

Hexabenz[4.4.4]propellane: A Helical Molecular Platform for the Construction of Electroactive Materials

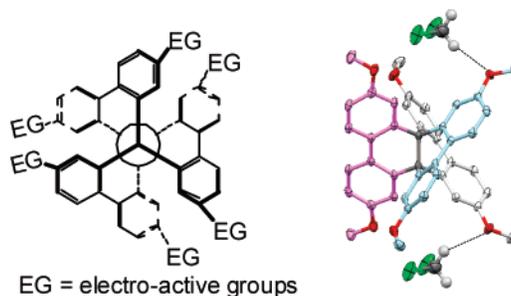
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ABSTRACT



Helical hexabenz[4.4.4]propellane (a relative of hexaphenylethane) and its derivatives are synthesized and their structures are established by X-ray crystallography. Isolation and X-ray crystallographic characterization of a robust trication-radical salt of hexamethoxypropellane derivative confirms that its framework is stable toward oxidative (aliphatic) C–C bond cleavage. It is also demonstrated that propellane can be easily brominated at the 4,4'-positions of the biphenyl linkages for its usage as a molecular platform for the preparation of electroactive materials.

Hexabenz[4.4.4]propellane¹ is a relative of hexaphenylethane (HPE) in which the phenyls of HPE from the opposite carbons are linked at the ortho positions to form biphenyl linkages (see structure A, Figure 1). Interestingly, unlike

central C–C bond,² hexabenz[4.4.4]propellane (referred to hereafter as propellane) is shown to be completely inert toward the reductive (aliphatic) C–C bond cleavage despite its close structural resemblance to the parent HPE.¹

Density functional theory (DFT) calculations at B3LYP/6-31G* level showed that the molecular geometry of propellane (D_{3h}) features three biphenyl moieties lying orthogonal to each other in a helical arrangement at an aliphatic C–C bond (i.e., Figure 1).³

It was conjectured that propellane may serve as a next-generation molecular platform containing three orthogonally

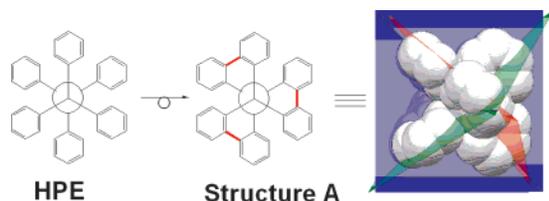


Figure 1. Orthogonal helical arrangement of the biphenyl moieties in parent propellane.

hexaphenylethane (HPE) which is yet to be isolated due to its significantly lengthened and consequently weakened

(1) Wittig, G.; Schoch, W. *J. Liebigs Ann. Chem.* **1971**, 749, 38. Also see: Kimura, M.; Kuwano, S.; Shimada, K.; Kamata, R.; Yasuda, S.; Sawaki, Y.; Fujikawa, H.; Noda, K.; Taga, Y.; Takagi, K. *Bull. Chem. Soc. Jpn.* **2006**, 79, 1793.

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(3) Note that propellane possesses geometric similarity to the metal-tris-bipyridyls in which three bipyridyl moieties lie almost orthogonally around the octahedral metal center.

juxtaposed and readily functionalizable biphenyl linkages (Figure 2) for the preparation of electroactive materials for

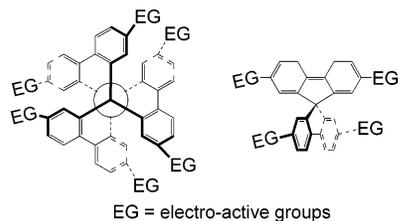


Figure 2. Comparison of (helical) propellane and spiro-bifluorene platforms for designing electroactive materials.

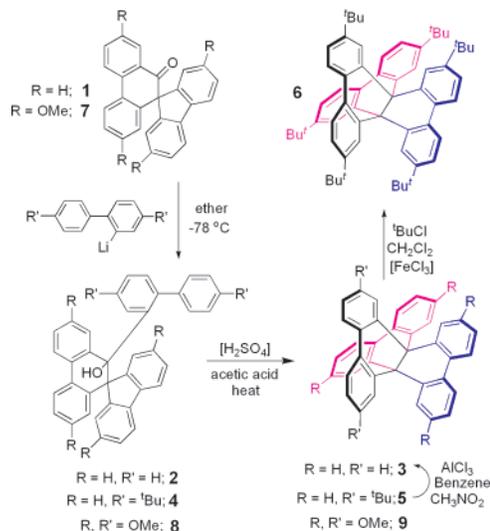
the applications in the emerging areas of molecular electronics and nanotechnology.⁴ In this context, it is important to note that spiro-bifluorene is extensively utilized as a platform for the preparation of molecular wires that lie orthogonal to each other at an insulating juncture,⁵ i.e., Figure 2.

Before undertaking the exploration of propellane and its derivatives for the preparation of electroactive materials, one needs to establish (i) that it is stable toward both reductive as well as oxidative cleavage of the central C–C bond and (ii) to demonstrate that it can be readily functionalized at the 4,4'-positions, i.e., Figure 2.

Accordingly, herein we present, for the first time, the structures of propellane and its derivatives by X-ray crystallography and establish that they are stable toward oxidative degradation by the isolation and X-ray crystallographic characterization of a stable tri-cation-radical salt of an electron-rich propellane. Furthermore, we will show that the parent propellane can be easily brominated at the 4,4'-positions of all three biphenyls for attachment of various electroactive groups using standard palladium-catalyzed coupling reactions.

Thus, parent propellane **3** (or structure A) was obtained in ~60% overall yield by a reaction of 2-biphenyllithium with readily available pinacolone **1** (derived from fluorenone)⁶ followed by an acid-catalyzed Wagner–Meerwein rearrangement/cyclization of the resulting carbinol **2** (Scheme 1) using a slightly modified procedure of Wittig.¹ A similar reaction with easily available 4,4'-di-*tert*-butyl-2-biphenyllithium⁷ similarly afforded di-*tert*-butylated derivative **5** in 75% yield. It is noteworthy that **5** can be easily and quantitatively de-*tert*-butylated to produce **3** by a reaction of **5** in benzene with AlCl₃–CH₃NO₂ as a catalyst⁷ (Scheme 1). Moreover, both **3** and **5** can be fully *tert*-butylated at the

Scheme 1. Preparation of Propellane and Its Derivatives



4,4'-positions by reaction with *tert*-butyl chloride in dichloromethane using ferric chloride as a catalyst⁸ (Scheme 1).

An electron-rich propellane derivative containing methoxy groups at the 4,4'-positions was also obtained using a similar strategy as summarized in Scheme 1. Thus, 2,7-dimethoxy-9-fluorenone⁹ was subjected to reductive coupling using Zn/ZnCl₂ in THF–H₂O followed by an acid-catalyzed rearrangement of the resulting pinacol to the corresponding pinacolone **7** in nearly quantitative yield (Scheme 1). A reaction of **7** with 4,4'-dimethoxy-2-biphenyllithium¹⁰ in anhydrous ether followed by acid-catalyzed rearrangement/cyclization of the corresponding carbinol **8** afforded propellane **9** in 53% isolated yield.

The molecular structures of **3**, **5**, **6**, and **9** were established with the aid of ¹H/¹³C NMR spectroscopy (see the Supporting Information) and were further confirmed by X-ray crystallography as follows.

The determination of precise molecular structures of various propellanes by X-ray crystallography (see Figure 3 for a representative structure) established that the central (aliphatic) C–C bond is only slightly elongated [**3**, 1.563(2) Å; **5**, 1.572(17) Å; **6**, 1.560(3) Å; and **9**, 1.564(3) Å] as compared to the standard value of 1.530 Å for a C(sp³)–C(sp³) bond.¹¹ It is also noted that the central C–C bonds in various propellanes are relatively shorter than the average value of 1.588 Å for the C–C bonds between two tertiary carbons.¹¹ The observation of relatively normal C–C bond length in various propellanes as compared to the calculated C–C bond length of 1.72 Å for hexaphenylethane² is easily reconciled by the fact that phenyl groups (due to the linkage

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(9) Epperson, J. R.; Bruce, M. A.; Catt, J. D.; Deskus, J. A.; Hodges, D. B.; Karageorge, G. N.; Keavy, D. J.; Mahle, C. D.; Mattson, R. J.; Ortiz, A. A.; Parker, M. F.; Takaki, K. S.; Watson, B. T.; Yevich, J. P. *Bioorg. Med. Chem.* **2004**, *12*, 4601.

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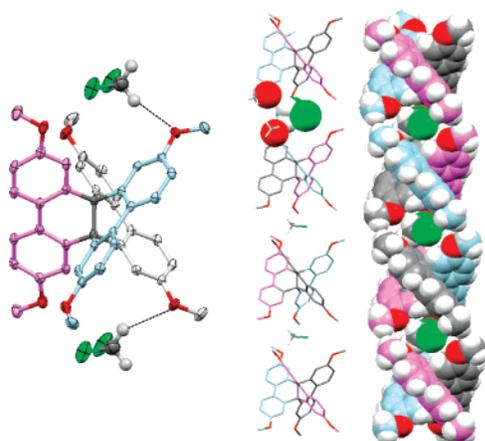


Figure 3. ORTEP diagram of $[9 \cdot \text{CH}_2\text{Cl}_2]$ and its triple helical packing arrangement.

at ortho-carbons) lie almost in (non-hindered) staggered arrangement along the central C–C bond, i.e., the average dihedral angles $\varphi(\text{Ph}-\text{C}-\text{C}-\text{Ph})$ are close to the ideal 60° value. (For a complete listing of important bond lengths, angles, and dihedral angles of various X-ray structures reported herein, see Table S1 in the Supporting Information).

Despite the inherent helicity (chirality) of the propellane framework and a very high barrier of racemization, the synthesis described in Scheme 1 produces only the racemic mixtures of various propellanes (i.e., **3**, **5**, **6**, and **9**). Expectedly, the crystallizations of the racemic **3**, **5**, and **6** yield the crystals containing closely packed stacks of molecules of alternating chirality. Interestingly, however, hexamethoxypropellane **9** forms triple helical columns by stacking molecules of one enantiomer onto each other (see Figure 3). The molecules of **9** in the helix are linked together via an alternating dichloromethane molecule by C–H \cdots O contacts with the distance and angle of 2.63 Å and 139° , respectively (see Figure 3). Note that “helices” of alternating chirality (formed from the enantiomers of **9**) pack adjacent to each other in the crystal with multiple contacts. As such, this observation suggests that propellane framework may represent an interesting building block for devising supramolecular helical arrays for interesting nonlinear optoelectronic properties and electrical conductivity.¹²

With the various propellane derivatives at hand, we next evaluated their electron-donor strength and the initial indication of the oxidative stability by cyclic voltammetry.

Thus, each propellane was subjected to electro-chemical oxidation at a platinum electrode as a 2 mM solution in dichloromethane containing 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte. Figure 4A shows the cyclic voltammograms of **9** with three reversible 1-electron oxidations occurring at the potentials of 1.17, 1.37, and 1.51 V vs SCE for the formation of mono-, di-, and trication radical,

(12) Compare: Rajca, A.; Safronov, A.; Rajca, S.; Shoemaker, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 488.

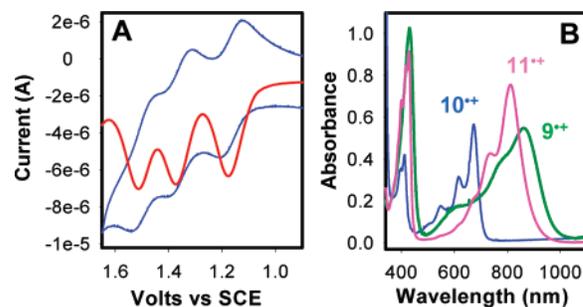
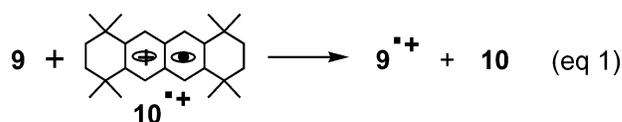


Figure 4. (A) Cyclic and square-wave voltammograms of 2×10^{-3} M **9** in CH_2Cl_2 (0.1 M *n*-Bu₄NPF₆) at a scan rate 200 mVs^{-1} . (B) Comparison of the UV–vis absorption spectra of cation radicals of **9** (green) and dimethoxybiphenyl **11** (pink), obtained using $10^{+\bullet}$ (blue) as an oxidant in CH_2Cl_2 at 22°C .

respectively.¹³ Similarly, *tert*-butylated derivatives **5** and **6** also showed reversible waves for the first oxidation at a potential of 1.60 and 1.55 V vs SCE, while the later oxidations occurring at relatively higher potentials with irreversible waves (see Figures S1 and S2 in the Supporting Information). The reversibility of electrochemical oxidations of **5**, **6**, and **9** indicates that the central C–C bond in these molecules do not undergo oxidative cleavage at least on the electrochemical time-scale.¹⁴

The electrochemical reversibility and relatively low oxidation potential of **9** prompted us to carry out its oxidation to the corresponding cation radical using a stable naphthalene cation radical ($10^{+\bullet}$)¹⁵ as an aromatic one-electron oxidant ($E_{\text{ox}} = 1.34 \text{ V vs SCE}$).

Thus, Figure 4B shows the spectrum of $9^{+\bullet}$ obtained by a reaction of a 6.1×10^{-5} M solution of $10^{+\bullet}$ ($\lambda_{\text{max}} = 672, 616, 503, \text{ and } 396 \text{ nm}$; $\epsilon_{672} = 9300 \text{ M}^{-1} \text{ cm}^{-1}$)¹⁵ with 1 equiv of **9** in dichloromethane at 22°C , i.e., eq 1.



The characteristic absorption spectrum of green-colored $9^{+\bullet}$ with a structured absorption band ($\lambda_{\text{max}} = 430, 861 \text{ nm}$) was expectedly similar to that of the 4,4′-dimethoxybiphenyl (**11**) cation radical¹⁶ ($\lambda_{\text{max}} = 428, 812 \text{ nm}$), i.e. Figure 4B. (For complete details for the generation of cation radicals of **9** and **11**, see Supporting Information.)

(13) There is little or no possibility of “through-space” interaction between the cationic biphenyl moieties in propellanes due to their orthogonal juxtaposition with respect to each other. Thus, splitting of the oxidation waves in **9** most likely arises due to the Coulombic repulsion amongst the orthogonally juxtaposed cationic biphenyls.

(14) The parent propellane (**3**) showed only an irreversible oxidation wave at $\sim 1.8 \text{ V}$. Such an observation does not necessarily imply the instability of the resulting cation radical towards C–C bond cleavage but most likely indicates its high electrophilic reactivity similar to that observed for the unsubstituted biphenyl cation radical.

(15) Rathore, R.; Le Mague’res, P.; Lindeman, S. V.; Kochi, J. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 809.

It is noteworthy that the green-colored 9^{3+} , obtained in eq 1, is highly persistent at ambient temperatures and did not show any decomposition during a 12 h period at 22 °C as confirmed by UV–vis spectroscopy. It is to be further noted that the reduction of 9^{3+} with zinc dust regenerated the neutral **9** quantitatively, as confirmed by $^1\text{H}/^{13}\text{C}$ NMR spectroscopy. The high stability of the 9^{3+} lends support to the fact that propellane derivatives are stable toward oxidative C–C bond cleavage, and thus, we next attempted the isolation of crystalline 9^{3+} as follows.

Treatment of a solution of **9** with triethyloxonium hexachloroantimonate ($\text{Et}_3\text{O}^+\text{SbCl}_6^-$)—an efficient $1e^-$ oxidant for the isolation of crystalline cation-radical salts¹⁷—in dichloromethane at ~ 0 °C immediately resulted in a dark-green solution which was spectrally identical to that obtained above as in eq 1. The green-colored solution was carefully layered with toluene and stored in a refrigerator at -10 °C for 2 days. The crystallographic analysis of the dark-colored crystals thus obtained, indicated that the crystals consisted of a tri-cation-radical salt [$9^{3+}3\text{SbCl}_6^-$], most likely formed by crystallization induced disproportionation [9^{3+}SbCl_6^-].¹⁸

Figure 5 shows that the crystal structure of [$9^{3+}3\text{SbCl}_6^-$] consists of columns of tricationic 9^{3+} with alternating

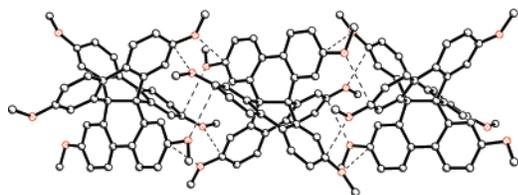


Figure 5. Packing arrangement of racemic tricationic **9** with multiple $\text{O}\cdots\text{Ar}$ contacts.

chirality as opposed to neutral **9** (vide supra) along one axis surrounded by 4 equiv of toluene molecules (two of them are rotationally disordered within molecular plane) and separated by layers containing 3 equiv of SbCl_6^- (two in general positions and two halves on 2-fold axes) and several heavily disordered solvent molecules. The columns of 9^{3+} are built on a 6-fold $\text{O}\cdots\text{Ar}$ contacts (as close as 3.05 Å) which may correspond to attractive interactions between the dipoles of the methoxy groups with delocalized positive charge on the aromatic moieties. Unfortunately, the low experimental precision severely limits discussion of the bond-length changes in 9^{3+} , but the averaged bond lengths are in a good agreement with the expected quinoidal distortion of dimethoxybiphenyl moieties (see Table S1 in the Supporting Information).

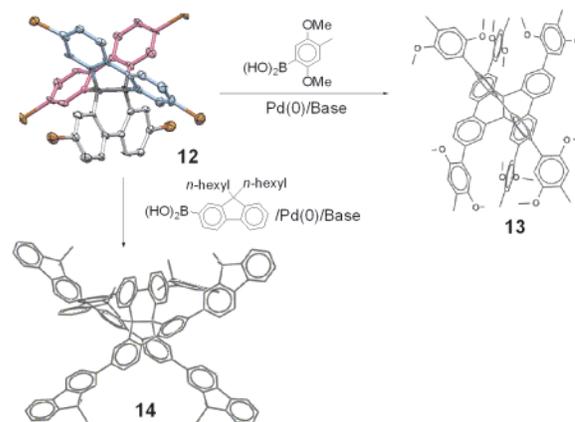
It is also noted that reduction of 9^{3+} using Zn dust or borane–dimethyl sulfide complex¹⁹ regenerated the neutral **9** in quantitative yield and thereby further attesting to the stability of the central C–C bond in propellanes toward oxidative cleavages.

Having established that propellanes are stable toward both reductive¹ and oxidative cleavage of the central C–C bond,

we next explored if they can be functionalized at the 4,4'-positions of three orthogonal biphenyl moieties (see Figure 2) for the preparation of electro-active materials as follows.

Thus, parent propellane **3** was subjected to a bromination reaction in dichloromethane in the presence of powdered iron as a catalyst for 4 h to afford **12** in quantitative yield with selective bromination at 4,4'-positions as established by X-ray crystallography (see Scheme 2). Moreover, hexabromopro-

Scheme 2. Preparation of Electroactive Propellanes



pellane **12** underwent efficient Suzuki coupling reactions with 2,5-dimethoxyphenylboronic acid and 9,9-dihexyl-2-fluoreneboronic acid, under standard conditions, to afford arylated derivatives **13** and **14** in excellent yields (see Scheme 2).

In summary, we have synthesized and established structures of propellane and its derivatives by X-ray crystallography. The helical propellane framework is stable toward both reductive and oxidative C–C bond cleavage as shown by isolation and X-ray crystallographic characterization of a stable trication-radical salt. Moreover, parent propellane **3** can be easily transformed to the hexabromopropellane **12** which in turn was utilized for the preparation of electroactive derivatives **13** and **14** (Scheme 2). These findings demonstrate that the propellane framework can serve as a platform for the preparation of futuristic electroactive materials for practical applications.

Acknowledgment. We thank the National Science Foundation (CAREER Award) for financial support.

Supporting Information Available: Synthetic details, $^1\text{H}/^{13}\text{C}$ NMR data, and X-ray structural data of **3**, **5**, **6**, **9**, and **12**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) Singular absence of any additional absorption bands (in near IR region) in hexamethoxypropellane cation radical when compared to 4,4'-dimethoxybiphenyl cation radical suggests the lack of electronic coupling amongst the orthogonally juxtaposed biaryl moieties in propellanes.¹³

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