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Reprint of “Indenone and cyclopentadienone energetics via mass spectrometry and computations: Are these species antiaromatic or “merely” nonaromatic?”☆

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In celebration of Veronica Bierbaum’s 65th birthday and years of scientific leadership and friendship.

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ABSTRACT

The heat of hydrogenation of indenone was measured via two partially independent thermodynamic cycles by carrying out energetic measurements (i.e., electron affinities, proton affinities and ionization potentials) on both negative and positive ions ($\Delta H^{\circ}_{\mathrm{H_2}} = 17.8 \pm 5.5$ and 17.5 ± 5.7 kcal mol^{-1}, respectively). High level G3 computations were also carried out to provide the heats of formation of indenone (16.8 kcal mol^{-1}) and cyclopentadienone (14.0 kcal mol^{-1}). These $4n$ π electron systems are found to be nonaromatic in contrast to previous views. A recent report on cyclopropenyl anion (J. Org. Chem. 2013, 78, 7370–7372) indicates that this ion is also nonaromatic, and suggests that NMR ring currents and nucleus independent chemical shift (NICS) calculations do not correlate with the energetic criterion for antiaromatic compounds.

1. Introduction

Cyclopentadienone (**1**) and its benzannulated derivative indenone (**2**) along with their substituted analogs are of wide interest with respect to natural product synthesis, drug development, combustion processes, and environmental chemistry [1–6]. They are also commonly viewed as antiaromatic $4n$ Hückel systems given the polarization of carbonyl groups (i.e., $\mathrm{C{=}O} \leftrightarrow {}^{+}\mathrm{C{-}O^{-}}$) and their relationship to cyclopentadienyl and indenyl cations (Fig. 1) [7–11]. The heats of formation of **1** and **2** have not been measured, however, despite recent studies showing that the pyrolysis of lignin, the major organic material in soil, affords **1** and fuel combustion produces **2** [2–4]. Moreover, cyclopropenyl anion, the prototypical antiaromatic anion, was recently found to be nonaromatic from an energetic point of view despite 50 years of claims to the contrary [12]. This raises the question, what about cyclopentadienone and indenone? Are they antiaromatic as routinely assumed or are they nonaromatic compounds? Mass spectrometry is especially valuable in addressing these questions because it can be used to measure the energetics of ions and neutral compounds even when they are quite unstable [13]. Herein, we report our measurement of the heat of hydrogenation of **2** via two thermodynamic cycles along with companion computations that enable us to estimate the heats of formation of **1** and **2**.

2. Experimental section

Indenone (**2**) and 2-inden-1-ol (**3**) were prepared as previously described [14–17]. In the latter case this was accomplished by oxygenation of 1-indenyllithium and the reduction of the

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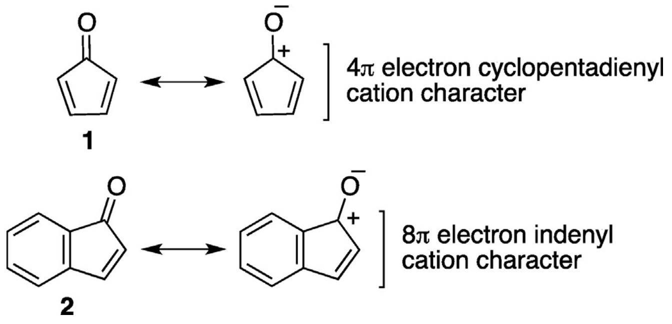


Fig. 1. Cyclopentadienone (**1**), indenone (**2**) and resonance structures that highlight their 4*n* (*n* = 1 or 2) π electron character.

Table 1
Bracketing results for the proton affinity of indenone radical anion ($2^{\bullet-}$).

Cmpd.	ΔH°_{acid} (kcal mol^{-1})	Proton transfer
$(CH_3)_3CSH$	352.5 ± 2.2	No
CD_3CO_2D	348.1 ± 2.2[a]	No
$CH_3CH_2OCH_2CO_2H$	342.0 ± 2.2	No
$ClCH_2CO_2H$	336.5 ± 2.2	No
$CF_3CH_2CO_2H$	333.9 ± 2.1	Yes

[a] Value for all protio acid. No H/D exchange was observed.

resulting hydroperoxide with potassium iodide in aqueous acetic acid. Recrystallization of the alcohol from a mixture of ether and light petroleum ether afforded **3** with a melting point of 56–57 °C.

A 3 T dual cell Fourier-transform mass spectrometer (FTMS) that previously has been described was used to carry out the gas phase experiments [18]. Electron ionization of a pulse of methanol to ~10^{-5} Torr for 0.5 s at 70 eV afforded $CH_3OH_2^+$ which was allowed to react with indenone to afford its $(M+1)^+$ ion at *m*/*z* 131. This cation was transferred to the second (source) cell where it was thermalized with a pulse of argon up to a pressure of ~10^{-5} Torr and then isolated by using a stored waveform inverse Fourier transform (SWIFT) excitation [19]. Likewise, the conjugate base of 2-inden-1-ol was generated by electron ionization of water at 8 eV for 0.7 s to afford HO^- which was then reacted with the alcohol to form the $(M-1)^-$ ion at *m*/*z* 131. This anion was transferred to the source cell and vibrationally cooled with a pulse of argon up to ~10^{-5} Torr before being isolated with a SWIFT excitation. The reactivity of this ion, however, indicated the presence of two isomers (O- and C-deprotonation). To eliminate this issue, 2-inden-1-ol-OD was deprotonated by F^-(produced by EI of CF_4 at 8.5 eV for 0.5 s) and both the $(M-H^+)^-$ and $(M-D^+)^-$ ions at *m*/*z* 132 and 131, respectively were transferred to the source cell. Both ions were cooled with a pulse of argon up to a pressure of ~10^{-5} Torr and then the former species at *m*/*z* 132 was isolated using a combination of CHIRP and SWIFT excitations [20]. Finally, the radical anion of indenone at *m*/*z* 130 was made by electron ionization at 6.5 eV for 500 ms. It was then transferred to the source cell where it was thermalized with a pulse of argon at a pressure of ~10^{-5} Torr and isolated via a SWIFT irradiation.

Computations were performed using Gaussian 03 and 09 at the Minnesota Supercomputer Institute for Advanced Computational Research [21]. B3LYP/6-31+G(d) geometry optimizations and vibrational frequencies were carried out initially to locate the structures that were used as the starting points for subsequent G3 energy determinations [22]. All of the calculated energies reported in this work are given at 298 K and correspond to G3 values. These results and the computed MP2 structures are provided in the supporting information or were taken from the literature [23,24].

3. Results and discussion

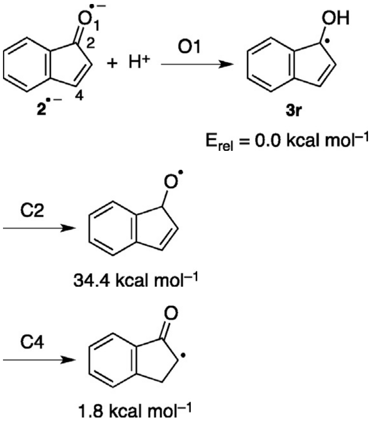
To measure the energetics of indenone (**2**) and assess its stability (i.e., antiaromatic character), the heat of hydrogenation of **2** to afford 2-inden-1-ol (**3**) was determined. This would be difficult to accomplish by reaction calorimetry because of the ease by which **2** polymerizes at room temperature. A thermodynamic cycle, consequently, was employed to overcome this difficulty and was supplemented by extensive G3 calculations. This computational approach was selected because it has been extensively benchmarked and the resulting energies often reproduce the experimental values to within ±2 kcal mol^{-1} [1 kcal = 4184 kJ].

3.1. Electron affinity of 2

Formation of the radical anion of indenone ($\mathbf{2}^{\bullet-}$) was accomplished by electron attachment to **2** and its electron binding energy (which is equivalent to the electron affinity (EA) of **2**) was determined by reacting $\mathbf{2}^{\bullet-}$ with reference reagents of known EA. 4-Nitrofluorobenzene and sulfur dioxide (EA = 1.12 ± 0.10 and 1.1070 ± 0.0080 eV, respectively) both react rapidly via electron transfer with rate constants of ~1.3×10^{-9} cm^3 molecule^{-1} s^{-1} whereas electron transfer was not observed with nitrobenzene and chloropentafluorobenzene (EA = 1.000 ± 0.010 and 0.82 ± 0.11 eV, respectively) [25]. This enables us to assign EA(**2**) = 1.05 ± 0.05 eV (24.2 ± 1.2 kcal mol^{-1}) which is reasonably reproduced by the G3 theory prediction of 1.21 eV (27.9 kcal mol^{-1}).

3.2. Proton affinity of $2^{\bullet-}$

The proton affinity (PA) of $\mathbf{2}^{\bullet-}$ was also measured by reacting it with a series of O–H and S–H Brønsted acids of known strength (Table 1). Chloroacetic acid is the strongest acid that was examined that did not protonate $\mathbf{2}^{\bullet-}$ whereas trifluoromethylacetic acid reacted at the collision limit (i.e., *k* = ~2.9×10^{-9} cm^3 molecule^{-1} s^{-1}). This indicates that PA ($\mathbf{2}^{\bullet-}$) = 335.2 ± 2.0 kcal mol^{-1} and as expected G3 theory indicates that oxygen-protonation is favored over carbon-protonation by 34.4 (C2) and 1.8 (C4) kcal mol^{-1} (Eq. (1a-c)(1)). The predicted value of 331.2 kcal mol^{-1} for O-protonation is also in reasonable accord with experiment.



(1a)

(1b)

(1c)

3.3. Electron and proton affinities of 3r and 3a

To complete a thermodynamic cycle for the heat of hydrogenation of indenone, the conjugate base of **3** (**3a**) was generated by proton abstraction. This is an unusual case where the carbon acidity at the benzylic carbon is expected to be much greater than at the hydroxyl group since indene is a much stronger acid than benzyl alcohol