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Journal of Physical Chemistry Letters, Vol. 8, No. 17 (2017): 4226-4230. DOI. This article is © American Chemical Society and permission has been granted for this version to appear in e-Publications@Marquette. American Chemical Society does not grant permission for this article to be further copied/distributed or hosted elsewhere without the express permission from American Chemical Society.

When Substituents Do Not Matter: Frontier Orbitals Explain the Unusually High and Invariant Oxidation Potential in Alkoxy-, Alkyl-, and H-Substituted Iptycenes

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Abstract

Frontier molecular orbitals (FMOs) have played a critical role in predicting reactivity/selectivity of pericyclic reactions. Here we show that the structurally similar iptycene-based hydroquinone ether (HE), that is, ^{MeO}Ipt and ^{BO}HE/^{BH}HE, molecules have drastically different ordering of bisallylic and quinoidal FMOs. They are almost degenerate in ^{BO}HE/^{BH}HE, while in ^{MeO}Ipt, the bisallylic orbital lies far below the quinoidal HOMO. Oxidation of ^{BO}HE/^{BH}HE induces coplanarization of the methoxy group and destabilizes the bisallylic HOMO, leading to a relatively low oxidation potential. In ^{MeO}Ipt, considerable energy must be invested in coplanarization of the methoxy group to bring about orbital swapping, resulting in an oxidation potential higher than that in structurally similar ^{BO}HE/^{BH}HE. As the quinoidal HOMO density does not extend to the substituent-bearing carbon in H-, alkyl-, and alkoxy-substituted iptycenes, their redox potentials remain invariant. This case study involving a simple visual inspection of the nodal arrangement as well as energetics of the FMOs and Walsh analysis could serve as a tool for the design of organic molecules with a desired redox potential.

Introduction

Development of tools to aid in the design of organic molecules with desired redox potentials would impact diverse areas of research from the syntheses of efficient molecular wires to redox shuttle additives for lithium-ion batteries to redox reagents for chemical synthesis.⁽¹⁻⁴⁾ We have recently shown that the redox potentials of *p*-hydroquinone ethers (HEs) can be fine-tuned in the range of 0.66–1.05 V (vs Fc/Fc⁺) by methylation (i.e., ^{Me2}HE and ^{Me4}HE) and/or double annulation of parent HE with bicyclo[2.2.1]heptane (i.e., ^{BH}HE) or bicyclo[2.2.2]octane (i.e., ^{BO}HE) frameworks ([Chart 1](#)).⁽⁵⁾

Chart 1

Chart 1. Molecular Structures of Various HEs and Other Relevant Molecules and Their Oxidation Potentials

Bearing a close structural resemblance to ^{BO}HE is a hydroquinone ether (^{MeO}Ipt) molecule, [Chart 1](#), which belongs to a well-known class of molecules, the iptycenes, [\(6\)](#) extensively explored for the preparation of functional materials for chemosensors, molecular machines, and supramolecular chemistry. [\(7-12\)](#) The dimethoxy iptycene ^{MeO}Ipt not only embodies the ^{BO}HE alkyl framework but also contains four additional phenylenes that should enhance through-space charge delocalization/stabilization. It is surprising, then, that the reversible redox potential of ^{MeO}Ipt is 300 mV *higher* than ^{BO}HE , while the parent iptycene (HIpt) and its alkyl-substituted analogues (AIpt) have similar oxidation potentials to ^{MeO}Ipt . This puzzling redox behavior of iptycene derivatives is further highlighted by the fact that a related set of bicyclo[2.2.1]heptane-annulated structures with methoxy (^{BH}HE), methyl (^{BH}XYL), and hydrogen (^{BH}Bz) substituents show the expected variation in their reversible redox potentials (see [Chart 1](#) and Figure S3 in the [Supporting Information](#)). [\(13\)](#)

In order to ascertain the origin of these unusual trends, we undertook experimental/computational analysis of the cation radicals produced via 1- e^- electrochemical/chemical oxidation of ^{MeO}Ipt , AIpt , and HIpt in comparison with other HEs in [Chart 1](#). This study will show that the interactions of the orbitals of the central aryl moiety in iptycenes with the orbitals of four additional phenylenes alter the energetic ordering of (parent benzene-like) HOMO/HOMO-1 (see [Chart 2](#)).

Chart 2

Chart 2. Isovalue Plots of Degenerate Frontier Molecular Orbitals of Benzene and Their Schematic Depiction Relevant to HEs

Unlike other HEs , which generally have a bisallylic orbital as the HOMO, in iptycenes, the quinoidal orbital is the HOMO. As the nodal arrangement of the quinoidal orbital prevents extension of the HOMO density at the carbons substituted by H, alkyl, and alkoxy groups in iptycenes, their HOMO energies do not vary, and consequently, their redox potentials are unaffected by the substituents.

This case study demonstrates that a simple visual examination of the frontier orbitals and their nodal arrangement can allow ready evaluation of the trends of redox/optical properties of electron donors and could serve as an important predictive tool for designing molecules with desired redox properties. The details of these findings are described below.

The parent iptycene (HIpt) and its derivatives ^{RO}Ipt ($R = CH_3$, ^{MeO}Ipt or $R = n$ -octyl, ^{AO}Ipt) and AIpt ($A = n$ -octyl) were synthesized by adaptation of literature procedures. [\(14\)](#) All compounds were characterized by $^1H/^{13}C$ NMR spectroscopy and MALDI mass spectrometry. Note that methoxy-substituted iptycene (^{MeO}Ipt) was sparingly soluble in CH_2Cl_2 , and therefore, a soluble octyloxy derivative (^{AO}Ipt) was also synthesized; see the [Supporting Information](#) for complete details.

Electrochemical oxidation of the parent iptycene and its derivatives and ^{BO}HE showed reversible cyclic voltammograms in CH_2Cl_2 ([Figure 1](#)). The oxidation potentials (E_{ox}) of ^{MeO}Ipt (1.15 V), AIpt (1.15 V), and HIpt (1.18 V) were found to be ~ 300 mV higher than that of ^{BO}HE (0.86 V). Expectedly, the oxidation potential of ^{AO}Ipt (1.10

V) was slightly lower (by 50 mV) than that of ^{MeO}Ipt due to the presence of alkoxy groups with long alkyl chains.⁽¹⁵⁾

Figure 1

Figure 1. Cyclic voltammograms of 2.0 mM ^{BO}HE, ^{MeO}Ipt, ^{AO}Ipt, ^{AI}Ipt, and ^{HI}Ipt in CH₂Cl₂ (0.1 M *n*-Bu₄NPF₆) at a scan rate of 200 mV s⁻¹ and 22 °C.

To examine these trends, we performed DFT calculations using the B1LYP-40/6-31G(d)+PCM(CH₂Cl₂) level of theory, which has been extensively benchmarked for the accurate description of electronic structures of a variety of π -conjugated cation radicals^(16, 17) and compared the frontier molecular orbitals (FMOs) of ^{MeO}Ipt with a series of hydroquinone ethers, including ^{BO}HE, in [Figure 2](#).

Figure 2

Figure 2. Compilation of FMOs of neutral HEs and ^{MeO}Ipt. For ^{MeO}Ipt, the relevant quinoidal HOMO and bisallylic HOMO–2 are shown; see the [Supporting Information](#) for additional details.

The degeneracy of the benzene-like FMOs in HEs is perturbed by substitution, with a substantial destabilization of the bisallylic orbital arising from methoxy groups lying in the aromatic plane and a modest change in the energy of the quinoidal orbital by the alkyl framework that varies depending on the nature and number of alkyl substituents ([Figure 2](#)).⁽⁵⁾ In the case of HE and its substituted derivatives, the extent of destabilization of the bisallylic orbital by the methoxy groups, when lying out of the aromatic plane, and of the quinoidal orbital by tetrasubstituted alkyl frameworks is similar and thus results in a negligible HOMO/HOMO–1 energy gap ([Figure 2](#)). A significantly larger energy gap arises in ^{MeO}Ipt (0.61 eV) due to the additional destabilization of its quinoidal orbital and stabilization of the bisallylic orbital by its four phenylenes, which also results in swapping of the order of quinoidal and bisallylic orbitals ([Figure 2](#)).

In contrast to the expected evolution of ionization potentials, that is, following Koopman's theorem and decreasing with increasing energy of the HOMO,⁽¹⁸⁾ the observed large energy gap (0.61 eV) and accompanying switching of the quinoidal (HOMO) and bisallylic (HOMO–1) orbitals in ^{MeO}Ipt (Figure 2) is insufficient to account for its unusually high oxidation potential. When considering thermodynamic oxidation potentials, one must also account for the energetic penalty associated with structural reorganization, such as the rotation of methoxy groups into a planar arrangement in order to stabilize the cationic charge in ^{BH}HE⁺⁺, ^{BO}HE⁺⁺, and ^{MeO}Ipt⁺⁺. Indeed, such a coplanarization of the methoxy groups in ^{BH}HE⁺⁺ and ^{BO}HE⁺⁺ is supported by X-ray crystallography.^(19, 20) In ^{BH}HE⁺⁺, the methoxy groups adopt a perfect in-plane arrangement due to the presence of the raised out-of-the-plane orientation of the bridgehead hydrogens in the bicyclo[2.2.1]heptane framework. On the other hand, in ^{BO}HE⁺⁺, the steric clash between in-plane bridgehead hydrogens from the bicyclo[2.2.2]octane framework and methoxy carbons resulted in reduced planarization of the methoxy groups (Figure S14 in the [Supporting Information](#)). The coplanarity of the methoxy groups with respect to the aromatic plane can be depicted by the dihedral angle C_{Ar}–C_{Ar}–O–Me, hereafter simply referred to as ϕ , which was $\sim 1^\circ$ and $\sim 20^\circ$ for ^{BH}HE⁺⁺ and ^{BO}HE⁺⁺, respectively (see structures in [Figure 3A](#)).

Figure 3

Figure 3. (A) X-ray crystal structures of ^{BH}HE⁺⁺ and ^{BO}HE⁺⁺.^(19, 20) Note that hydrogens and methyl groups from the ethoxy analogue of ^{BO}HE⁺⁺ are omitted for clarity. (B,C) Relative electronic energies [B1LYP-40/6-31G(d)+PCM(CH₂Cl₂)] of neutral (B) and cation radical (C) ^{BO}HE, ^{BH}HE, and ^{MeO}Ipt at varied orientations of the methoxy group. At each 5° increment, the dihedral angle between the methoxy group and the aromatic plane was fixed, while other geometrical parameters were optimized. Note that inclusion of thermal corrections leads to identical energies of bisallylic and quinoidal electronic structures of ^{MeO}Ipt⁺⁺. See Figures S7 and S8 in the [Supporting Information](#) for additional details.

Unfortunately, the crystal structure of ^{MeO}Ipt⁺⁺ was unavailable, which prevented experimental determination of the extent of coplanarity of its methoxy groups, relative to ^{BO}HE⁺⁺ and/or ^{BH}HE⁺⁺. Thus, in order to determine the extent of methoxy group rotation in ^{MeO}Ipt⁺⁺ and the associated (relative) energetic penalty with coplanarization of the methoxy groups in ^{MeO}Ipt (as well as ^{BH}HE and ^{BO}HE), we resorted to a computational approach. [Figure 3B,C](#) displays the relaxed potential energy surface scans, performed at both neutral and cation radical states, of

^{BO}HE, ^{BH}HE, and ^{MeO}Ipt against decreasing dihedral angle ϕ in the range of 90° (starting angle) to 0° (ending angle).

In accord with the X-ray crystallographic findings, presented above, the computed energy profiles in [Figure 3B](#) show that coplanarization of the methoxy groups in neutral ^{BH}HE results in a modest increase in its total energy (0.12 eV), as opposed to a significantly larger increase in the energies of ^{BO}HE and ^{MeO}Ipt (0.47 and 0.43 eV, respectively). Importantly, sigmoidal evolution of the energies of HEs vs ϕ in [Figure 3B](#) further shows that decreasing the ϕ below 30° in ^{BO}HE does not change its energy, while the energies of ^{BO}HE and ^{MeO}Ipt continue to increase up to $\phi = 0^\circ$ ([Figure 3B](#)).

While the computed energy profiles of the cation radicals in [Figure 3C](#) accurately reproduce the observed experimental differences in the redox potentials among ^{MeO}Ipt^{•+}, ^{BO}HE^{•+}, and ^{BH}HE^{•+}, a closer look is warranted as the evolution of the energies of the ^{MeO}Ipt^{•+} with varying ϕ are curiously different from that of ^{BO}HE^{•+} and/or ^{BH}HE^{•+}. The energy profiles show that in ^{BO}HE and ^{MeO}Ipt decreasing ϕ below 30° requires a sizable energetic penalty of ~0.1 eV and minimally lowers E_{ox} by 0.03 eV (compare panels B and C in [Figure 3](#)). In contrast, in ^{BH}HE, where at the same angle range there is almost no energetic penalty (i.e., ~0.01 eV) for the coplanarization of the methoxy groups, the oxidation potential decreases by 0.13 eV ([Figure 3B,C](#)). This analysis also suggests that multiple nearly isoenergetic structures of ^{BO}HE^{•+} are feasible with methoxy group orientations in the range of ($\phi =$) 0–30°. [\(21\)](#)

The energy profile of ^{MeO}Ipt^{•+} shows a marked change from ^{BO}HE^{•+} as well as ^{BH}HE^{•+} in the $\phi = 60$ –90° range ([Figure 3C](#)). First, two isoenergetic electronic structures of ^{MeO}Ipt^{•+} are feasible, that is, structures with out-of-the-plane ($\phi = 90^\circ$) and in-plane ($\phi = 0$ –30°) orientations of the methoxy groups, and their interconversion may involve a conical intersection (see Figures S7–S9 in the [Supporting Information](#) for additional details). While the computational analysis in [Figure 3C](#) fully corroborates the observed differences in the redox potentials among ^{MeO}Ipt^{•+}, ^{BO}HE^{•+}, and ^{BH}HE^{•+}, an intuitive understanding as to the origin of the observed (unusually) high redox potential of ^{MeO}Ipt is not immediately obvious.

We thus consider the fact that the energetic ordering of the (precursor) FMOs is expected to change upon removal of one electron from ^{BH}HE, ^{BO}HE, and ^{MeO}Ipt because of the accompanying rotation of out-of-the-plane methoxy groups into an in-plane arrangement. Therefore, we examined the Walsh-type diagrams showing the change in FMO energies against varied ϕ for ^{BH}HE, ^{BO}HE, and ^{MeO}Ipt in [Figure 4](#).

Figure 4

Figure 4. Energies [B1LYP-40/6-31G(d)+PCM(CH₂Cl₂)] of the bisallylic (blue) and quinoidal (red) FMOs of ^{MeO}Ipt, ^{BO}HE, and ^{BH}HE against varied dihedral angles between the methoxy group and the aromatic plane.

All three Walsh-type diagrams in [Figure 4](#) show that the energies of the quinoidal orbitals do not change with varying ϕ , irrespective of the sigma framework. In contrast, the energy of the bisallylic orbitals shows a large increase (~1.0 eV) with increasing coplanarity of the methoxy groups ([Figure 4](#)).

In accordance with the Koopman's theorem, as the HOMO energy increases, the oxidation energy lowers. For ^{BH}HE and ^{BO}HE, decreasing ϕ results in an increase in energy of the (bisallylic) HOMO, and as a consequence, the oxidation potentials decrease. However, in the case of ^{MeO}Ipt, the bisallylic orbital lies far below (0.61 eV) the quinoidal HOMO, and considerable energy needs to be expended as ϕ decreases until the bisallylic orbital can serve as the HOMO (compare [Figures 3](#) and [4](#)). Thus, the observed difference in the redox potentials between structurally similar ^{MeO}Ipt and ^{BO}HE arises because of a large energy gap between swapped quinoidal and bisallylic FMOs in ^{MeO}Ipt.

The possibility of two nearly isoenergetic electronic structures in the case of ^{MeO}Ipt^{•+} ([Figure 3C](#)) exists based on the similar energies of their corresponding quinoidal vs bisallylic HOMOs at $\phi \approx 30^\circ$ ([Figure 4](#), top). In the out-of-the-plane structure, the spin/charge distribution corresponds to a quinoidal orbital involving four additional phenylenes and without any energetic penalty for the rotation of methoxy groups. On the other hand, for the in-plane structure, a significant energetic penalty must be paid in advance to bring the methoxy groups in the aromatic plane to allow the bisallylic orbital to be involved in stabilization of the cation radical. The TD-DFT calculations showed that the two electronic structures of ^{MeO}Ipt^{•+} can be readily distinguished as the quinoidal cation radical contains transitions in the near-IR region, which are absent in bisallylic cation radical ([Figure S6](#) in the [Supporting Information](#)).

The cation radical spectrum of ^{MeO}Ipt^{•+}, generated using DDQ/MeSO₃H as an oxidant system ([22, 23](#)) in CH₂Cl₂ at ambient temperatures (red curve in [Figure 5](#)), showed a characteristic NIR transition, similar to those observed in other triptycene-like cation radicals, ([24](#)) suggesting dominance of the quinoidal electronic structure. ([25](#))

Figure 5

Figure 5. (A) Electronic absorption spectra and calculated spin densities of ^{MeO}Ipt^{•+}, ^AIpt^{•+}, and ^HIpt^{•+}. The spectrum of ^{BO}HE^{•+} is shown as a black dashed line. (B) HOMOs of neutral ^{MeO}Ipt, ^AIpt, and ^HIpt.

The DFT calculations clearly show that the lowest-energy electronic structures of H-, alkyl- and alkoxy-substituted iptycene cation radicals display similar spin-charge distributions arising from almost isoenergetic quinoidal HOMOs in each case ([Figure 5](#)). Indeed, this prediction is corroborated by our observation of a similar NIR transition in the electronic spectra of ^AIpt^{•+}, ^HIpt^{•+}, and ^{MeO}Ipt^{•+} ([Figure 5](#)).

In conclusion, the structurally similar ^{MeO}Ipt and ^{BO}HE/^{BH}HE molecules have drastically different ordering of FMOs, that is, bisallylic and quinoidal orbitals in ^{BO}HE/^{BH}HE are almost degenerate, while in ^{MeO}Ipt, the bisallylic orbital lies far below the quinoidal HOMO. It is well established that the oxidation of HEs induces coplanarization

of the methoxy group and destabilizes the bisallylic HOMO, leading to a relatively low oxidation potential. In contrast, in ^{MeO}Ipt, considerable energy must be invested in coplanarization of the methoxy group to bring about orbital swapping, resulting in an oxidation potential higher than that in structurally similar ^{BO}HE. Accordingly, electronic spectra of ^{MeO}Ipt^{•+} showed a characteristic NIR transition, suggesting the presence of a quinoidal electronic structure of ^{MeO}Ipt^{•+}. This was further supported by the spectra of H- and alkyl-substituted iptycene cation radicals (^HIpt^{•+} and ^AIpt^{•+}) that showed the presence of a similar NIR transition.

Finally, as the quinoidal HOMO in ^{MeO}Ipt, ^AIpt, and ^HIpt has no electron density at the substituent-bearing carbons, substitution by H, alkyl, and alkoxy groups has a minor impact on the energies of their HOMOs and thus provides a ready explanation for the striking invariance in their oxidation potentials.

This work should spur an interest in the design of organic molecules with desired redox potentials using a simple visual inspection of the nodal arrangement and energetics of the FMOs, akin to the prediction of the chemical reactivity of pericyclic reactions based on FMO analysis

Supporting Information

SYNTHESIS

Synthesis of parent iptycene (HIpt)1 dimethoxyiptycene (MeOIpt)1 was accomplished using a literature procedure.

^HIpt: Yield: 24%, mp >390 °C, mp¹ 483 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.44 (s, 2H), 7.30 (dd, J = 5.4, 3.2 Hz, 8H), 6.92 (dd, J = 5.4, 3.2 Hz, 8H), 5.32 (s, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 145.47, 142.55, 125.17, 123.53, 119.91, 54.03.

^{MeO}Ipt: Yield: 31%, mp >390 °C, mp¹ 400-402 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.34 (dd, J = 5.4, 3.1 Hz, 8H), 6.94 (dd, J = 5.4, 3.1 Hz, 8H), 5.67 (s, 4H), 3.88 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 147.05, 145.37, 136.47, 125.35, 123.68, 63.06, 48.29.

Synthesis of ^{RO}Ipt (R = n-octyl). Synthesis of dioctyloxyiptycene (^{RO}Ipt) was accomplished by a Williamson-type alkylation of iptycene-based hydroquinone S2² which was obtained from the readily available iptycenequinone S1³ by sodium borohydride reduction as follows.

To a suspension of iptycenequinone S1³ (2.0 g, 4.35 mmol) in anhydrous methanol (25 mL) and anhydrous THF (40 mL) under an argon atmosphere was added NaBH₄ (240 mg, 5.7 mmol) at 22 °C and the resulting mixture was stirred for 30 minutes. The solvent was evaporated and the crude product was used next step without further purification.

A mixture of iptycene-based hydroquinone S1 (1.0 g, 2.16 mmol), KOH (0.61 g, 10.8 mmol) and 1-bromooctane (1.12 mL, 6.48 mmol) in ethanol (60 mL) was refluxed under an argon atmosphere for 2h. An standard aqueous workup afforded a crude solid which was purified by column chromatography (0.62 g, 0.9 mmol, 42% yield). mp 245-247 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.31 (dd, J = 5.4, 3.2 Hz, 8H), 6.93 (dd, J = 5.4, 3.2 Hz, 8H), 5.64 (s, 4H), 3.90 (t, J = 6.8 Hz, 4H), 2.08 – 1.94 (m, 4H), 1.75 – 1.60 (m, 4H), 1.56 – 1.31 (m, 16H), 1.01 – 0.87 (m, 6H). ¹³C

NMR (101 MHz, CDCl₃) δ 146.22, 145.49, 136.34, 125.23, 123.66, 76.31, 48.51, 32.11, 30.71, 29.79, 29.59, 26.59, 22.89, 14.34.

Synthesis of ^AIpt (A = n-octyl). Synthesis of dioctylptycene^AIpt was accomplished by a two-step procedure using iptycenequinone³ as follows.

To a solution of 1-octyne (0.92 mL, 6.1 mmol) in THF (30 mL) at 0 °C was added nBuLi (2.5 mL, 6.25 mmol) was added with the aid of a syringe under an argon atmosphere. The resulting mixture was stirred for 1 hour and solid iptycenequinone (1.0 g, 2.2 mmol) was added. After stirring for 2 hours, the mixture was poured into water, then extracted with diethyl ether. The organic layer was separated and evaporated. The SnCl₂·H₂O (2.5 g) was dissolved in 30 mL of 50% acetic acid. The residue from the previous step was dissolved in 15 mL THF and added dropwise to SnCl₂ solution and stirred overnight. The mixture was poured into water and extracted with dichloromethane (3 × 30 mL). The organic layer was separated and dried over anhydrous MgSO₄ and evaporated to afford dioctyne S3 in 50% yield after column chromatography. mp 268-270 °C, ¹H NMR (400 MHz, cdcl₃) δ 7.32 (dd, J = 5.3, 3.2 Hz, 8H), 6.92 (dd, J = 5.3, 3.2 Hz, 8H), 5.78 (s, 4H), 2.74 (t, J = 6.8 Hz, 4H), 1.92 – 1.80 (m, 4H), 1.81 – 1.70 (m, 4H), 1.53 – 1.41 (m, 8H), 1.00 (t, J = 7.1 Hz, 6H). ¹³C NMR (101 MHz, cdcl₃) δ 145.30, 143.58, 125.20, 123.81, 115.04, 97.62, 76.39, 52.25, 31.72, 29.27, 28.95, 22.98, 20.09, 14.40.

Dioctyne S3 (1.0 g, 1.55 mmol) was dissolved in 50-mL ethyl acetate, then 50 mg of 10% Pd/C was added. The resulting mixture was stirred under H₂ atmosphere (40 psi) overnight. The resulting mixture was filtered through a celite pad and the solvent was evaporated and crude product was recrystallized from acetonitrile to afford pure A Ipt (1.0 g, ~100%). mp 248-250 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.29 (dd, J = 5.3, 3.2 Hz, 8H), 6.92 (dd, J = 5.3, 3.2 Hz, 8H), 5.56 (s, 4H), 3.07 (m, 4H), 1.59 (m, 8H), 1.38 (m, 16H), 0.94 (t, J = 6.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 145.86, 140.17, 129.98, 125.08, 123.44, 50.79, 32.13, 31.94, 30.27, 30.02, 29.52, 29.15, 22.94, 14.33.

¹H NMR of ^HIpt:

¹³C NMR of ^HIpt:

^1H NMR of MeOIpt :

^{13}C NMR of MeOIpt :

^1H NMR of $^{\text{RO}}\text{Ipt}$ (R = n-Octyl):

^{13}C NMR of $^{\text{RO}}\text{Ipt}$ (R = n-Octyl):

¹H NMR of S3:

¹³C NMR of S3:

¹H NMR of A₁pt (A = n-Octyl):

¹³C NMR of A₁pt (A = n-Octyl):

¹H NMR of ^{BO}HE

¹³C NMR of ^{BO}HE:

¹H NMR of ^{BH}HE

¹³C NMR of ^{BH}HE:

¹H NMR of BH₂Bz:

¹³C NMR of BH₂Bz:

¹H NMR of BH₂XYL

¹³C NMR of BH₂XYL

DENSITY FUNCTIONAL THEORY CALCULATIONS

Computational details

All electronic structure calculations were performed using density functional theory (DFT) as implemented in Gaussian 09, revision D.01⁵ using B1LYP-40/6-31G(d) level of theory.⁶⁻⁸ Solvent (CH₂Cl₂) effects were included using the implicit integral equation formalism polarizable continuum model (IEF-PCM)⁹⁻¹³. In all calculations, ultrafine Lebedev's grid was used with 99 radial shells per atom and 590 angular points in each shell. Tight cutoffs on forces and atomic displacement were used to determine convergence in geometry optimization procedure. Harmonic vibrational frequency calculations were performed for the optimized structures to confirm absence of imaginary frequencies for equilibrium geometries. For all cation radicals, wavefunction stability tests¹⁴ were performed to ensure absence of solutions with lower energy. Computed oxidation potentials (G_{ox}) are linearly correlated with the experimental oxidation potentials (Figure S1) and were scaled to experimental values as listed in Table S1.

Redox/optical properties of various HE and iptycene derivatives

Figure S1. Correlation plot between computed oxidation energies (G_{ox}) and experimental oxidation potentials (E_{ox}) with the linear best fit: $E_{ox} = 1.06 G_{ox} - 4.85$, $R^2 = 0.84$.

Table S1. Computed and scaled oxidation energies (G_{ox}) and experimental oxidation potentials (E_{ox})

Structure	G_{ox} , eV	G_{ox} (scaled), V	E_{ox} , V vs Fc/Fc ⁺
HE	5.34	0.82	0.92
Me ₂ HE	5.19	0.66	0.66
Me ₄ HE	5.57	1.07	1.05

^{BO} HE	5.45	0.94	0.86
^{BH} HE	5.23	0.71	0.67
^{MeO} Ipt	5.71	1.22	1.15
^A Ipt	5.54	1.04	1.15
^H Ipt	5.61	1.12	1.18
^{BH} XYL	5.51	1.01	0.99
^{BH} Bz	5.59	1.09	1.11

Experimental electronic absorption spectra of ^{MeO}Ipt^{•+}, ^AIpt^{•+}, and ^HIpt^{•+} were found to be uncannily similar with strongly red-shifted near-IR band, attesting to the triptycene-like delocalization of the cationic charge (Figure 5A in the manuscript). In contrast, spectrum of ^{BH}HE^{•+} did not show any transitions in the NIR region.

Computation of the vertical excitations in ^{MeO}Ipt^{•+}, ^AIpt^{•+}, and ^HIpt^{•+} using TD-DFT shows two peaks in the 790-1260 nm range (Figure S2). The nature of these transitions is identical across all three iptycene derivatives and involves transition to unoccupied “quinoidal” orbital. In contrast, ^{BH}HE^{•+} shows only one single bright transition at ~400 nm.

Figure S2. Left: Simulated stick spectra of ^{MeO}Ipt^{•+}, ^AIpt^{•+}, ^HIpt^{•+} and ^{BH}HE^{•+}. Right: orbitals involved in each transition calculated using TD-B1LYP-40/6-31G(d)+PCM(CH₂Cl₂).

Redox properties of ^{BH}HE, ^{BH}XYL, ^{BH}Bz

A set of BHHE derivatives with varied substitution showed expected variation in the redox potentials in the range of 0.44 V when substituents were changed from methoxy (^{BH}HE) to methyl (^{BH}XYL) to hydrogen (^{BH}Bz) as shown in Figure S3. DFT calculations reproduce a similar trend in the variation of the oxidation energies (Figure S4). In case of BHHE, upon oxidation the methoxy groups orient into the aromatic plane leading to the “bisallylic” electronic structure of the cation radical, while in the methyl- and hydrogen-substituted analogues (i.e. ^{BH}XYL and ^{BH}Bz), the electronic structure of their cation radicals remains “quinoidal”, and thus explains the drastically different oxidation potentials.

Figure S3. Cyclic voltammograms and square waves of 1,4-dimethoxybenzene and 1,4-dioctyloxybenzene (A) and $^{\text{BH}}\text{HE}$, $^{\text{BH}}\text{XYL}$ and $^{\text{BH}}\text{Bz}$ (B) in CH_2Cl_2 (0.1 M n-Bu4NPF6) at 200 mVs^{-1} and 22°C .⁴

$\text{MeO}^{\text{Ipt}^{+\bullet}}$

Figure S4. Structures, HOMO and spin-density plots of $^{\text{BH}}\text{HE}$ and its derivatives.

Redox/optical properties of “quinoidal” and “bisallylic” $\text{MeO}^{\text{Ipt}^{+\bullet}}$

DFT calculations showed that there are two stable equilibrium structures of $\text{MeO}^{\text{Ipt}^{+\bullet}}$ with in-plane ($\phi = 0^\circ$) and out-of-plane ($\phi = 90^\circ$) orientation of the methoxy groups. Spin density plots of the two $\text{MeO}^{\text{Ipt}^{+\bullet}}$ show completely different spin/charge distributions, which originate from ionization from “quinoidal” and “bisallylic” orbital (Figure S5).

Figure S5. Isovalue spin-density plots of “quinoidal” and “bisallylic” $\text{MeO}^+\text{Ipt}^{+\bullet}$.

Two conformations are isoenergetic with identical oxidation potentials ($G_{\text{ox}} = 5.71$ eV), however their electronic energies differ by 2.63 kcal/mol (Figure 6B in the manuscript and Table S2). Such difference arises mainly due to the thermal correction with the largest contribution from vibrational degrees of freedom. Despite their structural similarity, $\text{MeO}^+\text{Ipt}^{+\bullet}$. (90°) and $\text{MeO}^+\text{Ipt}^{+\bullet}$. (0°) contain slightly different vibration modes (see Table S3 for the lowest-energy frequencies), which contribute to the computed difference between electronic and Gibbs free energies.

Table S2. Thermodynamic data of “quinoidal” and “bisallylic” $\text{MeO}^+\text{Ipt}^{+\bullet}$. computed using B1LYP-40/6-31G(d)+PCM(CH_2Cl_2).

Absolute values, au	$\text{MeO}^+\text{Ipt}^{+\bullet}$ (90°)	$\text{MeO}^+\text{Ipt}^{+\bullet}$ (0°)
Electronic energy	-1536.853988	-1536.858186
ZPE	0.530574	0.533383
Thermal Correction	0.472155	0.476362
Gibbs Free Energy	-1536.381833	-1536.381823
Relative values, kcal/mol		
Electronic energy	2.63	0.00
ZPE	0.00	1.76
Thermal Correction	0.00	2.64

Table S3. Lowest energy frequencies of “quinoidal” and “bisallylic” $\text{MeO}^+\text{Ipt}^{+\bullet}$. computed using B1LYP-40/6-31G(d)+PCM(CH_2Cl_2). The table illustrates that despite structural similarity, modes of “quinoidal” and “bisallylic” $\text{MeO}^+\text{Ipt}^{+\bullet}$. may slightly differ.

$\text{MeO}^+\text{Ipt}^{+\bullet}$ (90°)			$\text{MeO}^+\text{Ipt}^{+\bullet}$ (0°)		
24	32	51	23	30	52
57	66	66	58	69	71
72	99	101	72	116	137
116	132	141	144	148	148
141	157	172	150	166	179
175	180	206	212	225	241
207	245	256	247	269	298
266	292	301	299	312	321
308	360	361	365	367	368
390	390	392	372	388	388
434	439	444	424	462	464
463	473	488	466	469	482
506	522	525	496	499	523

Predicted “quinoidal” and “bisallylic” electronic structures of $\text{MeO}^+\text{Ipt}^{+\bullet}$. can be easily distinguished using spectroscopy by observation of a near-IR transition from “quinoidal” cation radical due to the through-space charge delocalization in iptycene framework,¹⁵⁻¹⁷ while the “bisallylic” cation radical is expected to lack any absorption beyond 500 nm. Indeed, TD-DFT calculations show (Figure S6) that “quinoidal” and “bisallylic” $\text{MeO}^+\text{Ipt}^{+\bullet}$. can be readily distinguished as the “quinoidal” $\text{MeO}^+\text{Ipt}^{+\bullet}$. shows two transitions in the near-IR region, while “bisallylic” $\text{MeO}^+\text{Ipt}^{+\bullet}$. shows a single bright transition at ~400 nm.

Figure S6. Stick absorption spectra of “quinoidal” and “bisallylic” $\text{MeOIp}^{\bullet+}$. calculated using TD-B1LYP-40/6-31G(d)+PCM(CH_2Cl_2)

Relaxed potential energy surface (PES) scan of $\text{MeOIp}^{\bullet+}$. against $\text{C}_{\text{Ar}}\text{-C}_{\text{Ar}}\text{-O-Me}$ dihedral angle (ϕ), starting from the out-of-the-plane ($\phi = 90^\circ$) orientation and ending with the in-plane orientation ($\phi = 0^\circ$) at cation radical states (Figure S7) shows that “quinoidal” and “bisallylic” electronic structures of $\text{MeOIp}^{\bullet+}$. are separated by the conical intersection ($\phi = 60^\circ$) that is 0.15 eV (3.5 kcal/mol) higher in energy than “quinoidal” $\text{MeOIp}^{\bullet+}$. TD-DFT calculations further showed that $D_0 \rightarrow D_1$ transitions are dark (i.e., $f_{\text{osc}} = 0.0$) throughout the PES. Similarly to the ground state (D_0) PES, vertically excited state (D_1) PES also involves “quinoidal” and “bisallylic” electronic structures of $\text{MeOIp}^{\bullet+}$, which arise as the continuations of the respective curves at the ground state PES (see red and blue curves in Figure S7). Note that the energy gap at the conical intersection arises due to the absence of the structural reorganization at the D_1 state (calculations of the relaxed PES scan at the D_1 state were unsuccessful).

Figure S7. Relaxed potential energy surface scan (at each point, dihedral angle is fixed, while other geometrical parameters are optimized) of the ground state (D_0 , blue) and the vertically excited state of $\text{MeOIp}^{\bullet+}$ (i.e. at the optimized geometry of D_0 state) against dihedral angle between methoxy group and aromatic plane. (TD)-B1LYP-40/6-31G(d)+PCM(CH_2Cl_2) level of theory was employed.

A closer analysis of the electronic structures of $^{\text{MeO}}\text{Ipt}^{+\bullet}$, $^{\text{BO}}\text{HE}^{+\bullet}$, and $^{\text{BH}}\text{HE}^{+\bullet}$ along their PESs showed drastic differences in the evolution of their spin-density distributions (Figure S8). In particular, $^{\text{MeO}}\text{Ipt}^{+\bullet}$ shows a sharp switchover in the spin density distributions from “quinoidal” to “bisallylic” at the conical intersection ($\varphi = 60^\circ$). In contrast, although the starting ($\varphi = 90^\circ$) charge distribution is “quinoidal” in $^{\text{BH}}\text{HE}^{+\bullet}$, it continuously changes into the “bisallylic”, while in $^{\text{BO}}\text{HE}^{+\bullet}$ the charge distribution is “bisallylic” throughout the PES.

Figure S8. Top: Isovalue spin-density plots of $^{\text{BO}}\text{HE}^{+\bullet}$, $^{\text{BH}}\text{HE}^{+\bullet}$, and $^{\text{MeO}}\text{Ipt}^{+\bullet}$ at various points on the potential energy surface in the range of 50° - 90° angles. Bottom: Relative energies of $^{\text{BO}}\text{HE}^{+\bullet}$, $^{\text{BH}}\text{HE}^{+\bullet}$ and $^{\text{MeO}}\text{Ipt}^{+\bullet}$ against dihedral angle between methoxy group and aromatic plane.

Different nature of the spin/charge distributions in “quinoidal” and “bisallylic” $^{\text{MeO}}\text{Ipt}^{+\bullet}$ and $^{\text{BH}}\text{HE}^{+\bullet}$ is also reflected in their geometries as illustrated on the example of C-C bond in Figure S9. In $^{\text{BH}}\text{HE}^{+\bullet}$, there is a sharp but smooth shortening of the C-C bond that corresponds to continuous changes of the spin-density distributions from “quinoidal” to “bisallylic” (Figure S8). In contrast in $^{\text{MeO}}\text{Ipt}^{+\bullet}$, there is a discontinuity in the C-C bond length change that occurs at the conical intersection of “bisallylic” and “quinoidal” PES surfaces (compare Figures S7-S9). In $^{\text{BO}}\text{HE}^{+\bullet}$, no dramatic change in the C-C bond length occurs, as the spin/charge distributions remain “bisallylic” throughout the PES (Figure S9).

Figure S9. Plot of a representative C-C bond length against varied dihedral angle (as indicated) in $^{\text{BO}}\text{HE}^{+\bullet}$, $^{\text{BH}}\text{HE}^{+\bullet}$ and $^{\text{MeO}}\text{Ipt}^{+\bullet}$,

Walsh diagrams of BOHE and MeOIpt

To probe dependence of the FMOs ordering on the orientation of the methoxy group we performed a computational scan of FMO energies in $^{\text{BH}}\text{HE}$, $^{\text{BO}}\text{HE}$, $^{\text{MeO}}\text{Ipt}$ with respect to varied dihedral angle (ϕ) from 90° to 0° (Figures S10-S11 and Figure 4 in the manuscript). At each 5° increment, two dihedral angles were fixed, while other geometrical parameters were optimized. The scans show that the energy of the “bisallylic” orbital (filled blue circles) increase rapidly with decreasing angle, while the energy of “quinoidal” orbital (filled red circles) remains almost invariant to the orientation of the methoxy group. In $^{\text{MeO}}\text{Ipt}$, swapping of “quinoidal” and “bisallylic” orbitals occurs at 55° - 40° range. At this range HOMO and HOMO-1 represent a linear combination of “bisallylic” and “quinoidal” orbitals. In contrast in $^{\text{BH}}\text{HE}$, at the swapping between “quinoidal” and “bisallylic” occurs much more sharply as compared to $^{\text{MeO}}\text{Ipt}$ (compare Figures S10 and S11). Note the in $^{\text{MeO}}\text{Ipt}$ “bisallylic” orbital is HOMO-2 for equilibrium structure ($\phi = 90^\circ$), which swaps to HOMO-1 and then to HOMO upon rotation of the methoxy group.

Figure S10. Energies of the frontier orbitals (HOMO, HOMO-1 and HOMO-3) of $^{\text{MeO}}\text{Ipt}$ against varied orientation of the methoxy group relative to the aromatic plane [B1LYP-40/6-31G(d)+PCM(CH_2Cl_2)].

Figure S11. Energies of the frontier orbitals (HOMO and HOMO-1) of $^{\text{BH}}\text{HE}$ against varied orientation of the methoxy group relative to the aromatic plane [B1LYP-40/6-31G(d)+PCM(CH_2Cl_2)].

Figure S12. Three highest occupied FMOs of iptycene derivatives

MOLECULAR STRUCTURES OF ^{BO}HE⁺•, ^{BO}HE⁺• AND ^{MeO}IPT⁺•.

Figure S13. X-ray structures of ^{BO}HE⁺• and ^{BH}HE⁺•.^{18,19} Note that hydrogens and terminal methyl groups from the ethoxy analog of BOHE⁺• are omitted for clarity.

Figure S14. Stick and space-filling representations of ^{BH}HE⁺•, ^{BO}HE⁺• and ^{MeO}Ipt⁺•, showing different steric interactions between methoxy group and alkyl framework as indicated by difference interatomic distance between bridgehead hydrogen and methoxy carbon atoms.

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Optimized equilibrium structures of HIpt, Alpt, AOIpt, MeOIpt at neutral and cation radical states.

HIpt-N.log:

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1
GINC-HPC-CN35
FOpt
RBLYP
6-31G(d)
C34H22
0
```

```
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nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)
```

Optimization of neutral state

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C,0.3095200091,1.0303576203,1.6490146684
C,0.1523885626,1.2275447851,3.022976095
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C,3.7949220191,-4.4266755781,2.8356048245
C,1.6883927709,-3.3506680243,2.4338753629
C,2.5001550733,-3.5902889055,4.6952448392
C,3.6386742778,-4.2306493574,4.2008058189
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@

HIpt-CR.log:

1

1

GINC-HPC-CN26

FOpt

UBLYP

6-31G(d)

C34H22(1+,2)

0

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Optimization of cation radical

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S2=0.76672

S2-1=0.

S2A=0.750182

RMSD=9.304e-09

RMSF=1.188e-06

Dipole=-0.0000438,0.0000252,-0.0000072

Quadrupole=-12.3320209,-1.0280366,13.3600575,-0.5682799,2.1741999,-1.713476

PG=C01 [X(C34H22)]

@

AIpt-N.log:

1

1

GINC-HPC-CN118

FOpt

RBLYP

6-31G(d)

C40H34

0

```
#P BLYP IOP(3/76=0600004000)/6-31G(d) Opt(tight) SCRF(PCM,solvent=Dichloromethane)
nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)
```

Optimization of neutral state

```
0,1
C,0.4718136724,-0.2945288545,1.1375887934
C,0.0566511538,0.0421562326,3.9571531072
C,0.4000655158,-1.3868612535,2.0061501533
C,0.3222593301,0.969883594,1.7134438758
C,0.1283986022,1.1344882142,3.088591033
C,0.2062051823,-1.2222565088,3.3812984909
C,0.5202952731,-2.8603719193,1.6021160039
H,0.6611131863,-3.0081000101,0.5371300478
C,0.177898539,-2.5567063898,4.1345199552
H,0.0387981112,-2.4484250615,5.2045178473
C,0.3505776122,2.3043336696,0.9602242987
H,0.4896784045,2.1960527348,-0.1097736878
C,0.0081801275,2.6079987749,3.4926276688
H,-0.1326377526,2.7557252839,4.5576138333
C,1.4852486633,-3.2622225458,3.7979231802
C,3.7678924676,-4.5157454036,2.8422133005
C,1.6709855039,-3.4290173254,2.4221482993
C,2.4348460631,-3.7209258574,4.6931782105
C,3.5835393619,-4.3503996363,4.2080949139
C,2.8068354785,-4.0540440762,1.9399013992
H,2.2900727912,-3.5951739272,5.7578313686
H,4.3306801124,-4.7105756149,4.9013281071
H,2.950857411,-4.1844069882,0.8757333819
H,4.6586543431,-5.0043545882,2.4729512789
C,-0.9274366719,-3.3811410068,3.4876765046
C,-2.763230061,-4.8314454354,1.9969138267
C,-0.7418685697,-3.5444903513,2.1114142962
C,-2.0248801488,-3.9401683882,4.1172957111
C,-2.9474815534,-4.6688559747,3.3631563512
C,-1.6532625236,-4.2679416585,1.3632855418
H,-2.1684346349,-3.8149589166,5.1821397268
H,-3.8082162221,-5.1078990191,3.8478437082
H,-1.5087909299,-4.3974293508,0.2989933164
H,-3.4804882993,-5.3970894707,1.4188897147
C,1.2703521667,3.2921045279,2.9833329945
C,3.4759838575,4.4164408977,1.7315982169
C,2.1817545653,4.0155411012,3.731465406
C,1.4559206206,3.1287556179,1.6070709205
C,2.5533731215,3.6877687833,0.9774552266
C,3.2917318983,4.5790299153,3.0978408831
H,2.0372833995,4.1450269884,4.7957579191
H,2.6969289981,3.5625583305,-0.0873885074
H,4.0089980901,5.1446607208,3.6758681125
H,4.3367267978,4.8554710451,1.2469138176
C,-0.9567653654,3.0098631954,1.2968200454
C,-3.239392746,4.2634182475,2.2525268503
C,-1.1425024163,3.1766588238,2.6725944571
C,-1.9063541003,3.4685814429,0.4015636749
C,-3.0550391919,4.0980718531,0.8866453988
C,-2.2783442588,3.8017011981,3.1548399436
H,-1.761580098,3.3428297699,-0.6630894259
H,-3.8021726177,4.4582611193,0.1934111506
```

H,-2.4223658997,3.9320657095,4.2190078133
H,-4.1301473904,4.7520416293,2.6217876506
C,-0.1393960782,0.2197986439,5.4456425675
H,-0.7050446538,-0.6198956722,5.8498996849
H,-0.7532812807,1.099661997,5.638766221
C,0.6678621989,-0.472169902,-0.350900683
H,1.2817545514,-1.3520277813,-0.5440251286
H,1.2335033147,0.3675287476,-0.7551591569
C,-0.6520174235,-0.604157226,-1.1238892027
H,-1.2167888151,-1.4504574886,-0.7258874437
H,-1.2651256096,0.280881156,-0.9385706705
C,-0.4392818313,-0.7824415208,-2.6238717801
H,0.1456099346,-1.6795414787,-2.834644807
H,0.0965063527,0.0680027763,-3.0492966302
H,-1.3898913969,-0.8737716712,-3.1499397892
C,1.1804838078,0.3517753837,6.2186322718
H,1.7935865373,-0.5332663648,6.033311911
H,1.745260134,1.1980727452,5.8206315217
C,0.9677493409,0.5300582104,7.7186149151
H,0.4319512954,-0.3203812309,8.144037142
H,0.3828682581,1.4271643933,7.9293907252
H,1.9183603937,0.6213753948,8.2446822249

Version=EM64L-G09RevD.01

HF=-1543.8634809

RMSD=1.825e-09

RMSF=2.954e-07

Dipole=0.0000056,-0.0000011,0.0000002

Quadrupole=-2.1077366,-9.0453325,11.1530691,0.0467997,-1.5015115,2.5014156

PG=C01 [X(C40H34)]

@

AIpt-CR.log:

1

1

GINC-HPC-CN79

FOpt

UBLYP

6-31G(d)

C40H34(1+,2)

0

#P BLYP IOP(3/76=0600004000)/6-31G(d) Opt(tight) SCRF(PCM,solvent=Dichloromethane)
nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)

Optimization of cation radical

1,2

C,0.4811128464,-0.2974864193,1.1114677414

C,0.0473549828,0.0451048599,3.9832757733

C,0.3984388856,-1.3812213614,1.9827845129

C,0.3263462013,0.9589626429,1.6931350681

C,0.1300286924,1.1288398277,3.1119589541

C,0.2021249842,-1.2113438332,3.4016092177

C,0.504603136,-2.844392054,1.5891456587

H,0.6336920839,-2.9928799852,0.5243580437

C,0.18527544,-2.5374836172,4.1419779205

H,0.0566973843,-2.4289649005,5.2117374273

C,0.3432088455,2.2851031837,0.9527684361

H,0.471792612,2.1765850662,-0.1169904606

C,0.0238690264,2.5920100941,3.5055994003
H,-0.1052250791,2.7404969548,4.5703866119
C,1.5001633107,-3.2082048319,3.7809715059
C,3.8065457555,-4.3850755337,2.7940402656
C,1.6727733992,-3.3751631006,2.4024222169
C,2.4799521819,-3.6256513376,4.6685008085
C,3.6341117862,-4.2203567495,4.1671363525
C,2.8273931999,-3.9576904572,1.9023810976
H,2.3468675261,-3.4972777697,5.7333562541
H,4.4018839197,-4.5572389383,4.8482937154
H,2.9621495135,-4.0832240401,0.8374539504
H,4.7071535774,-4.848585659,2.4184774843
C,-0.938346986,-3.3267153798,3.4929907641
C,-2.8241860573,-4.7082165281,2.0070280283
C,-0.7663016103,-3.4911231996,2.1142475948
C,-2.0543932335,-3.8458216822,4.1311678213
C,-2.9956324694,-4.5433770398,3.3802125548
C,-1.7089043583,-4.178173097,1.3648140576
H,-2.1873479475,-3.7164974886,5.1958676279
H,-3.8656320599,-4.960709004,3.8659283385
H,-1.5772628158,-4.3057881135,0.2996155687
H,-3.5623620802,-5.2522463754,1.4359751112
C,1.2947815903,3.2387325578,2.9805059881
C,3.5241301261,4.2909670927,1.7145566822
C,2.2373861009,3.9257721806,3.7299466093
C,1.4668335204,3.0743255792,1.6017634807
C,2.582888402,3.5934226265,0.9635942195
C,3.3526770088,4.4558057308,3.087740499
H,2.1057394256,4.0533857688,4.795144658
H,2.7158488235,3.4640985415,-0.1011049018
H,4.0908551598,4.999826781,3.6587990582
H,4.3941371866,4.7082907504,1.2288471123
C,-0.9716763458,2.9558331545,1.313768356
C,-3.2780530394,4.1327243733,2.3006878003
C,-1.1442923896,3.1227914227,2.6923166876
C,-1.9514562582,3.3732896238,0.4262339153
C,-3.1056128982,3.9680058073,0.9275925731
C,-2.2989095512,3.7053286916,3.1923521206
H,-1.8183661269,3.2449167009,-0.6386209157
H,-3.873377478,4.3048971347,0.246431209
H,-2.4336708185,3.8308628246,4.2572785736
H,-4.1786581336,4.5962434777,2.6762460886
C,-0.1636667867,0.2214193977,5.4685942446
H,-0.742161872,-0.6155794009,5.8573893859
H,-0.7779663684,1.102542066,5.6486172602
C,0.6921377062,-0.4737969867,-0.3738509132
H,1.3064225041,-1.3549292477,-0.5538766629
H,1.2706484313,0.3631944802,-0.7626386018
C,-0.6199717912,-0.5973634722,-1.1624933369
H,-1.1946600289,-1.4417707589,-0.7761105961
H,-1.2322534037,0.2896545508,-0.9860848672
C,-0.380778505,-0.7734754056,-2.6581889002
H,0.2026470653,-1.6728989123,-2.8604857941
H,0.1643239137,0.0759320997,-3.0724142907
H,-1.3241350124,-0.8594167284,-3.1967715218
C,1.1484438641,0.3450122105,6.2572298609
H,1.7607379465,-0.5419982768,6.0808266313
H,1.7231186619,1.1894246416,5.8708382764
C,0.9092530863,0.5211333151,7.7529250054
H,0.3641671888,-0.3282800609,8.1671601271

H,0.3258125481,1.4205485021,7.9552158097
H,1.8526099535,0.6070960334,8.2915036458

Version=EM64L-G09RevD.01

HF=-1543.65832

S2=0.767503

S2-1=0.

S2A=0.7502

RMSD=5.658e-09

RMSF=9.774e-07

Dipole=0.0000093,-0.0000064,0.0000011

Quadrupole=-13.7313972,-3.6719851,17.4033823,-0.4495046,2.5395842,-1.4343274

PG=C01 [X(C40H34)]

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AOIpt-N.log:

1

1

GINC-HPC-CN85

FOpt

RBLYP

6-31G(d)

C40H34O2

0

#P BLYP IOP(3/76=0600004000)/6-31G(d) Opt(tight) SCRF(PCM,solvent=Dichloromethane)
nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)

Optimization of neutral state

0,1

C,0.3212412725,-0.1573178636,1.1455858852
C,0.2446635264,0.0002253151,3.9561117614
C,0.308190062,-1.3112441527,1.9218913409
C,0.2984752864,1.0761537168,1.7877089726
C,0.2577129875,1.1541515836,3.1798073291
C,0.2674279134,-1.2332460611,3.3139886424
C,0.3435187194,-2.7460148775,1.4068592459
H,0.3919623574,-2.8006824207,0.3241542098
C,0.243213027,-2.6015371033,3.9865544243
H,0.1946604769,-2.5347454669,5.0686092128
C,0.3226935761,2.4444447916,1.1151424195
H,0.3712500854,2.3776521513,0.033087979
C,0.2223824774,2.5889229195,3.6948376767
H,0.1739356482,2.643592281,4.7775424793
O,0.3845180967,-0.2340438658,-0.2246889606
O,0.1813885054,0.0769462255,5.3263869532
C,1.4529057046,0.1208159651,5.9789426077
H,2.0246692089,-0.7757498978,5.7254574465
H,2.0178929958,0.9852331654,5.6204217281
C,-0.8869976038,-0.277886189,-0.8772475269
H,-1.452002282,-1.1422942935,-0.5187308317
H,-1.4587456318,0.6186891231,-0.6237619739
C,1.4838846798,-3.3308253203,3.4829116259
C,3.6182183777,-4.5933732629,2.2386855914
C,1.5395130766,-3.4054338269,2.0860657445
C,2.4894705689,-3.8858448056,4.2536292063
C,3.5627762256,-4.5200650108,3.6236028211
C,2.6012238651,-4.0341314956,1.4614980971
H,2.4453580731,-3.8315273984,5.3331138985

H,4.3524830969,-4.9555949142,4.2195273776
H,2.6448077932,-4.0918502366,0.3823229793
H,4.4514562732,-5.0854003261,1.7569680743
C,-0.9473664437,-3.3421312534,3.3859148321
C,-2.9615957625,-4.6367316075,1.9832667849
C,-0.8916792369,-3.4238591675,1.9894798148
C,-2.0046351106,-3.9050567595,4.077205154
C,-3.0170625024,-4.5552232084,3.3677297578
C,-1.8927321289,-4.0689359705,1.2859229831
H,-2.0483658624,-3.8420826155,5.1560684286
H,-3.8468522063,-4.9964915068,3.9017320848
H,-1.8483433798,-4.1351369256,0.2071165001
H,-3.7478162139,-5.1419479792,1.4400700159
C,1.4575835333,3.2667644593,3.112220556
C,3.5829723114,4.3981234584,1.7339736545
C,2.4586369007,3.9118388429,3.8157786587
C,1.5132724941,3.1850383607,1.7157851954
C,2.5705434554,3.7479611621,1.0244963198
C,3.5275031455,4.4796316732,3.1184364079
H,2.4142474297,3.978040573,4.8945850825
H,2.6142750522,3.6849868754,-0.0543668786
H,4.3137237236,4.9848455934,3.6616352596
H,4.4127643995,4.83938945,1.199973196
C,-0.9179784174,3.1737346604,1.6187813279
C,-3.0523099126,4.4362899794,2.8630045049
C,-0.9736085892,3.2483437925,3.0156275465
C,-1.9235608262,3.7287584575,0.8480625541
C,-2.996864693,4.362983421,1.4780875802
C,-2.0353188767,3.8770437688,3.6401935859
H,-1.879446593,3.6744430716,-0.2314221557
H,-3.7865679829,4.7985175032,0.8821613552
H,-2.0789046453,3.9347620639,4.7193686135
H,-3.8855466974,4.9283201409,3.3447207289
C,1.2189462609,0.2091770771,7.4733359341
H,0.6266116849,-0.6525713028,7.7862638734
H,0.6187433501,1.0967500799,7.6816085826
C,2.527393913,0.2621480813,8.2569649909
H,3.1239619782,1.1307260986,7.9742153654
H,3.1321808223,-0.628439142,8.0798852834
H,2.3354078697,0.3255278484,9.3274320385
C,-0.653034865,-0.3662530704,-2.3716397841
H,-0.0606879792,0.495485323,-2.6845717843
H,-0.0528435677,-1.2538356584,-2.5799063846
C,-1.9614817971,-0.4192082557,-3.1552701531
H,-2.5662612678,0.4713828039,-2.9781832436
H,-2.5580576482,-1.2877836235,-2.8725291827
H,-1.7694945587,-0.4825790221,-4.2257374228

Version=EM64L-G09RevD.01

HF=-1694.2240725

RMSD=3.387e-09

RMSF=2.171e-07

Dipole=0.0000033,0.0000199,-0.0000018

Quadrupole=-2.5405708,-9.4475213,11.9880921,0.4561879,7.6509598,1.2468789

PG=C01 [X(C40H34O2)]

@

AOIpt-CR.log:

1

1

GINC-HPC-CN124
FOpt
UBLYP
6-31G(d)
C40H34O2(1+,2)
0

#P BLYP IOP(3/76=0600004000)/6-31G(d) Opt(tight) SCRF(PCM,solvent=Dichloromethane)
nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)

Optimization of cation radical

1,2
C,0.3003195466,-0.1638500345,1.1180933654
C,0.2655858771,0.0067527245,3.9836030925
C,0.3005131565,-1.3073676965,1.9059727842
C,0.291747641,1.0651967084,1.7650240437
C,0.2653941167,1.1502702358,3.1957237422
C,0.2741606455,-1.2222941186,3.3366724277
C,0.3367231284,-2.7342924113,1.4054903508
H,0.3802776425,-2.7923129285,0.3239627959
C,0.2487607739,-2.5800288986,4.0028951831
H,0.2041641038,-2.5103096357,5.0837058514
C,0.3171512814,2.4229319124,1.0988020351
H,0.3617495068,2.3532134722,0.0179913977
C,0.2291859678,2.5771948699,3.6962061986
H,0.1856298716,2.6352153308,4.7777337189
O,0.3618488442,-0.2444501782,-0.2385312055
O,0.2040547223,0.0873516052,5.3402277437
C,1.4757030515,0.1154496236,6.0152107535
H,2.0406190764,-0.782088745,5.7553931328
H,2.0454870072,0.9814763657,5.6724587667
C,-0.9097998596,-0.2725367564,-0.9135140221
H,-1.4795749838,-1.1385805119,-0.5707897507
H,-1.4747242717,0.6249872311,-0.6536659056
C,1.4974289011,-3.2763316287,3.4859454603
C,3.6592559987,-4.4691264581,2.2269024814
C,1.5458730967,-3.3552284943,2.0868427812
C,2.5312177123,-3.7882688112,4.2554467099
C,3.6113217286,-4.3908165072,3.6180980688
C,2.6276624555,-3.9464092971,1.4531300257
H,2.4945216552,-3.7274319032,5.3338723992
H,4.4188051386,-4.8017600726,4.2062723223
H,2.666068043,-4.0041431604,0.3747633557
H,4.5041725416,-4.9394527172,1.7454793613
C,-0.9544138137,-3.2880802926,3.4005764165
C,-3.0081062139,-4.5190997113,2.0042432196
C,-0.9056845603,-3.375656028,2.0021648953
C,-2.030876872,-3.8102479463,4.1006232888
C,-3.0566360877,-4.4314378875,3.3948881068
C,-1.9334159436,-3.986095346,1.2993909795
H,-2.0694456278,-3.7398144707,5.1782031921
H,-3.8973429908,-4.8493424794,3.9291362963
H,-1.8955762674,-4.0542226654,0.2215298559
H,-3.8109179811,-5.0052809741,1.4694614887
C,1.4715943652,3.2185581089,3.0995333195
C,3.6225485427,4.2743384201,1.7068129764
C,2.4993256301,3.8289961313,3.8023085297
C,1.5203249817,3.1309831136,1.7011221533
C,2.5967889425,3.6531503235,1.0010765765

C,3.5740174393,4.3619995752,3.0974577355
 H,2.4614854671,3.8971225454,4.8801696994
 H,2.6353588133,3.5827169038,-0.0765033011
 H,4.3768294424,4.8481791081,3.6322407291
 H,4.4632566489,4.6922417796,1.1725656835
 C,-0.9315178213,3.1192341243,1.6157501422
 C,-3.0933479343,4.3120255123,2.8747911764
 C,-0.9799637368,3.1981304913,3.0148527072
 C,-1.9653065955,3.631169735,0.8462478251
 C,-3.0454119663,4.2337160359,1.4835954271
 C,-2.0617547276,3.789309259,3.6485645875
 H,-1.9286093834,3.5703330078,-0.2321778315
 H,-3.8528952112,4.6446588274,0.8954203687
 H,-2.1001616277,3.8470423787,4.7269312413
 H,-3.9382658456,4.7823503441,3.3562133278
 C,1.2138993702,0.1861353161,7.5044137715
 H,0.6146243568,-0.6778682108,7.7960400135
 H,0.6141417514,1.073536457,7.7126656464
 C,2.5110219426,0.2251078647,8.3078173505
 H,3.1141720196,1.0953588567,8.0459070463
 H,3.1151206918,-0.6656902284,8.1307090848
 H,2.2997338279,0.2763228254,9.3748683704
 C,-0.6479968781,-0.3431703156,-2.4027199568
 H,-0.0487332944,0.5208504212,-2.694318695
 H,-0.0482279398,-1.230556739,-2.6110018297
 C,-1.9451197137,-0.3821342443,-3.2061236078
 H,-2.54923591,0.5086445322,-3.0289769702
 H,-2.5482522409,-1.2524080809,-2.9442493511
 H,-1.7338321661,-0.433299493,-4.2731771516

Version=EM64L-G09RevD.01

HF=-1694.0132039

S2=0.765311

S2-1=0.

S2A=0.750161

RMSD=9.031e-09

RMSF=4.121e-07

Dipole=-0.0000123,0.0000047,-0.0000024

Quadrupole=-13.8923014,-3.3297023,17.2220037,0.3997492,12.2182707,-0.9731305

PG=C01 [X(C40H34O2)]

@

MeOIpt-N.log:

1

1

GINC-HPC-CN102

FOpt

RBLYP

6-31G(d)

C36H26O2

0

#P BLYP IOP(3/76=0600004000)/6-31G(d) Opt(tight) SCRF(PCM,solvent=Dichloromethane)
 nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)

Optimization of neutral state

0,1

C,0.3749948078,-0.0992979357,1.142259229

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C,0.3737185479,-1.222644212,1.9618642476
C,0.3259443584,1.158032706,1.7341924058
C,0.2708404198,1.2895472674,3.1218154409
C,0.318615664,-1.0911294884,3.3494869378
C,0.4368197692,-2.6756014322,1.5035538976
H,0.4962572447,-2.7719335067,0.4243175966
C,0.3098892659,-2.4323291675,4.0749377708
H,0.2502500018,-2.324483794,5.1530671418
C,0.3346695557,2.4992335151,1.0087433765
H,0.3943107177,2.3913914609,-0.069386384
C,0.2077367239,2.7425038243,3.5801271992
H,0.1482975771,2.8388335589,4.6593633625
O,0.4521658708,-0.2283087304,-0.2243804242
O,0.1923935615,0.295208204,5.3080617298
C,1.4557758763,0.3842648233,5.9564110021
H,2.0527260338,-0.5112726222,5.7781837626
H,1.2541175142,0.4805248985,7.0195350584
H,2.0141295068,1.2555162671,5.6109516372
C,-0.8112162426,-0.3173521871,-0.8727314042
H,-1.3695874786,-1.1885864523,-0.5272564793
H,-0.6095567049,-0.4136359572,-1.9358529672
H,-1.4081493597,0.57820033,-0.6945224147
C,1.566706216,-3.1603938274,3.6109237591
C,3.7324544768,-4.4354277789,2.4358994714
C,1.6367285356,-3.2883295639,2.2186520738
C,2.5736059358,-3.6685254644,4.4116897907
C,3.6627444538,-4.3092185348,3.8163678811
C,2.7141735153,-3.9234528703,1.6284544869
H,2.5184277484,-3.5729046987,5.4878009438
H,4.4536020645,-4.7083601412,4.4357690738
H,2.7688862086,-4.0223991472,0.5527931331
H,4.5779171873,-4.9322398504,1.981165791
C,-0.8633165454,-3.2145998353,3.4931038449
C,-2.8439571042,-4.5942512628,2.1241636035
C,-0.7930931191,-3.3498368884,2.1015365246
C,-1.9184563742,-3.7665318499,4.196414388
C,-2.9138882756,-4.4597069907,3.5038308131
C,-1.7773436917,-4.0373512384,1.4147284774
H,-1.9735945504,-3.6621171666,5.2715207268
H,-3.741888718,-4.8927783724,4.0472230891
H,-1.7216821677,-4.1444161995,0.33975003
H,-3.617134841,-5.1324957767,1.5941454866
C,1.4376498158,3.4167415283,2.9821460869
C,3.5584453908,4.5266117547,1.5798522441
C,2.4218991401,4.104257612,3.6689541131
C,1.5078742552,3.2815040897,1.5905789025
C,2.563014253,3.8334358623,0.8872683012
C,3.48851267,4.6611575006,2.9595191883
H,2.366236581,4.2113238493,4.7439323369
H,2.6181531845,3.7290203997,-0.1878379165
H,4.2616897048,5.1994028811,3.4895374152
H,4.3864461841,4.9596830184,1.0364603997
C,-0.9221478652,3.2272975301,1.4727567703
C,-3.0878985082,4.5023289081,2.6477809054
C,-0.9921721448,3.3552312482,2.8650286321
C,-1.9290469047,3.7354305872,0.6719908433
C,-3.0181863873,4.3761221996,1.2673124713
C,-2.0696183211,3.9903527808,3.4552260802
H,-1.8738679842,3.6398119202,-0.404120474
H,-3.8090430529,4.7752645007,0.6479105415

H,-2.1243315532,4.0892970514,4.5308876023
H,-3.9333619608,4.9991399366,3.1025143597

Version=EM64L-G09RevD.01

HF=-1537.0655275

RMSD=4.466e-09

RMSF=2.696e-07

Dipole=0.,0.0000079,-0.0000019

Quadrupole=-1.3374587,-8.5350995,9.8725582,0.8409882,7.3652123,1.9252097

PG=C01 [X(C36H26O2)]

@

B-MeOIpt-CR.log:

1

1

GINC-HPC-CN69

FOpt

UBLYP

6-31G(d)

C36H26O2(1+,2)

17-May-2017

0

#P BLYP IOP(3/76=0600004000)/6-31G(d) Opt(tight) SCRF(PCM,solvent=Dichloromethane)
nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)

Optimization of cation radical

1,2

C,-0.0047792001,0.062999021,-0.0158222735
C,2.8184199745,0.0612135472,0.014784388
C,0.6877203741,0.0487041535,-1.249021663
C,0.7495996329,0.0763736686,1.2087831396
C,2.1259204281,0.0755092473,1.2479830878
C,2.0640412187,0.0478332137,-1.2098211865
C,0.1592957712,0.035975742,-2.6924704258
H,-0.915213738,0.0368330987,-2.7796099688
C,2.7318794271,0.0339752737,-2.5760609416
H,3.8120236621,0.0330603148,-2.5100665419
C,0.0817618617,0.0902252943,2.575023846
H,-0.9983824043,0.091131894,2.5090293233
C,2.6543457314,0.088242756,2.6914322759
H,3.7288555378,0.0873908799,2.7785714022
O,-1.3008300497,0.0657010184,0.1976893228
O,4.1144711474,0.0584996226,-0.1987239555
C,5.1427293548,0.0747125846,0.7967844473
H,5.0746802798,0.9783898467,1.3941205404
H,6.0676978422,0.0737384234,0.2336541686
H,5.0845077028,-0.8168838491,1.4131172993
C,-2.3290930011,0.0494880311,-0.7978144527
H,-2.2708871108,0.9410935007,-1.4141349194
H,-3.2540586459,0.0504463589,-0.2346793879
H,-2.2610351422,-0.8541813674,-1.3951623259
C,2.1767963832,1.2509222206,-3.3084793773
C,0.8431208522,3.3040775664,-4.6006700437
C,0.783537892,1.2494914824,-3.374009453
C,2.908416592,2.2763660944,-3.8791474725
C,2.2300964613,3.3081472348,-4.5302798002
C,0.1082852859,2.2688328729,-4.0198236729
H,3.9881723128,2.2775358026,-3.8269988634

H,2.7901755607,4.1137717485,-4.9828192989
 H,-0.9715330107,2.2649699845,-4.0766929743
 H,0.3271172128,4.1069395255,-5.1072820474
 C,2.1737436524,-1.1946817703,-3.2860950737
 C,0.8356693545,-3.2678903272,-4.5409831929
 C,0.7804864474,-1.1912256754,-3.3518493375
 C,2.9031637217,-2.2318887507,-3.8380118713
 C,2.2226321497,-3.2738219852,-4.4703704438
 C,0.1030101016,-2.2206465262,-3.9791727936
 H,3.9829319377,-2.2342785033,-3.7858438732
 H,2.7809386807,-4.0887605289,-4.9081847721
 H,-0.9768019924,-2.2156552184,-4.0367589688
 H,0.3179241802,-4.0786307129,-5.0330672323
 C,2.033147311,1.3154437172,3.35080561
 C,0.5909915042,3.3980444614,4.4693058388
 C,2.710618963,2.3448736056,3.9781201534
 C,0.6398900658,1.3188931979,3.2850505355
 C,-0.089534962,2.3561025154,3.8369567973
 C,1.9779544169,3.3921192279,4.5399198689
 H,3.7904310489,2.3398894199,4.0357091471
 H,-1.169303248,2.3584859559,3.7847889422
 H,2.4956949546,4.2028669068,5.0319968692
 H,0.0326809415,4.212984655,4.9071119273
 C,0.6368528114,-1.1267116903,3.3074458968
 C,1.9705396885,-3.1798629302,4.5996315274
 C,2.0301118602,-1.1252750471,3.3729733307
 C,-0.0947617378,-2.1521588108,3.8781156737
 C,0.5835640436,-3.1839375913,4.5292461041
 C,2.7053697116,-2.1446154554,4.0187837989
 H,-1.1745174726,-2.1533332972,3.8259684486
 H,0.0234890983,-3.9895639938,4.9817870946
 H,3.7851881305,-2.14074833,4.0756469176
 H,2.4865484403,-3.9827233256,5.106240882

Version=EM64L-G09RevD.01

HF=-1536.8581856

S2=0.768715

S2-1=0.

S2A=0.750152

RMSD=5.294e-09

RMSF=4.393e-06

Dipole=-0.0000051,0.0000016,0.0000014

Quadrupole=24.1037071,-14.8153717,-9.2883354,0.4386499,8.670536,0.0714402

PG=C01 [X(C36H26O2)]

@

Q-MeOIpt-CR.log:

1

1

GINC-HPC-CN73

FOpt

UBLYP

6-31G(d)

C36H26O2(1+,2)

0

#P BLYP IOP(3/76=0600004000)/6-31G(d) Opt(tight) SCRF(PCM,solvent=Dichloromethane)
 nosym scf(fermi,xqc,maxcyc=200) int(grid=ultrafine)

Optimization of cation radical

1,2

C,0.3602815673,-0.1033201636,1.115228319
C,0.2842706745,0.1702202615,3.9684520494
C,0.3684833442,-1.2180708426,1.9428646818
C,0.323398593,1.14852073,1.7150370804
C,0.2760727829,1.2849710897,3.1408158982
C,0.3211609962,-1.0816207984,3.3686435156
C,0.4341380919,-2.6613209311,1.4949809382
H,0.493126096,-2.7580263459,0.4169617368
C,0.3080944498,-2.4143283941,4.0839791417
H,0.247387626,-2.3061632719,5.1608230632
C,0.3364692267,2.4812289033,0.9997027282
H,0.3971781348,2.3730652012,-0.0771411605
C,0.2104203385,2.7282219955,3.588699417
H,0.1514305925,2.8249267767,4.6667184893
O,0.4408332273,-0.2322829927,-0.2379905694
O,0.2037091118,0.2991791768,5.3216711429
C,1.4630874722,0.3724142592,5.99724233
H,2.0507444536,-0.5283186448,5.822664735
H,1.2344422255,0.4626492221,7.0537031583
H,2.0311332288,1.2415961533,5.6671311818
C,-0.8185509562,-0.3054777403,-0.9135561358
H,-1.3866051851,-1.1746639475,-0.5834699895
H,-0.5899144212,-0.3956800323,-1.9700215456
H,-1.4061967264,0.5952560025,-0.7389452058
C,1.5747242734,-3.1082603122,3.609170717
C,3.7724541716,-4.3098611374,2.4227340432
C,1.6436041514,-3.2370369415,2.2144939961
C,2.606074487,-3.5746490406,4.410381287
C,3.704283298,-4.1817929735,3.8095071318
C,2.7433455182,-3.8328416605,1.6169360243
H,2.5539070585,-3.4752906832,5.4853412853
H,4.5102959879,-4.5575517885,4.4226762138
H,2.7973337961,-3.9287945022,0.5419985571
H,4.6313623173,-4.7832708803,1.9699766944
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C,-2.8891746395,-4.4782756599,2.1140440508
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C,-1.9528400277,-3.6776699525,4.1962211082
C,-2.9584214795,-4.3409337794,3.4998999816
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H,-2.0077745,-3.5687546344,5.2698582971
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H,-1.7594254041,-4.0596999964,0.3304324424
H,-3.6766159156,-4.9967877041,1.5868546051
C,1.450415047,3.3677937163,2.9852891976
C,3.6029868816,4.4078286772,1.5837860066
C,2.4581366155,4.0204035296,3.6791364687
C,1.5198203203,3.2303077906,1.5916948468
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C,3.5337370127,4.5451727049,2.969641194
H,2.4039827518,4.1266033982,4.7532509608
H,2.6523422767,3.6356480945,-0.1861731288
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H,4.4442541802,4.8199602205,1.0459638711
C,-0.9301608402,3.17516239,1.4745087978
C,-3.1278933078,4.3767641654,2.6609383008
C,-0.9990435053,3.3039405898,2.8691852333
C,-1.9615096798,3.6415477551,0.6732955415

C, -3.0597206586, 4.2486924661, 1.2741663039
C, -2.0987854569, 3.8997464672, 3.4667392928
H, -1.9093403025, 3.5421858979, -0.4016640427
H, -3.8657327425, 4.6244484037, 0.6609946634
H, -2.1527768411, 3.9957018934, 4.5416764352
H, -3.986802204, 4.8501738496, 3.1136943267

Version=EM64L-G09RevD.01
HF=-1536.8539882
S2=0.765154
S2-1=0.
S2A=0.750158
RMSD=7.641e-09
RMSF=4.063e-07
Dipole=-0.0000018, -0.0000255, 0.0000053
Quadrupole=-12.0980812, -1.6433735, 13.7414546, 0.6398901, 11.838085, -0.3634023
PG=C01 [X(C36H26O2)]

@

Acknowledgment

We thank the NSF (CHE-1508677) and NIH (R01-HL112639-04) for financial support. We also thank Professors Scott A. Reid, Qadir K. Timerghazin, and Marat R. Talipov for helpful discussions. The calculations were performed on the high-performance computing cluster Père at Marquette University and the Extreme Science and Engineering Discovery Environment (XSEDE).

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- [15](#) Note that a similar difference was observed in the reversible oxidation potentials of 1,4-dimethoxybenzene (0.92 V vs Fc/Fc⁺) and 1,4-dioctyloxybenzene (0.86 V vs Fc/Fc⁺) due to the increasing size of the alkyl chain in the alkoxy group.
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- [18](#) Note that the HOMO energy of ^{MeO}Ipt is far higher than that of ^{BO}HE or ^{BH}HE, suggesting that its ionization potential (IP) should be lower than that of ^{BO}HE or ^{BH}HE. This contrasting evolution of IP vs *E*_{ox1} in ^{MeO}Ipt, ^{BO}HE, and ^{BH}HE may suggest that the reorganization penalties are dramatically different for quinoidal vs bisallylic hole distributions. This unusual observation is under investigation and will be reported in due course.
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- [21](#) A nearly flat energy profile of ^{BO}HE⁺⁺ in the range of 0–30° ([Figure 3B](#)) suggests that ^{BO}HE⁺⁺ can exist with various orientations of the methoxy groups. Indeed, the observation of a dihedral angle of ~20° in ^{BO}HE⁺⁺ in its X-ray structure is understandable, and it is possible that crystal modification may exist where the methoxy group may adopt a completely in-plane arrangement with minimal energetic penalty.
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- [25](#) Unfortunately, due to high oxidation potential of ^{MeO}Ipt, quantitative generation of its cation radical was not feasible, and therefore, the presence of the bisallylic electronic structure of ^{MeO}Ipt⁺⁺ cannot be ruled out.