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Vincent J. Chebny
Marquette University

Tushar S. Navale
Marquette University

Ruchi Shukla
Marquette University

Sergey V. Lindeman
Marquette University, sergey.lindeman@marquette.edu

Rajendra Rathore
Marquette University

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X-ray Structural Characterization of Charge Delocalization onto the Three Equivalent Benzenoid Rings in Hexamethoxytryptcene Cation Radical

Vincent J. Chebny

Department of Chemistry, Marquette University, Milwaukee, WI

Tushar S. Navale

Department of Chemistry, Marquette University, Milwaukee, WI

Ruchi Shukla

Department of Chemistry, Marquette University, Milwaukee, WI

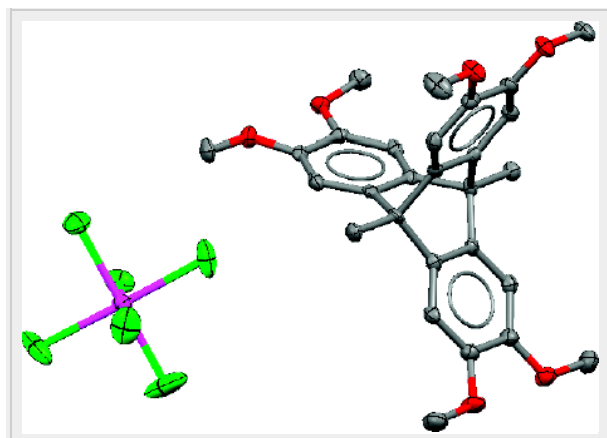
Sergey V. Lindeman

Department of Chemistry, Marquette University, Milwaukee, WI

Rajendra Rathore

Department of Chemistry, Marquette University, Milwaukee, WI

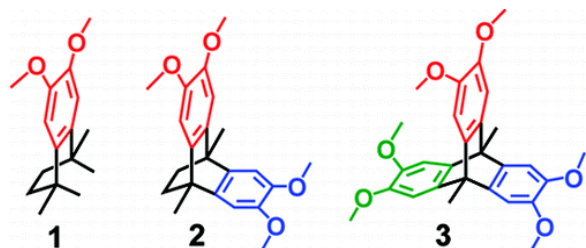
Abstract



Definitive X-ray crystallographic evidence is obtained for a single hole (or a polaron) to be uniformly distributed on the three equivalent 1,2-dimethoxybenzenoid (or veratrole) rings in the hexamethoxytryptycene cation radical. This conclusion is further supported by electrochemical analysis and by the observation of an intense near-IR transition in its electronic spectrum, as well as by comparison of the spectral and electrochemical characteristics with the model compounds containing one and two dimethoxybenzene rings.

Interactions between aromatic rings via π -stacking are at the origin of many phenomena of organic material science¹ and biological chemistry including the electron transport in DNA through stacked π -bases.² It has been noted in a number of recent studies that electronic coupling among the cofacially oriented aryl moieties does not necessarily require a perfect sandwich-like geometry. For example, we³ and others have shown⁴ that a hole (formed by the removal of a single electron) can hop among multiple cofacially oriented aryl moieties in various hexaarylbenzene derivatives as judged by the appearance of a characteristic near-infrared (NIR) intervalence transition in the absorption spectra of their cation radicals. From this standpoint, triptycene and its derivatives are fundamentally important molecules in which the three equivalent benzenoid rings are cofacially oriented at an angle of $\sim 120^\circ$. It has been shown with the aid of ESR and photoelectron spectroscopy that there is significant electronic coupling among the three benzenoid rings in triptycene and its derivatives.⁵ It is also important to note that the triptycene scaffold is being extensively explored⁶ for the preparation of modern materials for the potential use in the emerging areas of molecular electronics and nanotechnology.⁷

Our continued interest in the design, syntheses, and exploration of electronic coupling in the cofacially arrayed polybenzenoid structures⁸ led us to isolate a crystalline cation-radical salt of a hexamethoxytryptycene derivative (**3**), which provides definitive (X-ray) structural evidence that a single hole (or a polaron) is distributed evenly on the three equivalent 1,2-dimethoxybenzene (or veratrole) rings. Furthermore, the effective electronic coupling among the three cofacially oriented veratrole rings in **3** is further corroborated by comparison of the spectral and electrochemical characteristics with the model compounds containing one and two dimethoxybenzene rings (i.e., **1** and **2**).



The syntheses of **1–3** were easily accomplished by the adaptation of standard literature procedures,^{6c,9} and the relevant details along with the ¹H and ¹³C NMR spectral data are summarized in the [Supporting Information](#).

The electrochemical oxidations of **1–3** at a platinum electrode in CH₂Cl₂ were reversible for the removal of the first electron at varying scan rates of 25–400 mV s⁻¹; all anodic/cathodic peak current ratios were $I_a/I_c = 1.0$ (theoretical) at room temperature (Figure 1). A quantitative evaluation of the CV peaks and peak currents with added ferrocene (as an internal standard, $E_{ox} = 0.45$ V vs SCE) revealed that the first wave in the reversible cyclic voltammograms of **1–3** correspond to the production of the mono cation radical (by transfer of one electron) at $E_{ox1} = 1.22$, 1.11, and 1.00 (V vs SCE), respectively. The second oxidation in **2** ($E_{ox2} = 1.39$ V) and the second and third oxidations in **3** ($E_{ox2} = 1.29$ and $E_{ox3} = 1.78$ V) occur at relatively higher potentials (see Figure 1) and thus are indicative of the electronic coupling among the cofacially oriented veratrole moieties.¹⁰ As such, the lowered first oxidation potentials of **2** and **3** by ~110 and ~220 mV, respectively, as compared to the model donor **1** attest to the significant stabilization of the cationic charge by the cofacially arrayed veratrole rings in **2** and **3** owing to the electronic coupling among the cofacially oriented veratrole rings in **2** and **3**.¹⁰

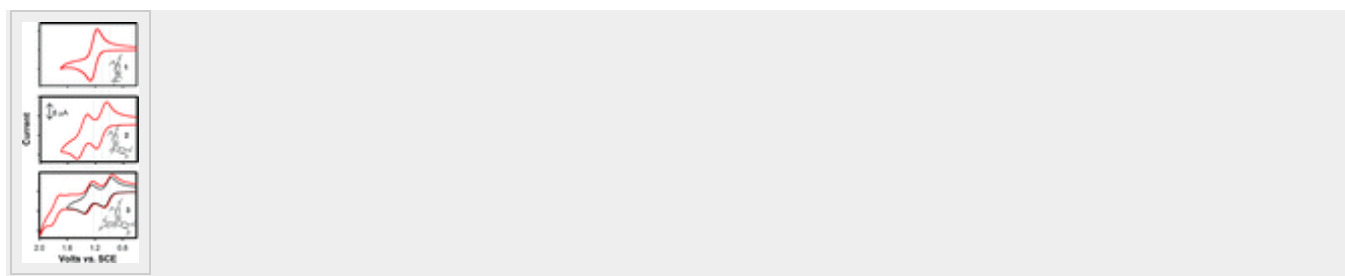


Figure 1. Cyclic voltammograms of **1**, **2**, and **3** (5 mM) in CH₂Cl₂ (containing 0.2 M nBu₄NPF₆ as the supporting electrolyte) measured at a scan rate of $v = 200$ mV s⁻¹ at 22 °C.

The electrochemical reversibility and relatively low oxidation potentials of **1–3** allow the generation of their cation radicals in solution using a hydroquinone ether cation radical (CRET⁺, $E_{red} = 1.14$ V vs SCE; $\lambda_{max} = 518$ nm; $\epsilon_{518} = 7300$ M⁻¹ cm⁻¹)¹¹ or a hindered naphthalene cation radical (NAP⁺, $E_{red} = 1.34$ V vs SCE; $\lambda_{max} = 672, 616, 503,$ and 396 nm; $\epsilon_{672} = 9300$ M⁻¹ cm⁻¹)¹² as stable (aromatic) one-electron oxidants.

Thus, Figure 2A shows the spectral changes observed upon an incremental addition of substoichiometric amounts of **3** to a solution of CRET⁺ in dichloromethane at 22 °C. A plot of formation of the **3**⁺ (i.e., increase in the absorbance at 1510 nm) against the increments of added neutral **3** (see Figure 2B) established that CRET⁺ was completely consumed after the addition of 1 equiv of **3**, and the resulting absorption spectrum

of $3^{+\bullet}$ ($\lambda_{\max} = 408, 1510 \text{ nm}$; $\epsilon_{1510} = 18300 \text{ M}^{-1} \text{ cm}^{-1}$) remained unchanged upon further addition of neutral **3** (i.e., eq 1).¹³

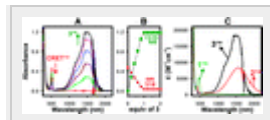
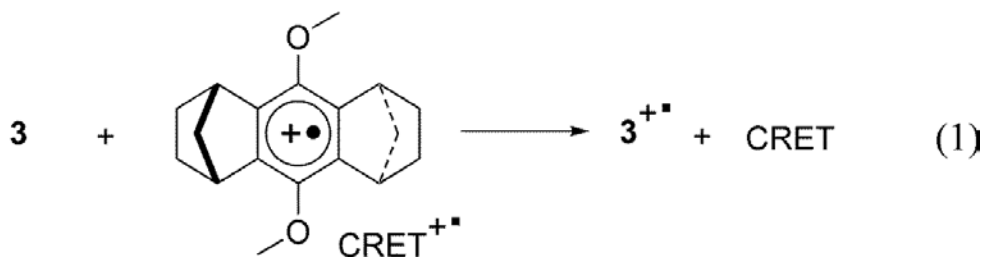


Figure 2. (A) Spectral changes observed upon the reduction of $6.5 \times 10^{-5} \text{ M}$ $\text{CRET}^{+\bullet}$ by an incremental addition of substoichiometric amounts of **3** in CH_2Cl_2 at 22°C . (B) Plot of depletion of absorbance of $\text{CRET}^{+\bullet}$ (red squares, at 518 nm) and an increase of the absorbance of $3^{+\bullet}$ (green circles, at 1510 nm) against the equivalent of added neutral **3** (data points from plot 2A). (C) Comparison of the molar absorptivity of the **1–3** cation radicals in CH_2Cl_2 at 22°C .

Similarly, the cation radical spectra of **1** and **2** were generated using $\text{NAP}^{+\bullet}$ and/or $\text{CRET}^{+\bullet}$ and are compared with the cation radical spectrum of triptycene **3** in Figure 2C. The observation of intense NIR transitions in the absorption spectra of bichromophoric $2^{+\bullet}$ ($\lambda_{\max} = 420, 1560 \text{ nm}$; $\epsilon_{1560} = 8400 \text{ M}^{-1} \text{ cm}^{-1}$) and trichromophoric $3^{+\bullet}$ ($\lambda_{\max} = 1510 \text{ nm}$) should be contrasted with a singular lack of any absorption beyond 500 nm in the absorption spectrum of the monochromophoric cation radical $1^{+\bullet}$ ($\lambda_{\max} = 461 \text{ nm}$; $\epsilon_{461} = 5200 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure 2C). Moreover, the fact that the NIR transition in $3^{+\bullet}$ ($\lambda_{\max} = 1510 \text{ nm}$) is roughly twice as intense as in $2^{+\bullet}$ ($\lambda_{\max} = 1560 \text{ nm}$) is most likely due to the increased probability of the hole migration over the three veratrole rings in $3^{+\bullet}$ as opposed to only the two rings in $2^{+\bullet}$.¹⁴

The cation radicals of donors **1–3**, obtained according to eq 1, are highly persistent at ambient temperatures and did not show any decomposition during a 12 h period at $\sim 22^\circ\text{C}$, as confirmed by UV-vis spectral analysis. The single crystals of the $3^{+\bullet}$, suitable for X-ray crystallography, were obtained by a slow diffusion of toluene into the dichloromethane solutions of $3^{+\bullet} \text{SbCl}_6^-$, prepared using equimolar $\text{NO}^+ \text{SbCl}_6^-$ as a 1- e^- oxidant, at -10°C during the course of 2 days (see the Supporting Information for the experimental details). Note that the repeated attempts to obtain single crystals of $1^{+\bullet} \text{SbCl}_6^-$ and $2^{+\bullet} \text{SbCl}_6^-$, suitable for X-ray crystallography, have been thus far unsuccessful.

The crystallographic analysis of the highly colored crystals of $3^{+\bullet} \text{SbCl}_6^-$ revealed that cationic triptycenes pack in layers in the crystallographic plane *ac* with embedded toluene molecules, and in between these layers lie the hexachloroantimonate anions and additional solvent (i.e., disordered toluene) molecules (Figure 3A). Within a layer, each independent molecule of the cationic triptycene ($3^{+\bullet}$) makes a centrosymmetric dimer over the centers of symmetry $[0\ 0\ 0]$ and $[0\ 0\ 1/2]$ by forming a pseudo-1/2-translation along the *z*-axis (i.e., Figure 3B). These dimeric units, in turn, form infinite chains along the *z*-axis in which two out of the three veratrole rings of each cationic triptycene moiety is involved in face-to-face interactions with the neighboring molecules with a center to center distance of $\sim 3.3\text{--}3.4 \text{ \AA}$. The remaining

third veratrole ring of the cationic triptycene makes a somewhat limited contact between the triptycene moieties of the neighboring chains, as well as more distinct face-to-face contacts with the toluene molecules (see Figure 3B).

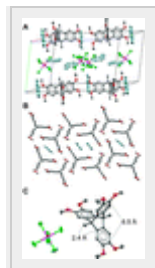
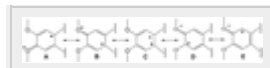


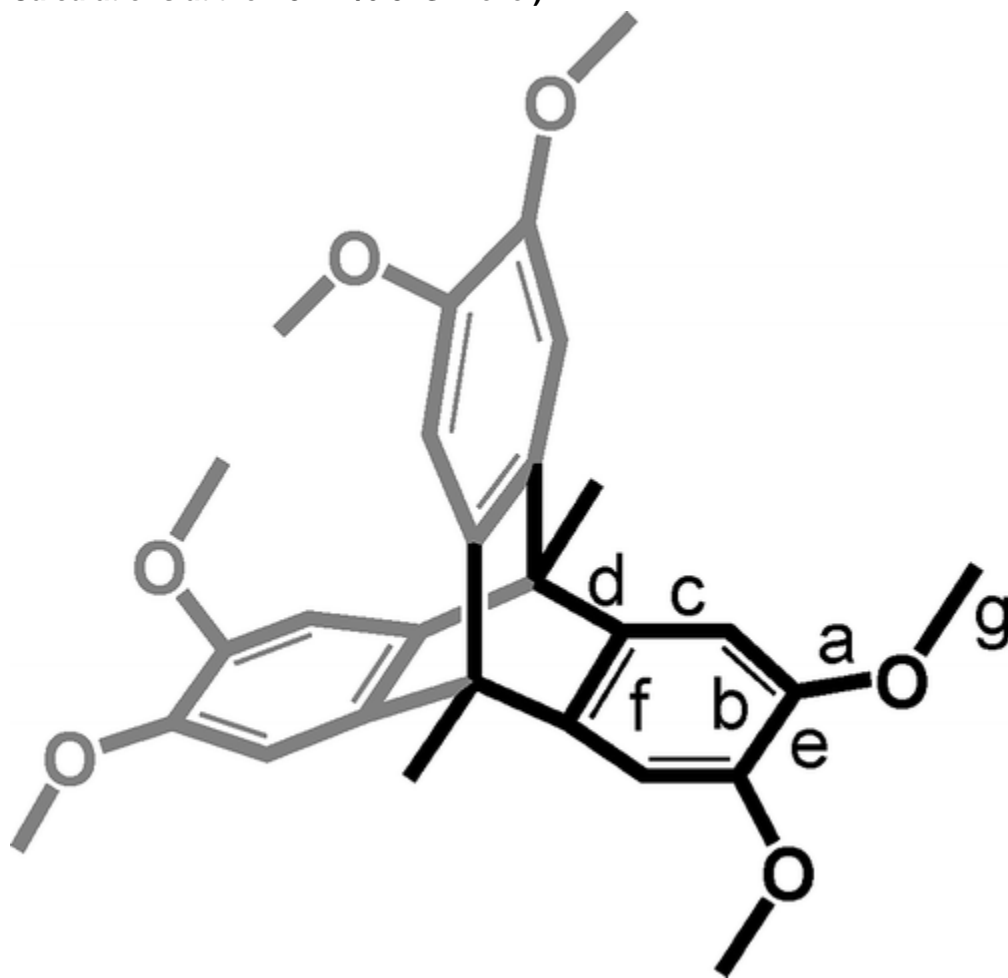
Figure 3. (A) Packing diagram of $3^{\bullet+}$ SbCl_6^- cation radical showing the toluenes and SbCl_6^- counteranions embedded between the layers of cationic triptycenes and additional toluene molecules. (B) Arrangement of cationic triptycenes and toluene molecules within a single layer. (C) ORTEP diagram of $3^{\bullet+}$ SbCl_6^- showing the closest (2.4 Å) and farthest (6.5 Å) separation between the veratrole moieties in the cationic triptycene.¹⁵

A closer look at the structural parameters of the veratrole groups in $3^{\bullet+}$ suggests that the three crystallographically unique benzenoid rings undergo similar structural changes (within the experimental precision of ~ 0.006 Å for various C–C/C–O bond lengths) and thus suggests that the cationic charge is evenly distributed over all three veratrole moieties.¹⁵ Furthermore, the bond length changes in the cation radical $3^{\bullet+}$, together with a comparison of its neutral form, the structure of which was established by X-ray crystallography, correspond to the predominant contributions from *p*-quinoidal resonance structures **A/B**, as judged by the significant shortening of bonds labeled “a” and elongation of bonds labeled “e” and “f”, along with only marginal shortening of the bonds labeled “b” and “c” (see Scheme 1 and Table 1). It is also noted that the alternate resonance structures **C–E** do not seem to contribute to the stabilization of the cationic charge in any significant way.



Scheme 1. Resonance Structures for the Stabilization of the Cationic Charge in $3^{\bullet+}$

Table 1. Experimental (X-ray) and Theoretical (DFT- B3LYP/6-31G* level) Bond Lengths of the Neutral and Cation Radical of 3 in Picometers (pm) (Two Views of the HOMO of 3 Obtained by DFT Calculations at the B3LYP/6-31G* Level)



bond	B3LYP/6-31G*		X-ray data	
	3 ^{•+}	$\Delta(3^{•+}-3)$	3 ^{•+}	$\Delta(3^{•+}-3)$
a	136.61	134.3-2.3	137.21	135.0-2.2
b	139.81	139.6-0.2	139.21	138.4-0.8
c	139.61	139.5-0.1	139.01	138.9-0.1

	B3LYP/6-31G*		X-ray data	
bond ^a	3 ⁺	$\Delta(3^{++}-3)$	3 ⁺	$\Delta(3^{++}-3)$
d	154.21	53.4-0.8	154.01	53.0-1.0
e	141.31	43.4+2.1	141.11	42.3+1.2
f	139.61	41.2+1.6	138.81	40.5+1.7
g	141.51	42.7+1.2	142.71	43.8+1.1
σ			0.4	0.6

^a Average of equivalent bonds.

It is noteworthy that the experimental observations of the similar bond length changes in all three veratrole moieties together with a significant shortening of the bonds labeled “d” in 3⁺ were found to be in reasonable agreement with the calculated values obtained using DFT calculations at the B3LYP/6-31G* level (see Table 1).¹⁶ Furthermore, it is noted that the bonds which undergo the most dramatic lengthening (i.e., bonds e and f) and shortening (i.e., bonds a–d) in 3⁺ are the bonds on which the HOMO shows the largest bonding and antibonding character, respectively (see Table 1 and Figure 4).

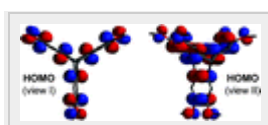


Figure 4. Two views of the HOMO of **3** obtained by DFT calculations at the B3LYP/6-31G* level.

In summary, we have demonstrated that hexamethoxytriptycene (**3**) and the model compounds containing one and two veratrole moieties (i.e., **1** and **2**) undergo reversible electrochemical oxidation and form stable cation-radical salts. The significantly lowered first oxidation potentials of bichromophoric **2** and triptycene **3** by ~110 and ~220 mV, respectively, as compared to the monochromophoric donor **1**, as well as the observation of intense NIR transitions in 3⁺ ($\lambda_{\max} = 1510$ nm) and 2⁺ ($\lambda_{\max} = 1560$ nm), and a complete absence of the NIR transition in monochromophoric 1⁺, attest to the effective electronic coupling among the cofacially arrayed veratrole rings in **2** and **3**. The isolation and X-ray crystal structure determination of the neutral and cation radical of **3**, as well as the DFT calculations now provide unequivocal evidence that a single charge (or polaron) is evenly distributed over all three veratrole moieties. Efforts are now underway to construct polyaromatic arrays based on the triptycene scaffold to explore their conducting properties as well as potential applications in the emerging areas of molecular electronics and nanotechnology.⁷

Acknowledgment

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- 10Note that the removal of the first electron from **2** and **3** results in the corresponding cation radicals where a charge is delocalized over two (pre-organized) cofacial veratrole moieties in **2** and over three veratrole moieties in **3**, and thereby rendering the ejection of the second electron from both **2**^{•+} and **3**^{•+} difficult by roughly ~280 and 290 mV, respectively. It is also noted that owing to the delocalization of charges in the dicationic **3**²⁺ makes the ejection of the third electron much more difficult (i.e., by 490 mV)
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- [15](#)Although, the geometrical parameter of all three benzenoid rings in the triptycene cation radical are similar (within experimental precision), each ring is crystallographically unique, and therefore, this structure does not suffer from the problem of static crystalline disorder. Furthermore, the X-ray crystallography together with the observation of the intense NIR intervalence transitions in **2** and **3** cation radicals suggests that these intervalence system belongs to Robin Day borderline class II/III systems. Compare: Sun, D.-L.; Lindeman, S. V.; Rathore, R.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1585
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