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

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*

X-ray Structural Characterization of Charge Delocalization onto the Three Equivalent Benzenoid Rings in Hexamethoxytriptycene 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 hexamethoxytriptycene 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 science and biological chemistry including the electron transport in DNA through stacked π-bases. 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, we and others have shown that a hole (formed by the removal of a single electron) can hop among multiple cofacially oriented aryl moieties in various hexaarylbenezene 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 ~120°. 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. It is also important to note that the triptycene scaffold is being extensively explored for the preparation of modern materials for the potential use in the emerging areas of molecular electronics and nanotechnology.

Our continued interest in the design, syntheses, and exploration of electronic coupling in the cofacially arrayed polybenzenoid structures led us to isolate a crystalline cation-radical salt of a hexamethoxytriptycene 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, and the relevant details along with the ‘H 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 Ia/Ic = 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, Eox = 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 Eox1 = 1.22, 1.11, and 1.00 (V vs SCE), respectively. The second oxidation in 2 (Eox2 = 1.39 V) and the second and third oxidations in 3 (Eox2 = 1.29 and Eox3 = 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. 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.

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 ν = 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•+, Ered = 1.14 V vs SCE; λmax = 518 nm; ε518 = 7300 M−1 cm−1) or a hindered naphthalene cation radical (NAP•+, Ered = 1.34 V vs SCE; λmax = 672, 616, 503, and 396 nm; ε672 = 9300 M−1 cm−1) 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+ (λ_{max} = 408, 1510 nm; ε_{1510} = 18300 M^{-1} cm^{-1}) remained unchanged upon further addition of neutral 3 (i.e., eq 1).

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

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 ~22 °C, as confirmed by UV–vis spectral analysis. The single crystals of the 3+, suitable for X-ray crystallography, were obtained by a slow diffusion of toluene into the dichloromethane solutions of 3+ SbCl6−, prepared using equimolar NO+ SbCl6− 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+ SbCl6− and 2+ SbCl6−, suitable for X-ray crystallography, have been thus far unsuccessful.

The crystallographic analysis of the highly colored crystals of 3+ SbCl6− 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+) 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 ~3.3–3.4 Å. 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).

A closer look at the structural parameters of the veratrole groups in 3•+ 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. Furthermore, the bond length changes in the cation radical 3•+, 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.
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)

<table>
<thead>
<tr>
<th>Bond</th>
<th>B3LYP/6-31G*</th>
<th>X-ray data</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>136.6134.3–2.3</td>
<td>137.2135.0–2.2</td>
</tr>
<tr>
<td>b</td>
<td>139.8139.6–0.2</td>
<td>139.2138.4–0.8</td>
</tr>
<tr>
<td>c</td>
<td>139.6139.5–0.1</td>
<td>139.0138.9–0.1</td>
</tr>
</tbody>
</table>
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). 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).

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•+ (λ_max = 1510 nm) and 2•+ (λ_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.
Acknowledgment

We thank the National Science Foundation (CAREER Award) and Marquette University for financial support.

References


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•+ makes the ejection of the third electron much more difficult (i.e., by 490 mV)

11Rathore, R.; Burns, C. L.; Deselnicu, M. I. Org. Synth. 2005, 82, 1


13It should be noted that the addition of up to 10 equiv of neutral 3 to the solution of 3•+ or increasing the concentration of 3•+ by 10-fold did not show any change in its absorption spectrum

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
