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Synthesis and Studies of 1,4,5,8,9,12,13,16-Octamethoxytetraphenylene[†]

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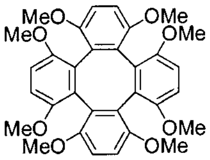
ABSTRACT



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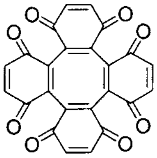

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The synthesis of 1,4,5,8,9,12,13,16-octamethoxytetraphenylene (6) is accomplished in five steps from 3,6-dimethoxy-2-nitroaniline (8). Its inclusion property and the electrochemical data of the corresponding tetraquinone 7 are presented.

Since the first successful synthesis of tetraphenylene by Rapson, Shuttleworth, and Niekerk in 1943,[1] extensive efforts have been made to explore its chemistry as well as that of its derivatives. Their inclusion properties toward solvent molecules[2] as well as their electronic and physical properties[3] have been carefully studied. Recently, 2,3,6,7,10,11,14,15-octamethoxytetraphenylene has been suggested to be a potential redox indicator on the basis of its redox-controlled reversible C−C bond formation.[4]

Although many aspects concerning the chemistry of tetraphenylene were studied, the construction of supermolecules consisting of tetraphenylene derivatives as building blocks is still not known. Triggered by the aforementioned reasons, we have started a research project with the eventual aim to construct three-dimensional molecular scaffolds using tetraphenylenols or their derivatives as building blocks. In our project, we would like to prepare all five tetraphenylenols **1**−**5** as shown in Figure 1.

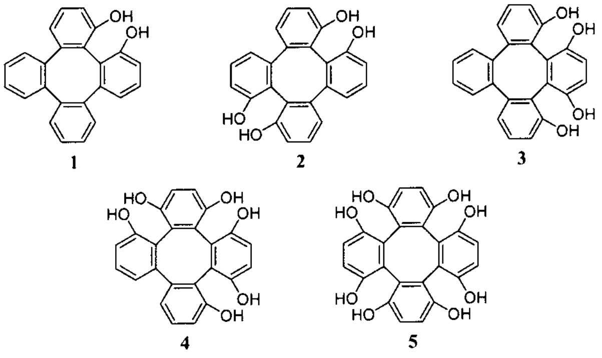

Figure 1. Five tetraphenylenols **1**−**5** for the construction of molecular scaffolds.

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(1) Rapson, W. S.; Shuttleworth, R. G.; Niekerk, J. N. *J. Chem. Soc.* **1943**, 326.

(2) (a) Mak, T. C. W.; Wong, H. N. C. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, P., Eds.; Pergamon Press: Oxford, 1996; Vol. 6, pp 351−369. (b) Mak, T. C. W.; Wong, H. N. C. *Top. Curr. Chem.* **1987**, *140*, 141. (c) Huang, N. Z.; Mak, T. C. W. *Chem. Commun.* **1982**, 543.

(3) (a) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; W. A. Benjamin: New York, 1966; pp 122−125, 468−470. (b) Rashidi-Ranjbar, P.; Man, Y. M.; Sandström, J.; Wong, H. N. C. *J. Org. Chem.* **1989**, *54*, 4888.

(4) Rathore, R.; Le Magueres, P.; Lindeman, S. V.; Kochi, J. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 809.

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We herein report the synthesis of 1,4,5,8,9,12,13,16-octamethoxytetraphenylene (**6**). The inclusion property of **6** and the electrochemical data of its corresponding tetraquinone **7** will also be delineated.

The synthesis of **6** is described in Figure 2. Sandmeyer reaction between diazotized 3,6-dimethoxy-2-nitroaniline (**8**)[5] and potassium iodide gave 2-iodo-3,6-dimethoxy-1-nitrobenzene (**9**) in 80% yield. Ullmann coupling reaction[6] of **9** afforded the symmetrical 3,3′,6,6′-tetramethoxy-2,2′-dinitrobiphenyl (**10**) in 51% yield. The two nitro groups in **10** were reduced to amino groups in 71% yield by hydrazine reduction in the presence of palladium on charcoal in refluxing methanol.[6]

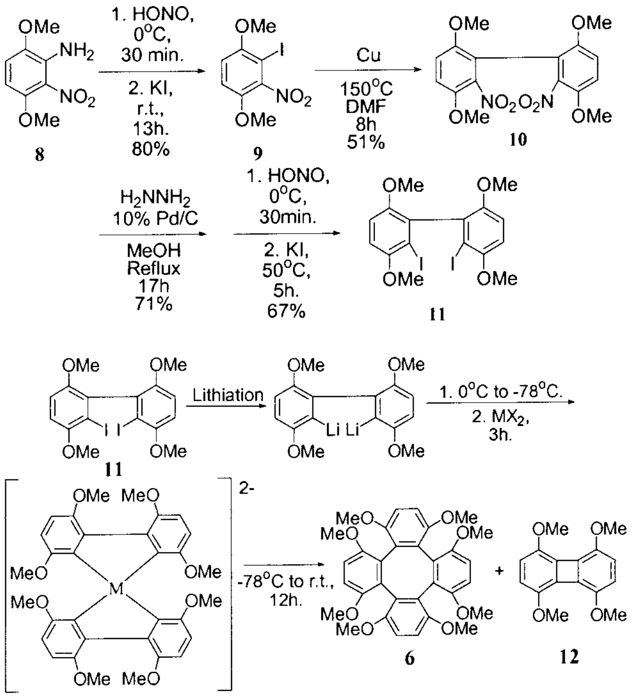

Figure 2. Synthesis of 1,4,5,8,9,12,13,16-octamethoxytetraphenylene (**6**) from 3,6-dimethoxy-2-nitroaniline (**8**).

Another Sandmeyer reaction between diazotized 2,2′-diamino-3,3′,6,6′-tetramethoxybiphenyl and potassium iodide completed the synthesis of 2,2′-diiodo-3,3′,6,6′-tetramethoxybiphenyl (**11**) in 67% yield.[6]

The results in Table 1 show the reaction conditions for the conversion of **11** to **6**. In agreement with the literature,[7] treatment of **11** with *n*-BuLi in diethyl ether as solvent led to **6** as the major product, whereas the use of tetrahydrofuran only gave 1,4,5,8-tetramethoxybiphenylene (**12**)[5] as the major product. The use of *n*-BuLi at 0 °C resulted in smooth lithiation of **11** after 8 h. From thin-layer chromatographic studies, lithiation at −78 °C remained incomplete after prolonged treatment, and prominent deterioration of the lithiated species was observed at room temperature. With the exception of $CuCl_2$, both $CuBr_2$ and $ZnCl_2$ gave exclusively **12** as the only product. The optimum conditions for the realization of **6** in 31% yield are therefore *n*-BuLi, Et_2O, 0 °C with $CuCl_2$.

Table 1. Attempted Conditions for the Conversion of **11** to **6**

type of alkyllithium	lithiation temp (°C)	solvent	metal salt	isol yield of **6** (%)	isol yield of **12** (%)
n-BuLi	−78	Et_2O	$CuCl_2$	10	4
(2.1 equiv)	0	Et_2O	$CuCl_2$	31	8
	rt	Et_2O	$CuCl_2$	16	7
	0	THF	$CuCl_2$	3	21
	0	Et_2O/THF (1/1)	$CuCl_2$	5	13
t-BuLi	−78	Et_2O	$CuCl_2$	3	2
(2.1 equiv)	0	Et_2O	$CuCl_2$	1	4
t-BuLi (4.5 equiv)	−78	Et_2O	$CuCl_2$	4	2
n-BuLi	0	Et_2O	$CuBr_2$	0	10
(2.1 equiv)	0	Et_2O	$ZnCl_2$	0	5

It was found that **6** formed a 1:2 clathrate inclusion compound with dichloromethane. Many attempts have been made to examine the inclusion properties of **6** toward other organic solvents to no avail. However, in mixed solvent systems, the host−guest selectivity between **6** and dichloromethane is remarkable: for example, in $CH_2Cl_2/C_6H_5Me/C_6H_6/C_6H_{14}$ (1:1:1:1), $CH_2Cl_2/C_5H_5N/p\text{-}C_6H_4Me_2$ (1:1:1), $CH_2Cl_2/C_6H_5OMe/p\text{-}C_6H_4Me_2$ (1:1:1), $CH_2Cl_2/CH_2Br_2/CH_2I_2/p\text{-}C_6H_4Me_2$ (1:1:1:1), $CH_2Cl_2/CHCl_3/CCl_4/p\text{-}C_6H_4Me_2$ (1:1:1:1), and $CH_2Cl_2/MeCOMe/H_2O$ (1:1:1) solvent systems, only the 2:1 complex of dichloromethane and **6** was formed, which was confirmed by an X-ray crystallographic analysis[9] (Figures 3 and 4) and NMR spectroscopic data.

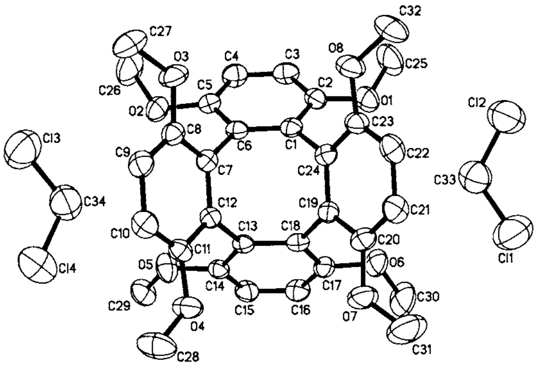

Figure 3. Molecular structure and atom labeling of $6{\cdot}2CH_2Cl_2$. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. The average formal single and double bonds in the central ring are 1.495(5) and 1.390(4) Å, respectively.

Figure 5 shows the conversion of **6** to its corresponding tetraphenylenol and quinone derivatives. Deprotection of the

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(5) Rees, C. W.; West, D. E. *J. Chem. Soc. C* **1970**, 583.

(6) Hine, J.; Hahn, S.; Miles, D. E.; Ahn, K. *J. Org. Chem.* **1985**, *50*, 5092.

(7) Kabir, S. M. H.; Iyoda, M *Synthesis* **2000**, *13*, 1839.

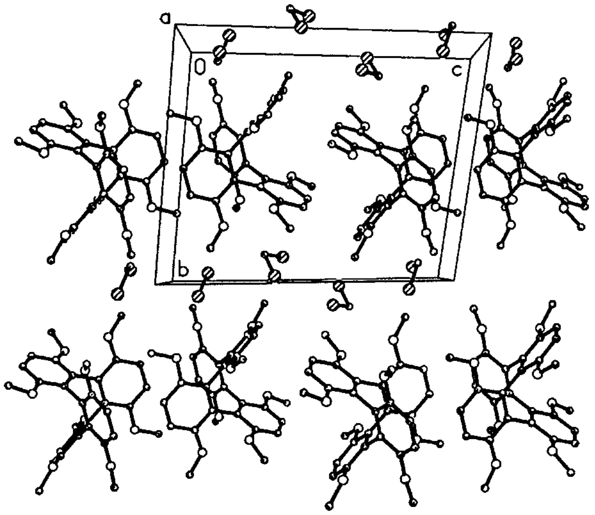


Figure 4. Stereoview of $6 \cdot 2CH_2Cl_2$. In the crystal structure, molecules of **6** are arranged in a layer matching the plane (020), and between such adjacent layers lie the CH_2Cl_2 solvate molecules.

methoxy groups of **6** employing boron tribromide at ambient temperature afforded 1,4,5,8,9,12,13,16-octahydroxytetraphenylene (**5**) in quantitative yield. Phenol **5** was oxidized to its corresponding tetraquinone **7** in 67% yield by the use of lead tetraacetate.

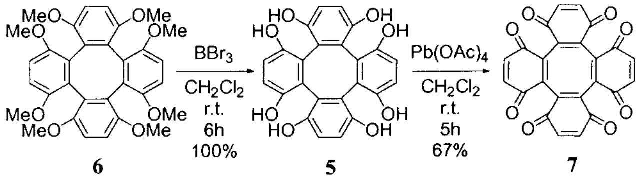


Figure 5. Synthesis of 1,4,5,8,9,12,13,16-octahydroxytetraphenylene (**5**) and its corresponding quinone **7**.

To examine the electrochemical property of **7**, a cyclic voltammetric method was employed. As shown in Figure 6, the cyclic voltammogram of **7** indicates three reversible couples at $E° = -0.597$, -0.813, and -1.296 V, respectively (see footnote b of Table 2).

In the first two couples, both reversible processes exhibit an equal peak separation of 116 mV and nearly equal anodic and cathodic peak currents at cathodic potentials. Table 2 gives the reduction potentials for other *p*-quinones as well as those of tetraquinone **7**.[7] The $E°$ values were taken from cyclic voltammetry peak potentials as $(E_a + E_c)/2$. The data show that the potential difference between the addition of the first and second electron is exceptionally small in **7** ($\Delta E° = 0.2$ V). One of the likely explanations is that charge transfer occurs between the semi-quinone and the opposite *p*-benzoquinone unit. Owing to the characteristic saddle shape of tetraphenylene, face-to-face interaction may occur between two opposite *p*-benzoquinone units that facilitate the distribution of charge. It is therefore likely that the second electron requires less energy to overcome the repulsive force inside the semi-quinone. However, the actual cause of the small $\Delta E°$ is still unclear to us. In addition, a cyclic voltammetric method was also applied to **6**. Although the anodic peak corresponding to the oxidation of **6** to $\mathbf{6}^{2+}$ is ill defined, on the return scan the cathodic peak at $E_{red} = 0.172$ V representing the reduction of $\mathbf{6}^{2+}$ to **6** is clear.[4]

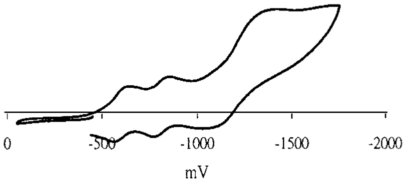
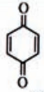
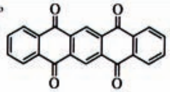
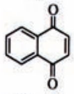
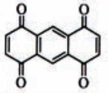
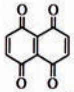
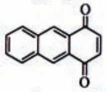
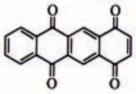


Figure 6. Cyclic voltammogram of **7**: CH_2Cl_2, 0.12 M $[Bu_4N]^+$-$[BF_4]^-$, scan rate = 100 mV s^{-1}.

In summary, the synthesis of 1,4,5,8,9,12,13,16-octamethoxytetraphenylene **6** has been accomplished. A 1:2 clathrate inclusion compound was obtained between **6** and dichloromethane. In addition, the cyclic voltammogram of tetraquinone **7** shows extraordinarily small $\Delta E°$ between two

Table 2. Electrochemical Data of *p*-Quinones and Tetraquinone **7**[a]

	$E°$ (V, SCE)		$\Delta E°$		$E°$ (V, SCE)		$\Delta E°$
	-0.43	-1.34	0.91		-0.42	-0.92	0.50
	-0.61	-1.41	0.80		-0.25	-0.74	0.49
	+0.14	-0.59	0.73		-0.60^b	-0.81^b	0.21
	-0.69	-1.41	0.72				
	-0.30	-0.85	0.55				

[a] Compound **7** shows exceptionally small $\Delta E°$ values as compared with that of *p*-benzoquinone. [b] All potentials are referenced to the ferrocenium/ferrocene couple. The $E°$ values were taken from cyclic voltammetry peak potentials as $(E_a + E_c)/2$.

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(8) Almlof, J. E.; Feyereisen, M. W.; Jozefiak, T. H.; Miller, L. L. *J. Am. Chem. Soc.* **1990**, *112*, 1206.

(9) Crystal data for $6 \cdot 2CH_2Cl_2$: $C_{34}H_{36}Cl_4O_8$, $M_w = 714.43$, triclinic, $P\bar{1}$ (No. 2), with $a = 9.460(2)$ Å, $b = 12.892(3)$ Å, $c = 15.324(3)$ Å, $\alpha = 90.929(5)°$, $\beta = 104.420(5)°$, $\gamma = 110.950(4)°$, $V = 1678.8(6)$ Å^3, and $D_c = 1.413$ g cm^{-3} for $Z = 2$. The structure was solved by direct methods and refined to R1 = 0.0488 and wR2 = 0.0887 for 5279 observed data. In the crystal structure, molecules of **1** are arranged in a layer matching the plane (020) and between such adjacent layers lie the CH_2Cl_2 solvate molecules. CCDC reference no. 189269.

reduction potentials. It is believed that charge transfer may occur intramolecularly between a semi-quinone and the opposite *p*-benzoquinone unit in **7**. Further investigation of the electrochemical properties of **7** and inclusion properties of **5** are in progress.

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Supporting Information Available: Experimental procedures and full characterization for compounds **5**−**7** and **9**−**11**. The X-ray crystallographic data of 1:2 clathrate inclusion compound between **6** and dichloromethane in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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