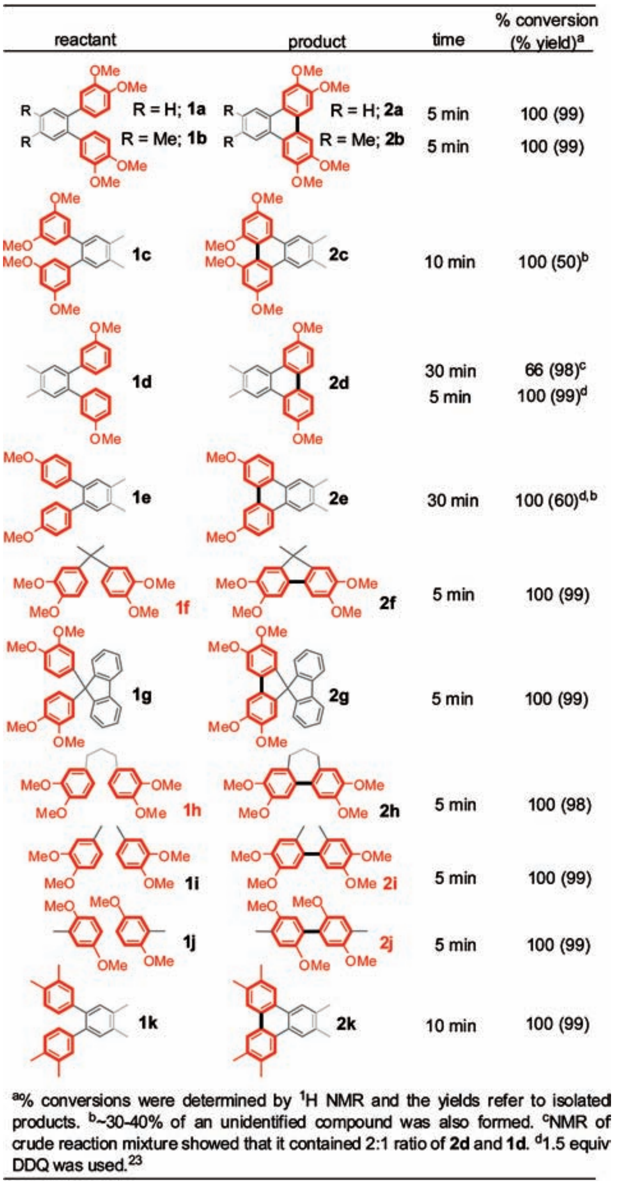
Scheme 1. Formation of Tetramethoxytriphenylene **2a**, Using a Combination of DDQ and Various Protic Acids and Lewis Acids in CH_2Cl_2 at 22 °C



CH_2Cl_2 (9 mL)/$MeSO_3H$ (1 mL)	Yield: 100%
CH_2Cl_2 (9 mL)/CF_3CO_2H (1 mL)	Yield: 100%
CH_2Cl_2 (9 mL)/HBF_4-OEt_2 (1 mL)	Yield: 100%
CH_2Cl_2 (9 mL)/BF_3-OEt_2 (10 equiv.)	Yield: 100%
CH_2Cl_2 (9 mL)/$AlCl_3$ (10 equiv.)	Yield: 100%

With use of the protocol developed in eq 4, a variety of Scholl precursors (Figure 1) were subjected to the reaction with DDQ in the presence of readily available and cheap methanesulfonic acid, under the standard conditions described in eq 4, to afford the corresponding cyclodehydrogenated products in excellent yields (see Table 1). It is noteworthy that the Scholl reaction with the DDQ/acid oxidation system was equally effective with substrates undergoing both *intramolecular* and *intermolecular* aryl−aryl C−C bond formations (see entries **1f** and **1j** in Table 1). Interestingly, King and co-workers[22] have recently reported that substrates **1c** and **1e** afforded no or poor yield of cyclized products using either phenyliodine(III) bis(trifluoroacetate)/BF_3 or $MoCl_5$ as oxidants; however, usage of the DDQ/H^+ system produces respectable yields of the cyclized products[23] from **1c** and **1e** (see Table 1).

Table 1. Scholl Reaction and Products Obtained under the Standard Set of Conditions, Using DDQ/$MeSO_3H$ in CH_2Cl_2



reactant	product	time	% conversion (% yield)[a]
R = H; **1a**	R = H; **2a**	5 min	100 (99)
R = Me; **1b**	R = Me; **2b**	5 min	100 (99)
1c	**2c**	10 min	100 (50)[b]
1d	**2d**	30 min 5 min	66 (98)[c] 100 (99)[d]
1e	**2e**	30 min	100 (60)[d,b]
1f	**2f**	5 min	100 (99)
1g	**2g**	5 min	100 (99)
1h	**2h**	5 min	100 (98)
1i	**2i**	5 min	100 (99)
1j	**2j**	5 min	100 (99)
1k	**2k**	10 min	100 (99)

[a]% conversions were determined by ^1H NMR and the yields refer to isolated products. [b]~30-40% of an unidentified compound was also formed. [c]NMR of crude reaction mixture showed that it contained 2:1 ratio of **2d** and **1d**. [d]1.5 equiv DDQ was used.[23]

[a] Percent conversions were determined by ^1H NMR and the yields refer to isolated products. [b] ∼30−40% of an unidentified compound was also formed. [c] NMR of the crude reaction mixture showed that it contained a 2:1 ratio of **2d** and **1d**. [d] 1.5 equiv of DDQ was used.[23]

The versatility of the DDQ/acid system for the oxidative cyclodehydrogenation is further demonstrated by the preparation of soluble hexa-*peri*-hexabenzocoronenes (HBC's) from hexakis(4-isoalkylphenyl)benzenes **1*l*−n**,[24] where 6 new C−C bonds are formed in one step, in excellent yields and high purity. Thus, a reaction of a 0.01 M solution of hexaarylbenzene **1*l*** in a mixture of dichloromethane and methanesulfonic acid (10%, v/v) was treated with 6 equiv of DDQ under an argon atmosphere at ∼0 °C. The resulting dark-colored mixture was stirred

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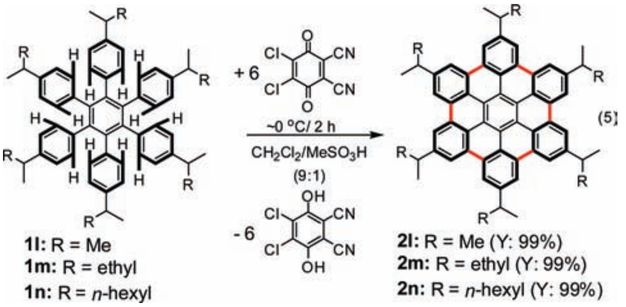
(19) The instantaneous appearance of green coloration in the reaction in eq 4 is due to the formation of the cation radical of tetramethoxytriphenylene **2a**. For example, when a solution of **2a** in a 9:1 mixture of $CH_2Cl_2-CH_3SO_3H$ was exposed to $^1/_2$ equiv of DDQ, the solution immediately took on the characteristic green coloration and the UV−vis spectral analysis and a spectral comparison with an authentic spectrum of the $\mathbf{2a}^{+\bullet}$ [generated with $CRET^{+\bullet}$,[15] as a robust 1-electron oxidant] confirmed the formation of the $\mathbf{2a}^{+\bullet}$ (λ_{max} = 410, 613, 684, and 762 nm) in eq 4.

(20) Hageman, L.; McNelis, E. *J. Org. Chem.* **1975**, *40*, 3300–3301.

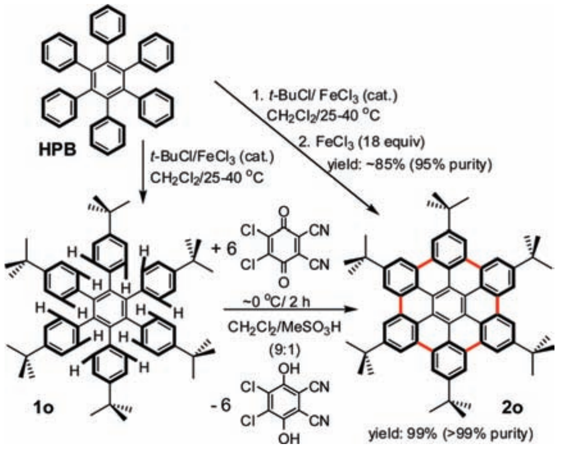
(21) The Scholl precursors in Figure 1including hexaphenylbenzene derivatives do not undergo any cyclization reaction when exposed to various protic and Lewis acids (Scheme 1) without DDQ for extended periods (up to ∼24 h) and the starting precursors can be recovered quantitatively by treatment with aqueous sodium bicarbonate. Similarly, various Scholl precursors did not show any reaction when exposed to DDQ alone in dichloromethane at 22 °C for 24 h.

for 2 h and a standard aqueous workup afforded pure HBC **2*l*** in a quantitative yield, i.e., eq 5. Similarly, **2m** and **2n** were also obtained in excellent yield.



We have reported earlier[25] that hexa-*tert*-butyl HBC (**2o**) can be obtained in a one-pot procedure from hexaphenylbenzene (HPB) in good yield; however, the resulting HBC **2o** required careful column chromatography and crystallization to obtain the analytically pure sample (Scheme 2). Herein, we show a two-step procedure in which the HPB was first *tert*-butylated with *tert*-butyl chloride and a catalytic amount of $FeCl_3$ in dichloromethane to afford **1a**,[25,26] which was then subjected to a reaction with 6 equiv of DDQ under standard conditions (see eq 5) to afford a clean sample of HBC **2o**, as judged by ^{1}H NMR spectroscopy.[27]

Scheme 2. A One-Step versus Two-Step Synthesis of HBC **2o**, Using Readily-Available Hexaphenylbenzene as a Precursor



Single crystals of HBC **2o**, suitable for X-ray crystallography, were readily obtained by a simple crystallization of the crude **2o** from a mixture of tetrahydrofuran and ethanol, and its structure was confirmed by X-ray crystallography (see Figure 2).

In summary, we have demonstrated that the DDQ/H$^+$ oxidation system, which is known to oxidize a variety of aromatic donors with oxidation potential as high as ~1.7 V to the corresponding cation radicals, can be effectively employed for the preparation of a variety of polyaromatic hydrocarbons including graphitic hexa-*peri*-hexabenzocoronenes. The procedure described herein with DDQ/H$^+$ instead of most commonly utilized oxidants such as $FeCl_3$, $MoCl_5$, or $SbCl_5$ for Scholl reactions obviates problems such as chlorination of the polyaromatic products and the use of a large excess of oxidants. We are presently examining the mechanistic dichotomy,[28] i.e., the arenium ion versus cation radical pathways for the Scholl reaction involving diamagnetic carbocations and paramagnetic cation radicals as different types of reactive intermediates using various oxidants including DDQ; and the details of these finding will be presented in due course.

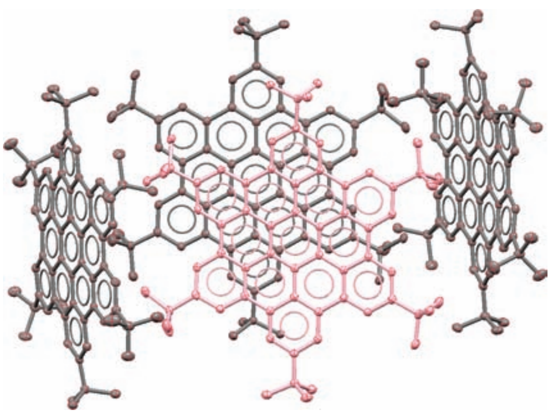


Figure 2. The crystal structure of HBC **2o** showing the herringbone packing of centrosymmetric dimers of **2o** via π,π-stacking (interplanar distance = 3.35 Å) and C−H···π interactions. The thermal ellipsoids are shown in 50% probability and the hydrogens are omitted for the sake of clarity.

Acknowledgment. We thank the National Science Foundation (CAREER Award) and Sergey V. Lindeman (Marquette University) for the X-ray crystallography.

Supporting Information Available: Synthetic details, ^{1}H/^{13}C NMR data of various compounds, and X-ray data of HBC **2o**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) King, B. T.; Kroulík, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007**, *72*, 2279–2288.

(23) For the complete consumption of the Scholl precursor **1d**, 1.5 equiv of DDQ was needed owing to the fact that part of the DDQ was used up for the conversion of the resulting triphenylene **2d** into its cation radical.[19] Also, the triphenylene cation radicals $\mathbf{2c}^{+\bullet}$ and $\mathbf{2e}^{+\bullet}$ are not stable under the reaction conditions and may have undergone additional oxidation reactions to thus far unidentified products.

(24) Chebny, V. J.; Gwengo, C.; Gardinier, J. R.; Rathore, R. *Tetrahedron Lett.* **2008**, *49*, 4869–4872.

(25) Rathore, R.; Burns, C. L. *J. Org. Chem.* **2003**, *68*, 4071–4074.

(26) Hexakis(4-*tert*-butylphenyl)benzene (**1a**) can also be prepared by $Co_2(CO)_8$-catalyzed trimerization of the bis-4,4(di-*tert*-butylphenyl)acetylene.[27]

(27) Compare: Herwig, P. T.; Enkelmann, V.; Schmelz, O.; Muellen, K. *Chem.—Eur. J.* **2000**, *6*, 1834–1839.

(28) For example, see: (a) Wadumethrige, S. H.; Rathore, R. *Org. Lett.* **2008**, *10*, 5139–5142. (b) Rathore, R.; Wygand, U.; Kochi, J. K. *J. Org. Chem.* **1996**, *61*, 5426–5436. (c) Also see: King, B. T. in ref 22. (d) Dou, X.; Yang, X.; Bodell, G. J.; Wagner, M.; Enkelmann, V.; Müllen, K. *Org. Lett.* **2007**, *9*, 2485–2488, and references cited therein.