Ferrocene Acidity and C–H Bond Dissociation Energy via Experiment and Theory

Published as part of The Journal of Physical Chemistry virtual special issue “Leo Radom Festschrift”.

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Supporting Information

ABSTRACT: The gas-phase acidity of ferrocene (ΔH° acid(1) = 391.5 ± 1.3 kcal mol⁻¹) and electron affinity of the ferrocenyl radical (EA(Ir) = 1.74 ± 0.08 eV) were measured in a Fourier transform mass spectrometer and combined in a thermodynamic cycle with the known ionization energy of the hydrogen atom to afford the C–H bond dissociation energy of 1 (BDE(1) = 118.0 ± 2.3 kcal mol⁻¹).

Companion M06-2X but not B3LYP computations reproduce each of these thermodynamic quantities and are in accord with an unusually strong aromatic C–H BDE. Natural population analysis and atomic polar tensor charges indicate that a covalent description of ferrocene with a neutral iron atom is a better representation of this compound than an ionic one with a doubly charged Fe²⁺ center. Predicted structural differences upon deprotonation of MCp₂, M = Fe and Mg, are also in accord with this view.

INTRODUCTION

Ferrocene (FeCp₂, 1) was first reported by Kealy and Pauson in 1951, and its sandwich structure was correctly assigned the following year.⁴⁻⁵ This led to the development, characterization, and investigation of the class of compounds now known as metallocenes. Over the intervening years, these species were extensively studied for a wide variety of uses spanning from a fuel additive for diesel engines⁶ to medical applications given the antianemic and cytotoxic properties of 1.⁷,⁸ This led to the incorporation of ferrocene into the anticancer drug tamoxifen and has resulted in the ferrocifen family, which consists of six groups and about 200 compounds.⁹⁻¹² Ferrocene derivatives also have been used in areas ranging from biological sensors¹³ and materials chemistry to organic synthesis and asymmetric catalysis.¹⁴⁻¹⁶ Despite all of these efforts, relatively few investigations addressing the energetics of these species have been carried out.

Ferrocene is commonly used as a reference electrode in electrochemical measurements because it readily undergoes reversible one-electron oxidation to the ferrocenium ion (1⁺, E₁/₂ = 624 mV in CH₂CN).¹⁷ Polarographic reduction potential determinations of R₂Hg, RHgCl, and CpFe(CO)₂R (R = H, Me) confirmed and Gubin to suggest that ferrocene is more acidic than benzene, and by using Streitwieser and Perrin-type calculations the half-wave potentials and acidities of 1 were obtained for ferrocene.¹⁸ Additional determinations of 1 do not appear to have been carried out. It has also been found that alkyl and phenyl radicals do not abstract a hydrogen atom from ferrocene,¹⁹,²⁰ but its C–H bond dissociation energy (BDE) to the best of our knowledge has not been experimentally determined.

In the gas phase, the ionization energy (6.82 ± 0.08 eV),¹¹ proton affinity (207 ± 1 kcal mol⁻¹),²¹ and homolytic CpFe–Cp BDE (91 ± 3 kcal mol⁻¹)²² of 1 have been reported. More recently, the adiabatic detachment energies (ADEs) of mono- and doubly deprotonated 1,1′-ferrocenedicarboxylic acid were measured by Wang and Wang et al.,²³ and the vertical detachment energy (VDE) of the conjugate base of ferrocene (1.79 eV) was reported by Bowen et al.²⁴ In this work, the gas-phase acidity (ΔH° acid) of ferrocene and the electron affinity (EA) of the ferrocenyl radical (CpFeC₅H₃⁺) are reported and combined in a thermodynamic cycle to afford the C–H BDE of 1. These experimental determinations are compared to B3LYP and M06-2X calculations, and the ionic (1i) vs covalent (1c) nature of ferrocene (Figure 1) is briefly addressed.

Figure 1. Commonly provided representations of ferrocene corresponding to ionic (1i) and covalent (1c) bonding descriptions.

Received: May 8, 2019
Revised: June 20, 2019
Published: June 21, 2019

DOI: 10.1021/acs.jpca.9b04382
J. Phys. Chem. A 2019, 123, 6016–6021

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### EXPERIMENTAL SECTION

**Mass Spectrometry.** A previously described dual-cell Fourier transform mass spectrometer outfitted with a 3 T superconducting magnet and operated with IonSpec’s Omega version 8.0.325 software package was employed for this work. Anionic bases corresponding to the conjugate acids of ammonia, diethylamine, dimethylamine, pyrazine, and water were generated by 7.0–8.3 eV electron ionization of these compounds at static pressures. The desired anions were mass isolated using a stored-waveform inverse Fourier transform (SWIFT) excitation and transferred to the second cell of the instrument where they were allowed to react with a static pressure of \(\sim 2.9 \times 10^{-8}\) Torr of ferrocene. The resulting ferrocenyl anion was thermally cooled with a \(\sim 10^{-5}\) Torr pulse of argon followed by a 1000 ms delay before product ions were ejected and subsequent reactions were monitored. Alternatively, ferrocenyl anion was generated in the first cell by chemical ionization of a mixture of a constant pressure of ferrocene \((\sim 2.9 \times 10^{-8}\) Torr) and a pulse of ammonia up to a pressure of \(\sim 1 \times 10^{-6}\) Torr. The resulting \((\text{M}–\text{H})^−\) ion at \(m/z\, 185\) was isolated with a SWIFT excitation and transferred to the second cell where it was cooled with an argon pulse. Its reactions with static pressures \((\sim 2.9 \times 10^{-8}\) Torr) of neutral reagents were subsequently monitored as a function of time. Observed rate constants obtained from these data were unaffected for pressure differentials that sometimes exist between the reaction region and the ionization gauge.

**Computational Methods.** Geometries were initially optimized using Gaussian 2003 with the B3LYP density functional method and the 6-31+G(d) basis set. Vibrational frequencies were subsequently computed for each stationary point, and they all were found to correspond to energy minima and transition structures with zero and one imaginary modes, respectively. Gaussian 2016 was employed to carry out analogous M06-2X optimizations and vibrational frequency determinations with both the aug-cc-pVDZ and aug-cc-pVTZ basis sets. Natural population analyses were carried out on the latter structures, and all of the acidities, EAs, and BDEs are given as enthalpies at 298 K. Unscaled vibrational frequencies were used in this regard, and small modes that contribute more than 0.5% to the thermal energy were replaced by 0.5% for the BDE computations, the experimental ionization energy of hydrogen \((313.6\) kcal mol\(^{-1}\)) was employed. VDEs were computed from the EAs by replacing the electronic energies for the optimized structures of the radicals with those obtained for the radicals using the anion geometries.

### RESULTS

The gas-phase acidity \(\Delta H^\circ_{\text{acid}}\) of ferrocene was measured by reacting it and its conjugate base with a series of standard reference acids and bases to observe the series of standard reference of proton transfer \((\text{eq }1)\). Pyrazine anion \((\Delta H^\circ_{\text{acid}} = 2.5\) kcal mol\(^{-1}\)) and stronger bases were protonated ferrocene, whereas hydroxide \((\Delta H^\circ_{\text{acid}} = 0.01\) kcal mol\(^{-1}\)) did not. Likewise, pyrazine did not protonate the conjugate base of ferrocene, whereas hydroxide did not. These bracketing results, summarized in Table 1, enable us to assign \(\Delta H^\circ_{\text{acid}} = 391.5\) ± 1.3 kcal mol\(^{-1}\) for the acidity of ferrocene.

### Table 1. Bracketing Results for the Acidity of Ferrocene in kcal mol\(^{-1}\)

<table>
<thead>
<tr>
<th>Acid (HX)</th>
<th>(\Delta H^\circ_{\text{acid}})</th>
<th>Proton Transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH(_3)</td>
<td>403.4 ± 0.3</td>
<td>yes</td>
</tr>
<tr>
<td>CH(_3)(_2)NH(_2)</td>
<td>399.3 ± 1.1</td>
<td>yes</td>
</tr>
<tr>
<td>(CH(_3)(_2))(_2)NH</td>
<td>396.4 ± 0.9</td>
<td>yes</td>
</tr>
<tr>
<td>pyrazine</td>
<td>392.6 ± 2.5</td>
<td>yes(^a)</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>390.3 ± 0.01</td>
<td>no</td>
</tr>
</tbody>
</table>

\(^a\)\(k = 7.1 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) \((k_{\text{ADDO}} = 1.32 \times 10^{-9}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), 54\% efficiency); 17.7 Å\(^3\) (from the M06-2X/aug-cc-pVTZ calculation) was used for the polarizability. \(^b\)\(k = 1.0 \times 10^{-5}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) \((k_{\text{ADDO}} = 1.75 \times 10^{-9}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), 57\% efficiency).

Analogous electron transfer reactions were carried out on the ferrocenyl anion \((1a)\) with a series of reference compounds with known EAs to determine the EA of the ferrocenyl radical \((1r)\). Our results are summarized in Table 2.

### Table 2. Bracketing Results for the EA of Ferrocenyl Radical in eV

<table>
<thead>
<tr>
<th>cmpd</th>
<th>EA</th>
<th>Electron Transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_6)H(_4)NO(_2)</td>
<td>1.00 ± 0.01</td>
<td>no</td>
</tr>
<tr>
<td>3-F-C(_6)H(_4)NO(_2)</td>
<td>1.24 ± 0.10</td>
<td>no</td>
</tr>
<tr>
<td>2-CF(_3)C(_6)H(_4)NO(_2)</td>
<td>1.33 ± 0.10</td>
<td>no</td>
</tr>
<tr>
<td>3-CF(_3)C(_6)H(_4)NO(_2)</td>
<td>1.41 ± 0.10</td>
<td>no</td>
</tr>
<tr>
<td>(CF(_3))(_2)CO</td>
<td>1.52 ± 0.11</td>
<td>no</td>
</tr>
<tr>
<td>4-O(_2)NC(_6)H(_4)CHO</td>
<td>1.691 ± 0.087</td>
<td>no</td>
</tr>
<tr>
<td>3,5-(CF(_3))(_2)C(_6)H(_4)NO(_2)</td>
<td>1.79 ± 0.10</td>
<td>yes(^a)</td>
</tr>
<tr>
<td>1,4-C(_6)H(_4)O(_3)</td>
<td>1.860 ± 0.005</td>
<td>yes(^a)</td>
</tr>
</tbody>
</table>

\(^a\)1,4-Benzoquinone. \(^b\)\(k = 4.79 \times 10^{-9}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) \((k_{\text{ADDO}} = 1.14 \times 10^{-9}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)); \(\mu_\alpha = 1.93\) D and \(\alpha = 1.48\) Å\(^2\) were used. A small amount \((\sim 10\%)\) of an adduct anion was also observed.

and because \(1a\) does not undergo electron transfer with \(p\)-nitrobenzaldehyde \((\text{EA} = 1.691 ± 0.087\) eV\) but does transfer an electron to 3,5-bis(trifluoromethyl)nitrobenzene \((\text{EA} = 1.79 ± 0.10\) eV\), we assign \(\text{EA}(1r) = 1.74 ± 0.08\) eV \((40.1 ± 1.9\) kcal mol\(^{-1}\)). This value is nearly the same as the VDE of 1.79 eV reported by Bowen et al. and reveals that the ADEs and VDEs are similar for this radical. The \(C–H\) BDE for ferrocene can be determined by combining the acidity and EA measurements above in a thermodynamic cycle as shown in eq 2, where all of the values are given in kcal mol\(^{-1}\). A BDE of 118.0 ± 2.3 kcal mol\(^{-1}\) is obtained for this quantity, and this value is 5–6 kcal mol\(^{-1}\) larger than the bond energies for benzene \((113.5 ± 0.5\) kcal mol\(^{-1}\)) and naphthalene \((112.2 ± 1.2\) \((\alpha)\) and 111.9 ± 1.4 \((\beta)\) kcal mol\(^{-1}\)). This result is also in accord with previous reports that phenyl and alkyl radicals do not abstract a
DISCUSSION

Measured electrochemical reduction potentials of organomercuric and cyclopentadienyliron dicarbonyl derivatives in different solvents (i.e., 90% dioxane, dimethylformamide, and acetonitrile) by Denisovich and Gubin led to correlations with dimethyl sulfoxide pK_a values that resulted in an acidity for benzene of 38 ± 4 kcal mol⁻¹.¹⁸ This indicates that 1 is more acidic than benzene because the latter compound has a reported pK_a of 43.0 ± 0.2.⁴⁵ In accord with these liquid-phase estimates, our determination of ΔH^°_acid(1) = 391.5 ± 1.3 kcal mol⁻¹ reveals that ferrocene is more acidic in the gas phase than benzene (ΔH^°_acid = 401.7 ± 0.5 kcal mol⁻¹)⁴² and naphthalene (394.2 ± 1.2 and 395.5 ± 1.3 kcal mol⁻¹ for the α and β positions, respectively).⁴³ The latter compound is used as a point of comparison because it is an aromatic hydrocarbon with the same number of carbon atoms as 1. Our acidity determination is also well reproduced by M06-2X/aug-cc-pVTZ and M06-2X/aug-cc-pVTZ predictions of 392.6 and 393.7 kcal mol⁻¹, respectively.

One might naively assume that the acidity of ferrocene can be used to distinguish between the ionic and covalent bonding descriptions for this compound in that the former bonding view should lead to a less acidic compound due to charge repulsion between the negatively charged cyclopentadienide ring and the carbanion center formed upon deprotonation. The covalent bonding model for ferrocene is reminiscent of an aromatic benzene ring, but because 1 has the same number of carbon atoms as naphthalene, one might expect it to be more acidic than benzene and similar to naphthalene. Our measured value indicates that 1 is 10 kcal mol⁻¹ more acidic than benzene and 3–4 kcal mol⁻¹ more acidic than naphthalene. This seems to suggest that 1 is a better description of ferrocene than 1, and in accord with this view, the computed M06-2X/aug-cc-pVTZ Mulliken, atomic polar tensor (APT), and natural population analysis (NPA) charges on the iron in 1 and 1a are close to zero (i.e., -0.03 and -0.02 (Mulliken), -0.16 and -0.15 (APT), and 0.03 and 0.00 (NPA), where the first and second numbers in each pair are for 1 and 1a, respectively). The real bonding situation, of course, is more complex, and an attractive Coulombic interaction in 1a between the negatively charged centers and a 2+ iron center in the ionic bonding model cannot be discounted.⁴⁶,⁴⁷

To address this issue further, the acidity of bis-(cyclopentadienyl)magnesium (MgCp₂) was calculated because Mg is more electropositive than Fe (i.e., the Pauling electronegativities are 1.31 and 1.83, respectively)⁴⁸ and the former does not have occupied d orbitals. Consequently, it seems reasonable to expect that MgCp₂ has more ionic character than FeCp₂. In accord with this view, the M06-2X/aug-cc-pVTZ APT and NPA charges on Mg are 0.89 and 1.80, respectively. An intuitively unreasonable Mulliken charge of -0.49 was also obtained, but this method is well-known to have a number of deficiencies and changes sign with the computational approach (i.e., the B3LYP/6-31+G(d) charge is +0.50).⁴⁹

Computed acidities for MgCp₂ of 390.9 (B3LYP/6-31+G(d)), 389.4 (M06-2X/aug-cc-pVDZ), 390.3 (M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ), and 390.4 kcal mol⁻¹ (M06-2X/aug-cc-pVTZ) all indicate that this metalloocene is a little more acidic than FeCp₂. This suggests that this thermodynamic quantity is not a reliable indicator of the covalent vs ionic character in these species; however, the structural changes upon proton abstraction are illuminating. That is, upon deprotonation of ferrocene, the Fe–C⁻ separation increases by 0.06 Å, whereas for MgCp₂, the Mg–C⁻ separation decreases by 0.15 Å. The latter change is in accord with the predicted values above.

Table 3. Computed Acidities, EAs, VDEs, and BDEs for Ferrocene or Ferrocenyl Radical

<table>
<thead>
<tr>
<th>Method</th>
<th>ΔH^°_acid</th>
<th>EA</th>
<th>VDE</th>
<th>BDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>M06-2X/aug-cc-pVDZ</td>
<td>392.6</td>
<td>1.67</td>
<td>1.60</td>
<td>117.6</td>
</tr>
<tr>
<td>M06-2X/aug-cc-pVTZ</td>
<td>393.7</td>
<td>1.74</td>
<td>1.77</td>
<td>120.3</td>
</tr>
<tr>
<td>M06-2X/aug-cc-pVTZ sp</td>
<td>393.7</td>
<td>1.74</td>
<td>1.77</td>
<td>120.3</td>
</tr>
<tr>
<td>M06-2X/aug-cc-pVDZ sp</td>
<td>391.5 + 1.3</td>
<td>1.74 ± 0.08</td>
<td>1.79d</td>
<td>118.0 ± 2.3</td>
</tr>
</tbody>
</table>

Acidities and BDEs are in kcal mol⁻¹, whereas EAs and VDEs are in eV. aEA = ADE. bM06-2X/aug-cc-pVTZ sp = M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVDZ. dSee ref 25.
with a predominantly electrostatic interaction that brings the oppositely charged centers closer together. Electron repulsion presumably accounts for the opposite behavior in ferrocene and suggests that covalent bonding is dominant for this compound.\textsuperscript{\textit{46,47}}

Ferrocenyl anion previously was reported in the gas phase, and its VDE was determined to be 1.79 eV by photoelectron spectroscopy.\textsuperscript{\textit{25}} Companion CAM-B3LYP/6-31+G(d,p) computations (1.77 eV) are in excellent accord with this result and led to a prediction of 1.44 eV for the EA of the ferrocenyl radical. Our B3LYP/6-31+G(d) calculations give nearly the same results, but the M06-2X computations indicate that the VDE and EA are nearly equal and reproduce the experimental determinations for both of these quantities. Given the similar geometries of 1\textit{a} and 1\textit{r}, it is not surprising that the VDE and EA are almost the same. Moreover, because ferrocene is more acidic than benzene and naphthalene and five-membered aromatic ring compounds have 5–10 kcal mol$^{-1}$ larger carbon–hydrogen bond energies than six-membered ring species,\textsuperscript{\textit{14}} we would expect 1\textit{r} to have a larger EA than 1\textit{a} (1.085 ± 0.006 eV)$^{\textit{94}}$ and both naphthyl radicals (1.30 ± 0.02 ($\alpha$) and 1.47 ± 0.02 ($\beta$) eV).\textsuperscript{\textit{43}} A reasonable estimate based upon these acidity and BDE differences which is in excellent accord with the M06-2X predictions of 1.67–1.75 eV and our experimental determination of 1.74 ± 0.08 eV.

The nature of the ferrocenyl radical was also explored. Upon the basis of the APT and NPA 1\textit{a}–1\textit{r} charge differences, it is apparent that the loss of an electron from the ferrocenyl anion primarily comes from the iron atom and the $\pi$-system. This is in accord with the Mulliken spin density of 1.30 at the Fe center and a plot of the spin density (Figure 3). In contrast, the Mulliken 1\textit{a}–1\textit{r} charge differences and the B3LYP/6-31+G(d) results are in accord with a $\sigma$-radical. We suspect that the former view provides a better description of

<table>
<thead>
<tr>
<th>cmpd/site</th>
<th>charge</th>
<th>spin density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mulliken</td>
<td>APT</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>−0.03</td>
<td>−0.16</td>
</tr>
<tr>
<td>C</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>1\textit{a}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>−0.02</td>
<td>−0.15</td>
</tr>
<tr>
<td>C$^-$</td>
<td>−1.47</td>
<td>−0.44</td>
</tr>
<tr>
<td>C–C$^-$</td>
<td>0.39</td>
<td>−0.07</td>
</tr>
<tr>
<td>C–C–C$^-$</td>
<td>−0.06</td>
<td>−0.10</td>
</tr>
<tr>
<td>Cp$^b$</td>
<td>−0.04 to −0.03</td>
<td>−0.02 to −0.01</td>
</tr>
<tr>
<td>1\textit{r}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.00</td>
<td>0.29</td>
</tr>
<tr>
<td>C$^*$</td>
<td>−1.22</td>
<td>−0.43</td>
</tr>
<tr>
<td>C–C$^*$</td>
<td>0.42</td>
<td>0.06</td>
</tr>
<tr>
<td>C–C–C$^*$</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>Cp$^b$</td>
<td>0.00 to 0.07</td>
<td>−0.02 to 0.01</td>
</tr>
</tbody>
</table>

$^a$All values are from M06-2X/aug-cc-pVTZ structures and calculations. $^b$Remote cyclopentadienyl ring carbons, all of which fall in the indicated range.

The nature of the ferrocenyl radical was also explored. Upon the basis of the APT and NPA 1\textit{a}–1\textit{r} charge differences, it is apparent that the loss of an electron from the ferrocenyl anion primarily comes from the iron atom and the $\pi$-system. This is in accord with the Mulliken spin density of 1.30 at the Fe center and a plot of the spin density (Figure 3). In contrast, the Mulliken 1\textit{a}–1\textit{r} charge differences and the B3LYP/6-31+G(d) results are in accord with a $\sigma$-radical. We suspect that the former view provides a better description of

Figure 3. Electron density from the spin density of the ferrocenyl radical (isovalue = 0.002) using the M06-2X/aug-cc-pVTZ optimized geometry.
the ferrocenyl radical, but a spectroscopic investigation of 1r would be useful.

Our experimentally determined C–H BDE of 118.0 kcal mol$^{-1}$ for ferrocene is 4.5 ± 2.4 kcal mol$^{-1}$ larger than that for benzene and 5.8 ± 2.6 and 6.1 ± 2.7 kcal mol$^{-1}$ larger than those for naphthalene. This unusually large BDE is in accord with liquid-phase observations and is well reproduced by M06-2X computations but not those with the B3LYP density functional. It is also in accord with separate predictions by Hadad et al. and Guo et al. for five-membered aromatic ring compounds, which were found to have larger C–H bond energies than six-membered species.\textsuperscript{30,31} This was reasonably attributed to the smaller C–C–C bond angles in five-membered rings, resulting in additional angle strain in the corresponding radical. Diminished hyperconjugation may also play a role in the large C–H BDE of 1.

### CONCLUSIONS

Ferrocene was found to be more acidic than benzene and naphthalene in the gas phase, and its conjugate base is harder to oxidize than phenyl or naphthyl anions. That is, the EA of the ferrocenyl radical is significantly larger than those for phenyl and both naphthyl radicals. These results are in accord with a relatively stable ferrocene conjugate base and the well-known synthetically useful metalation chemistry of 1 in the liquid phase. These findings are also well reproduced by M06-2X computations and lead to a covalent bonding description of ferrocene rather than an ionic one.

The C–H BDE of ferrocene is significantly larger than the CpFe–Cp ligand bond energy (118.0 ± 2.3 vs 91 ± 3 kcal mol$^{-1}$) and the carbon–hydrogen BDEs of benzene and naphthalene. This can be attributed to the relatively high energy of the ferrocenyl radical and the greater stability of an aromatic carbon radical in a six-membered ring than in a five-membered one. This also accounts for the dearth of synthetic transformations proceeding through the intermediary of 1r.

### ASSOCIATED CONTENT

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.9b04382.

Computed structures and energies along with complete citations to refs 28 and 31 (PDF)

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**Notes**

There is no competing financial interest.

This work was taken in part from Speetzen, B., M. S. Thesis, University of Minnesota, 2007.

**ACKNOWLEDGMENTS**

Generous support from the National Science Foundation (CHE-1665392) and the Minnesota Supercomputer Institute for Advanced Computational Research is gratefully acknowledged.

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