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Hydrocarbon Anions with High Stability. Part 2.[1) Structure and Stability of Cyclopentadienide Ions with Condensed Aromatic Rings

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The ionization-potential and oxidation-potential values have been examined as stability parameters in the gas and solution phase, respectively, for cyclopentadienide ions with from one to four condensed aromatic rings. They indicate that, without solvation effects, the condensed aromatic rings intrinsically stabilize the cyclopentadienide ion in solution as well as in the gas phase, and that *an apparent destabilization effect* by the aromatic rings in solution is most probably ascribed to a decrease in the stabilizing solvation effects due to charge delocalization on the carbanions. Theoretical investigations from governing orbital interactions using the frontier orbital theory demonstrate that the essential stability of the cyclopentadienide ions is dependent on the structure, itself.

Cyclopentadienide ion (**1**$^-$) is a very stable carbanion with 6π electrons, as designated by E_{ox} +0.028 V[2)] and +0.04 V[3)] in DMSO (referenced to SHE) and by pK_a 18.0[2)] and 18.2[3)] in DMSO and 18.2 in THF,[4)] 16.7 in cyclohexylamine (CHA),[5)] 16.0 in water,[5)] and 15 in DMSO–EtOH[6)] for its conjugate acid, cyclopentadiene (**1H**). Introducing condensed aromatic rings to **1**$^-$ was successfully carried out to give indenide (**2**$^-$) and fluorenide ion (**3**$^-$), which were also stable, but less so than **1**$^-$, as shown by E_{ox} − 0.200 V[2)] in DMSO for **2**$^-$ and by pK_a 18.2,[7)] 18.5,[8)] and 20.1[2)] in DMSO, 18.2[8)] in H_2O, and 17.8,[8)] 19.9,[9)] and 20.2[10)] in CHA for its conjugate acid, indene (**2H**), and by E_{ox} − 0.320 V[2)] in DMSO for **3**$^-$ and by pK_a 20.5,[7,8)] 21.1,[11)] and 22.6[2,12)] in DMSO, 20.5 in DMSO–MeOH,[7)] 20.5 in H_2O,[8)] and 20.6,[8)] 22.7,[9)] 22.8,[10)] and 22.9[13)] in CHA for fluorene (**3H**). The stability decreases according to the sequence **1**$^-$ > **2**$^-$ > **3**$^-$. This stability sequence led to a recognition that the condensed aromatic rings *destabilized* the cyclopentadienide ion because annelation might cause the electrons to be less available to the five-membered ring of the cyclopentadienide ion.[14)] However, the electron affinities of the cyclopentadienyl, indenyl, and fluorenyl radicals (**1**$^\bullet$, **2**$^\bullet$, and **3**$^\bullet$, respectively) slightly increase in the reverse order, **1**$^\bullet$ < **2**$^\bullet$ < **3**$^\bullet$, in the gas phase.[15)] Also, although among cyclopentadienide ions with condensed aromatic rings (Fig. 1), dibenzo[*b*,*h*]fluorenide (**6**$^-$) (pK_a 21.4 in DMSO–EtOH for its conjugate acid[16)]) might be less stable than **1**$^-$, its isomers dibenzo[*a*,*i*]fluorenide (**7**$^-$) and dibenzo[*c*,*g*]fluorenide (**8**$^-$) (pK_a 17.5 and 16.8 in DMSO–EtOH for their conjugate acids, respectively[16)]) might be almost equal and more stable, respectively, than **1**$^-$ in solution, although the measuring solvent contained ethanol other than DMSO.

In this work, we theoretically and experimentally studied the correlation between the structure and the stability for cyclopentadienide ions with condensed aromatic rings (**1**$^-$—**8**$^-$: Fig. 1) in order to shed light on the substantial effects of the condensed aromatic rings in the gas phase and in solution.

Results and Discussion

Stability in the Gas Phase. The ionization potential values (I_p) were calculated for the cyclopentadienide ions with one, two, and four condensed aromatic rings (**1**$^-$—**8**$^-$) by a semi-empirical molecular-orbital method (AM1) using MOPAC version 6.01. We can find a fairly good correlation (a correlation coefficient 0.924) between the I_p values and the observed electron affinities[15)] for **1**$^\bullet$, **2**$^\bullet$, and **3**$^\bullet$ in the gas phase. The I_p values as a substantial parameter for stability in the gas phase indicate that the stability increases in the order **1**$^-$ < **2**$^-$ < **4**$^-$ < **3**$^-$ < **5**$^-$≈**6**$^-$ < **7**$^-$ < **8**$^-$ (Table 1); the greater is the number of condensed aromatic rings, the more stable is the cyclopentadienide ion in the gas phase. The condensed aromatic ring, therefore, intrinsically *stabilizes* the cyclopentadienide ion in the gas phase, owing to its charge-delocalization effects. On the other hand, the ionization potentials of polycyclic aromatic hydrocarbon molecules depend inversely on the ionic radius, due to the proportionality of the HOMO energy to the molecular size.[15)]

Stability in Solution. The stability of **1**$^-$—**5**$^-$ and **8**$^-$ was experimentally evaluated for single-electron oxidation in DMSO. Some of their precursors, 1*H*-benzo[*f*]indene (**4H**),

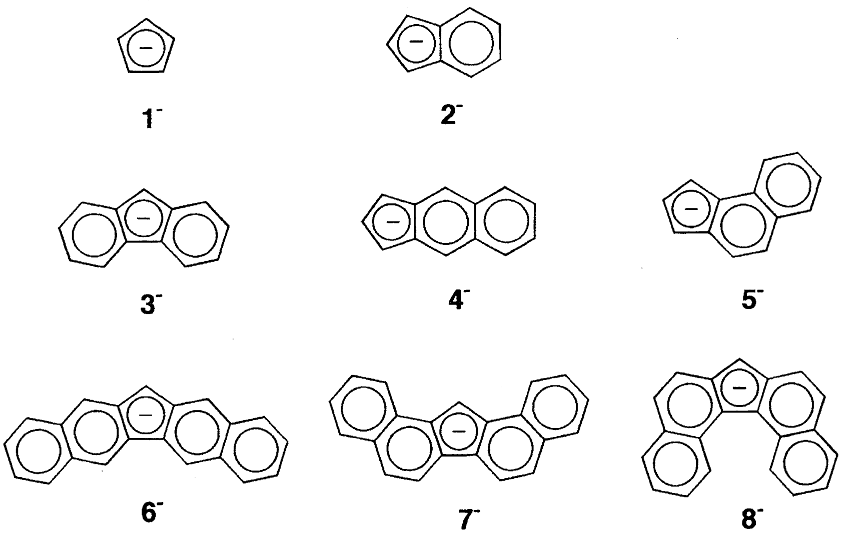

Fig. 1. Cyclopentadienide ions with condensed aromatic rings.

Table 1. Ionization Potential and Oxidation Potential Values for Cyclopentadienide Ions with Condensed Aromatic Rings ($\mathbf{Cp}^-$) and pK_a Values for Their Conjugate Acids in DMSO

$\mathbf{Cp}^-$ ion	I_p/eV[a]	E_{ox}/V[b]	p$K_{a)}$ (RH)[c]
$\mathbf{1}^-$	2.30	+0.035 −0.028[d] +0.04[e]	18.0[d] 18.2[e] 18.2 (in THF)[f] 16.7 (in CHA)[g] 16.0 (in H_2O)[g] 15 (in DMSO–EtOH)[h]
$\mathbf{2}^-$	2.52	−0.180 −0.200[d]	18.2[j] 18.5[j] 20.1[d] 17.8,[j] 19.9,[k] 20.2[l] (in CHA) 18.2 (in H_2O)[j]
$\mathbf{3}^-$	2.74	−0.264 −0.320[d]	20.5[i,j] 21.1[m] 22.6[d,n] 20.5 (in DMSO–MeOH)[i] 20.6,[j] 22.7,[k] 22.8,[l] 22.9[o] (in CHA)
$\mathbf{4}^-$	2.69	−0.339	24[p]
$\mathbf{5}^-$	3.03	+0.019	18[p]
$\mathbf{6}^-$	3.03	−0.21 (in DMSO–EtOH)[q,r]	21.4 (in DMSO–EtOH)[r]
$\mathbf{7}^-$	3.39	+0.020 (in DMSO–EtOH)[q,r]	17.5 (in DMSO–EtOH)[r]
$\mathbf{8}^-$	3.43	+0.044 +0.060 (in DMSO–EtOH)[q,r]	17.1[p] 16.8 (in DMSO–EtOH)[r]

a) Calculated by AM1 using MOPAC version 6.01. b) Irreversible oxidation potentials measured in DMSO with a ferrocene–ferrocenium standard, referenced to SHE, unless otherwise noted. c) In DMSO, unless otherwise noted. d) Cited from Ref. 2. e) Cited from Ref. 3. f) Cited from Ref. 4. g) Cited from Ref. 5. h) Cited from Ref. 6. i) Cited from Ref. 7. j) Cited from Ref. 8. k) Cited from Ref. 9. l) Cited from Ref. 10. m) Cited from Ref. 11. n) Cited from Ref. 12. o) Cited from Ref. 13. p) Estimated from the observed E_{ox} value by using the correlation equation between E_{ox} and pK_a (Ref. 20). q) Estimated from the reported pK_a value (Ref. 16) by using the correlation equation between pK_a and E_{ox} (Ref. 20). r) With EtOH/EtONa; cited from Ref. 16.

3*H*-benzo[*e*]indene (**5H**), and 7*H*-dibenzo[*c*,*g*]fluorene (**8H**) were synthesized in overall yields of 24, 11, and 15% (lit, 40%,[17] 23%,[18] and 47%[19]), respectively, according to the reported methods.[17—19] For $\mathbf{1}^-$—$\mathbf{5}^-$ and $\mathbf{8}^-$, which were generated from the corresponding precursor hydrocarbons with $CH_3SOCH_2^-K^+$, all the oxidation potential values (E_{ox})

were actually measured as E_{pa} of irreversible oxidation waves vs. an Ag/Ag$^+$ electrode with a ferrocene–ferrocenium standard and tetrabutylammonium perchlorate as a supporting electrolyte in DMSO under argon by a CV method and referenced to SHE (Table 1). The irreversibility in these cyclic voltammograms exhibits that the corresponding radicals to these carbanions are sufficiently unstable to undergo a coupling reaction.

The E_{ox} value for $\mathbf{8}^-$ was estimated to be +0.060 V from a reported pK_a value[16] for **8H** in DMSO–EtOH using a correlation equation between the E_{ox} and pK_a values, which was first proposed by Bordwell and his coworkers.[20] The estimated value closely agreed with the observed one (+0.044 V) in DMSO (Table 1). Therefore, no significant difference could be perceived in the E_{ox} values between the observed one for the anion in DMSO and the estimated one from the pK_a value for its corresponding conjugated acid in DMSO–EtOH. Then, those for $\mathbf{6}^-$ and $\mathbf{7}^-$, which were both isomers of $\mathbf{8}^-$, were estimated to be -0.21 V and +0.020 V, respectively, from the reported pK_a values[16] for their conjugate acids in DMSO–EtOH in a similar manner as for $\mathbf{8}^-$. Consequently, the stability for single-electron oxidation increases in the sequence $\mathbf{4}^- < \mathbf{3}^- < \mathbf{6}^- < \mathbf{2}^- < \mathbf{5}^- < \mathbf{7}^- < \mathbf{1}^- < \mathbf{8}^-$ in DMSO. We can find no simple relationship between the structure and the stability in the solution.

Correlation between Gas- and Solution-Phase Stability. The ionization potential values are plotted against the oxidation potential values for $\mathbf{1}^-$—$\mathbf{8}^-$ to display no simple linear relationship (Fig. 2). However, for each set of isomers $\mathbf{3}^-$, $\mathbf{4}^-$, and $\mathbf{5}^-$ with two condensed aromatic rings and $\mathbf{6}^-$, $\mathbf{7}^-$, and $\mathbf{8}^-$ with four ones, a linear correlation (slope: 0.970 and 1.57, correlation coefficient: 0.996 and 1.00, respectively) is found to exhibit that the stability is proportional in the solution to that in the gas phase, $\mathbf{4}^- < \mathbf{3}^- < \mathbf{5}^-$ and $\mathbf{6}^- < \mathbf{7}^- < \mathbf{8}^-$. For $\mathbf{1}^-$, $\mathbf{2}^-$, and $\mathbf{3}^-$, the stability increases in the order $\mathbf{3}^- < \mathbf{2}^- < \mathbf{1}^-$ in solution, whereas it increases in reverse order in the gas phase, as mentioned above. Similar phenomena are known for the reversal in the acidities of simple aliphatic alcohols[21] and cyclopentadienes with *t*-butyl substituents[3] between in the gas and in solution phases; in the latter case, *t*-butyl substituents showed a destabilizing effect on cyclopentadienide ion in solutions, contrary to a stabilizing effect in the gas phase, owing to steric inhibition of solvation and an increase in the inductive effect in the carbanion.[3,22] On the other hand, simple proportional relationships were observed between the ionization potentials in the gas phase and the oxidation potentials in DMSO solution for cyclopendienide ions with phenyl substituents[23] and for polycyclic aromatic hydrocarbons, such as naphthalene and phenanthrene.[24]

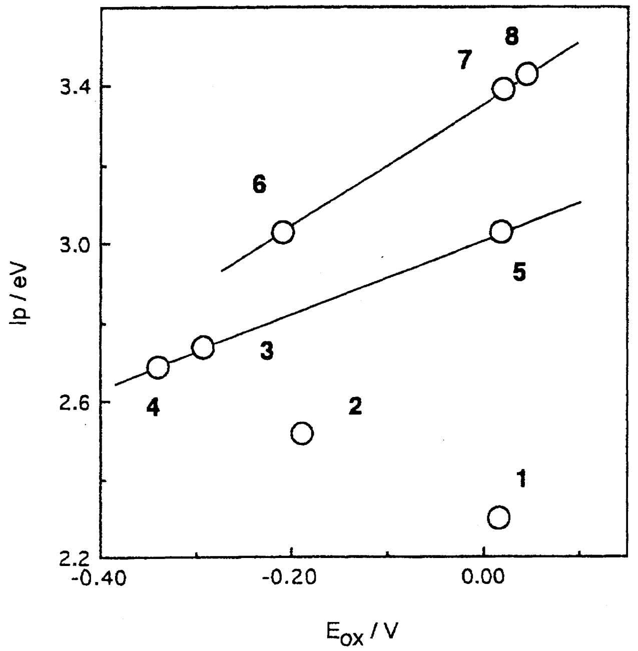

Fig. 2. Ionization potentials (I_p) vs. oxidation potentials (E_{ox}) in DMSO for cyclopentadienide ion with condensed aromatic rings (see Fig. 1 for $\mathbf{1}^-$—$\mathbf{8}^-$). E_{ox} for $\mathbf{6}^-$ and $\mathbf{7}^-$: estimated from the reported pK_a value for **6H** and **7H**, respectively, (Ref. 16) by using the correlation equation between pK_a and E_{ox} (Ref. 20).

The stability of carbanions may be affected by the solvent and their counter cations, since they form ion pairs in solution.[25] However, it was reported that ion pairing was not significant to the K$^+$ counter ion for $\mathbf{1}^-$ in DMSO.[23] Compared with a variation of less than 0.355 V in the E_{ox} values for $\mathbf{1}^-$, $\mathbf{2}^-$, and $\mathbf{3}^-$, that was virtually less than 0.050 V for K$^+$ and Li$^+$ as a counter cation of $\mathbf{1}^-$—$\mathbf{5}^-$ and $\mathbf{8}^-$. On the other hand, a replacement of DMSO by THF as a solvent caused a difference of 0.02—0.16 V in the E_{ox} values for these cyclopentadienide ions. In addition, the E_{ox} value for $\mathbf{1}^-$ (with K$^+$) in DMSO is about 0.34 V more positive than that for $\mathbf{1}^-$ (with Li$^+$) in HMPA–THF (17 : 83).[26] These data demonstrate that solvation has very large effects on the stability of these carbanions, as is known.[15] Also, the heat of solvation of aromatic radical anions decreased with increasing size of the radical anion.[27] Accordingly, the apparent stability sequence of $\mathbf{1}^- > \mathbf{2}^- > \mathbf{3}^-$ in solution is most probably attributable to a decrease in the stabilizing solvation effects by charge delocalization on the larger cyclopentadienide ions.

Stability–Structure Correlation. To understand the stability–structure correlation for cyclopentadienide ions with condensed aromatic rings, we analyzed the governing orbital interactions using frontier orbital theory.[28] Three isomers ($\mathbf{3}^-$, $\mathbf{4}^-$, and $\mathbf{5}^-$) can be theoretically partitioned into indenide ion and 1,3-butadiene fragments, combinations of which at positions *a*, *f*, and *e* in indenide give the three isomers $\mathbf{3}^-$, $\mathbf{4}^-$, and $\mathbf{5}^-$, respectively, as shown in Fig. 3. In view of the HOMO (-2.551 eV) and LUMO (5.100 eV) of indenide and the HOMO (-9.468 eV) and LUMO (2.634 eV) of butadiene, we expect from qualitative second-order perturbation theory that the interaction between the HOMO of indenide ion and the LUMO of butadiene plays a dominant role for coupling these assumed fragment molecules. The other interaction between the LUMO of the indenide ion and the HOMO of butadiene is less important because the energy separation is much larger. That is, the indenide ion acts as

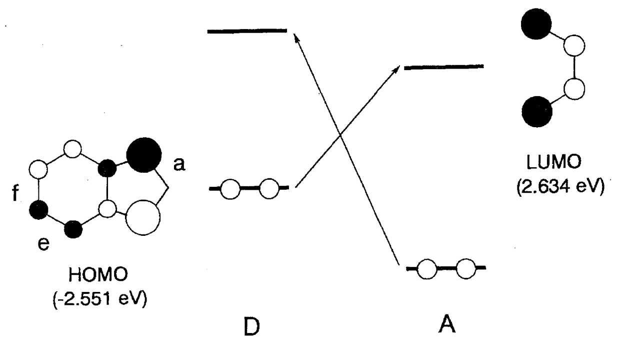

Fig. 3. Orbital interactions between the HOMO of indenide ion (D) and the LUMO of 1,3-butadiene (A).

an electron donor (D) and butadiene as an electron acceptor (A). Let us next look at the interactions between the two frontier orbitals, the HOMO of indenide ion and the LUMO of butadiene in terms of stereoselection rules.[28] The HOMO-LUMO interaction clearly favors coupling of the two fragment molecules at position *e*, and disfavors that at position *f* because of the in-phase and out-of-phase orbital interactions, respectively. A close inspection of the orbital interactions demonstrates that the stabilization energy decreases in the position sequence $e > a > f$, and, accordingly, the stability of the formed carbanions is likely to decrease in the sequence $\mathbf{5}^- > \mathbf{3}^- > \mathbf{4}^-$. These predictions are well consistent with the order of stability for single-electron oxidation in the gas phase and in the DMSO solution (I_p and E_{ox}, respectively), as given above in Table 1.

Clearly, $\mathbf{4}^-$ and $\mathbf{5}^-$ can be viewed as the isoelectronic structures of anthrecene and phenanthrene, respectively. It is well known that anthrecene and phenanthrene are strikingly different in their reactivities; Fukui[29] and Hosoya[30] theoretically explained the reason why phenanthrene is energetically more stable than anthracene. Detailed theoretical analyses of the electronic structures of the cyclopentadienide ions will be reported in a future paper.

For benzofluorenide ions with three condensed aromatic rings, the stability decreases in the sequence, benzo[*c*]fluorenide ion > benzo[*a*]fluorenide ion > benzo[*b*]fluorenide ion,[9,10] which is in agreement with their stability order on the basis of a similar bonding interaction of the HOMO of fluorenide ion with the LUMO of butadiene. For three isomers of the dibenzofluorenide ion, also, the stability sequence by the analogous HOMO-LUMO bonding interaction is consistent with the observed stability sequence for their conjugated acids, dibenzo[*c*,*g*]fluorenide ion > dibenzo[*a*,*i*]fluorenide ion > dibenzo[*b*,*h*]fluorenide ion.[16]

Conclusion. The condensed aromatic rings intrinsically stabilize the cyclopentadienide ion without any solvation effects in solution as well as in the gas phase. The apparent destabilizing phenomena by the condensed aromatic rings are most probably due to a decrease in the stabilizing solvation effects by charge delocalization on the carbanions. The stability of the carbanions with this type is dependent on the structure, itself.

Experimental

^{1}H and ^{13}C NMR spectra were taken with JEOL model JNM EX-400KS and EX-270J instruments (^{1}H: 400 and 270 MHz; ^{13}C: 100 and 68 MHz, respectively). IR spectra were recorded with a Perkin–Elmer model 1640 FTIR spectrophotometer. Mps were measured on a Yamato model MP-21 apparatus. MPLC was performed with a CHEMCO chromatograph system, which comprised an FMI model RP-SY-2 pump and a Merck silica gel 60 column. AM1 calculations were carried out using the MOPAC package on an IBM RS/6000 computer.[31]

The reagents were of analytical reagent-grade quality. Anhydrous solvents were used for syntheses and cyclic voltammetry by purification using the standard procedures.

Synthesis of Benzo[*f*]indene. Benzo[*f*]indene was synthesized by a known method.[17] A reaction of 1,2-bis(dibromomethyl)benzene with cyclopent-2-en-1-one in the presence of NaI provided benzo[*f*]indan-1-one in 27% yield, which was reduced with $LiAlH_4$ to benzo[*f*]indan-1-ol and a subsequent dehydration with 10% aq H_2SO_4 afforded benzo[*f*]indene in an overall 24% yield (lit,[17] 40%).

Synthesis of 1*H*- and 3*H*-Benzo[*e*]indene. 1*H*- and 3*H*-benzo[*e*]indene was prepared through five-step pathways from naphthalene and maleic anhydride in a manner like that previously reported[18] in a total yield of 5.5% (lit,[18] 23%). A reaction of naphthalene with maleic anhydride in the presence of $AlCl_3$ produced a mixture of 4-(1-naphthyl)- and 4-(2-naphthyl)-4-oxobut-2-enoic acids, which were isomerized in the presence of $AlCl_3$ in molten NaCl to give a mixture of 1-oxobenzo[*e*]indane-3-carboxylic acid and 3-oxobenzo[*e*]indane-1-carboxylic acid. The mixture was heated at 200—208 °C to yield a mixture of 1*H*-benzo[*e*]indan-1-one and 3*H*-benzo[*e*]indan-3-one, which was subsequently reduced with $LiAlH_4$ to a mixture of 1*H*-benzo[*e*]indan-1-ol and 3*H*-benzo[*e*]indan-3-ol. The alcohol mixture was dehydrated with oxalic acid and isolated by MPLC to afford a mixture of 1*H*- and 3*H*-benzo[*e*]indene as a slightly yellow solid.

Synthesis of 7*H*-Dibenzo[*c*, *g*]fluorene. 7*H*-Dibenzo[*c*,*g*]fluorene was provided in overall 4.7% (lit,[19] 62%) via three steps reactions from 2-(bromomethyl)naphthalene and α-tetralone.[19] A reaction of 2-(bromomethyl)naphthalene and α-tetralone gave rise to 2-(2-naphthyl)-α-tetralone, which was treated in liquid HF afforded 8,9-dihydro-7*H*-dibenzo[*c*,*g*]fluorene. A solution of the 8,9-dihydrodibenzofluorene and DDQ in benzene was heated at reflux for 5 min and separated by MPLC to produce 7*H*-dibenzo[*c*,*g*]fluorene with mp 154.9—155.8 °C (lit,[19] 152—152.5 °C) as slightly gray crystals.

Cyclic Voltammetry. The oxidation-potential values were measured by cyclic voltammetry. Cyclic voltammetry was performed with a BAS CV-50W instrument equipped with a MCA microcell. A three-electrode cell, consisting of a BAS 11-2012 glassy carbon working electrode, a Pt wire counter electrode, and a $Ag/AgNO_3$ (0.01 M in DMSO) ($1\ \mathrm{M} = 1\ \mathrm{mol\,dm^{-3}}$) reference electrode, was used. The measurements were carried out at a scan rate of 100 mV s^{-1} for DMSO solutions containing 1 mM of sample, 1 mM of ferrocene as an internal standard, and 0.1 M of tetrabutylammonium perchlorate as a supporting electrolyte.

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