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Energetics of Electrode Reactions. II.[1] The Relationship between Redox Potentials, Ionization Potentials, Electron Affinities, and Solvation Energies of Aromatic Hydrocarbons

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Abstract: Reversible oxidation and reduction potentials for alternant aromatic hydrocarbons (AAH) correlate linearly with ionization potentials (IP) and electron affinities (EA), and the slopes of the correlation lines were found to be equal to unity indicating that the solvation energies of AAH ions do not vary throughout the series. Oxidation and reduction potentials for AAH were observed to be symmetrically disposed about a common potential M_{AAH} (−0.31 V vs. SCE). The solution redox potentials were found to be related to IP and EA in the gas phase by $E_{\mathrm{M}} = \mathrm{IP} - \phi + (\Delta G°_{\mathrm{solv}})^{\pm} = \phi - \mathrm{EA} + (\Delta G°_{\mathrm{solv}})^{\pm}$, where ϕ is equal to 4.4 eV, and $(\Delta G°_{\mathrm{solv}})^{\pm}$ is equal to one-half of the sum of the solvation energies of the positive and negative ions. Furthermore, it was concluded that the solvation energies of the positive and negative ions of AAH are the same and equal to −1.94 eV. The value of the solvation energies calculated as above was verified by identity with those obtained from $-(E_{\mathrm{O}} - E_{\mathrm{R}}) = \mathrm{EA} - \mathrm{IP} - 2(\Delta G°_{\mathrm{solv}})^{\pm}$, where the sums of the redox potentials are independent of a reference potential. Correlation of E_{sum} with IP and EA indicated that the quantity is zero for the hypothetical AAH having IP = 6.27 and EA = 2.35 eV, indicating that the compound should be 50% ionized in solution. AAH having EA values greater than 2.36 eV would be completely ionized in acetonitrile solution according to: $2\mathrm{AAH} \rightleftarrows \mathrm{AAH}^+ + \mathrm{AAH}^-$. The driving force for the ionization reaction is the solvation energies of the ions.

Numerous correlations of oxidation and reduction electrode potentials with ionization potentials and electron affinities have been reported[2] and discussed.[3,4] The comment has been made[5] that it is best to use reversible potentials in order to obtain meaningful correlations. However, it was implied that the use of reversible potentials is not completely necessary. The reported correlation lines invariably have slopes somewhat less than unity and this is generally attributed to changes in solvation energies in a series of compounds.[2] However, most correlations have involved the use of irreversible half-wave potentials and, since the ions of compounds exhibiting the highest ionization potentials and lowest electron affinities are also the most reactive, the deviations observed in slope could just as well arise from kinetic behavior.

In a preliminary report of this work, it was suggested that, since the chemical solvation energies of the positive and negative ions of alternant aromatic hydrocarbons (AAH) are expected to be equal, the oxidation and reduction potentials should also be symmetric about zero, and that the common midpoint potential for AAH should be considered the zero point against which to measure the energy change of an electrode reaction. Attempts to calculate "absolute" electrode potentials[6] have not been successful due to the lack of an exact value for a solvation energy, lack of knowledge of surface potentials of metals, and lack of an absolute value for the chemical potential of the electron.[7] Real solvation energies of AAH ions have been calculated from redox potentials referred to an "absolute" scale leading to the result that, in acetonitrile, the positive ions invariably have significantly higher real solvation energies.[8]

In this paper the recently developed techniques for measuring reversible oxidation[9] and reduction[10] potentials in aprotic solvents are employed to give reversible redox potentials for several AAH and the reversible potentials are correlated with the recently calculated IP and EA values.[2]

Correlation Method

The energetics of reduction in solution as compared with the gas phase electron affinity (EA) for aromatic hydrocarbons was first analyzed in detail by Hoijtink,[11] and essentially the same derivation has been used by more recent authors.[2,3] When an electron adds to a molecule in the gas phase, energy is liberated which is equal to −EA (eq 1). In solution, the free energy change reflected by the half-wave potential of a reversible one-electron reduction is given by (2) or (3). $(\Delta G°)_{\mathrm{solv}}$ is the difference in free energies of solvation of the hydrocarbon and its anion. Neglecting entropy effects, substitution of EA into (3) gives (4).

$$\mathrm{R} + \mathrm{e} \rightarrow \mathrm{R}^- \qquad \Delta H° = -\mathrm{EA} \tag{1}$$

$$\Delta G° = (G°_{\mathrm{R}})_{\mathrm{sol}} - (G°_{\mathrm{R}^-})_{\mathrm{sol}} + (G°_{\mathrm{electron}})_{\mathrm{Hg}} \tag{2}$$

$$\Delta G° = (G°_{\mathrm{R}})_{\mathrm{gas}} - (G°_{\mathrm{R}^-})_{\mathrm{gas}} + (G°_{\mathrm{electron}})_{\mathrm{Hg}} + (\Delta G°)_{\mathrm{solv}} \tag{3}$$

$$\Delta G° = \mathrm{EA} + (G°_{\mathrm{electron}})_{\mathrm{Hg}} + (\Delta G°)_{\mathrm{solv}} \tag{4}$$

Table I. Redox Potentials and Calculated Solvation Energies of AAH Ions in Acetonitrile

Compd	$(E_p + 30\text{ mV})_{red}$[a,b]	$(E_p - 30\text{ mV})_{ox}$[a,b]	Midpoint	E_M[c]	$(-\Delta G°)_{solv}$[d]	$(-\Delta G°)_{solv}$[e]
Anthracene (II)	−1.97, R	1.37, r	0.30	1.67	1.97	1.99
Benzanthracene (VI)	−2.02, R	1.44, r	0.29	1.73	1.97	1.97
Chyrsene (XVI)	−2.27, R	1.64, r	0.32	1.95	1.90	1.89
Perylene (XXXII)	−1.66, R	1.06, R	0.30	1.37	2.02	2.01
Pyrene (XLIV)	−2.04, R	1.36, R	0.34	1.70	1.91	1.95
Benzopyrene (XLVI)	−1.84, R	1.16, R	0.34	1.50	1.91	1.91
Benzoperylene (XXXVI)	−1.91, R	1.35, R	0.28	1.63	1.88	1.91
Triphenylene (IX)	−2.48, R	1.88, i	0.30	2.17[f]	1.94	1.93
Naphthalene (I)	−2.50, R	1.84, i	0.33	2.19[f]	2.01	2.05
Benzene (0)		2.79, i		3.10[g]	1.93	
Phenanthrene (V)	−2.49, R	1.83, r	0.33	2.16	1.93	1.92

[a] V vs. SCE. [b] R = reversible, r = reaches limiting value at high sweep rates, i = irreversible. [c] Potential for oxidation and reduction referred to the midpoint, SCE − 0.31 V. [d] Calculated from eq 21 with $\phi = 4.34$ eV. [e] Calculated from E_{sum} (Table IV) using eq 20. [f] Reduction potential plus 0.31 V. [g] Oxidation potential minus 0.31 V.

If free energy is expressed in volts, the half-wave potential is given by (5).

$$E_{1/2} = -\Delta G° + (RT/F)\ln(f_R D_R{}^{-1/2}/f_{R\text{-}} D_R{}^{1/2}) \quad (5)$$

The second term of (5) is generally neglected on the basis that the activity coefficients (f) are believed to be close to unity and the diffusion coefficients (D) of the substrate and the ion are assumed to be equal. These assumptions have been shown to hold reasonably well for voltammetric oxidations of aromatic hydrocarbons. A comparison of redox equilibria determined voltammetrically and spectrophotometrically revealed comparable results for the two methods,[12] and the ratio of the diffusion coefficients of aromatic compound and the corresponding cation radical have been found to be of the order of 1.2-1.5 for several substrate-cation pairs.[13]

Another derivation[8] correctly omits the term due to the energy of the electron in the electrode and replaced it with a constant which is characteristic of the reference electrode. The latter treatment resulted in equations similar to (6) and (7) for reduction and oxidation, respectively.

$$E_R = \text{EA} - C - (\Delta G°)_{solv} \quad (6)$$

$$E_O = \text{IP} - C + (\Delta G°)_{solv} \quad (7)$$

For the reference half-cell, 0.1 N Et_4NClO_4, 0.01 N $AgClO_4$, CH_3CN-Ag, the value of C was given as 4.70 V at 25°C.[7]

Results

Relationship between Gas Phase and Solution Redox Potentials. Molecular orbital (MO) theory indicates that the MO's of AAH occur in pairs of bonding and antibonding orbitals of energy $-\epsilon$ and $+\epsilon$. Thus, the ionization potential (IP) and the electron affinity (EA) of an AAH can be related to the energies of the highest bonding and lowest antibonding orbitals by (8) and (9). For graphite, the largest member of the AAH series, IP is equal to EA (eq 10), the values being the work function ϕ[14] which has been determined to be equal to 4.39 eV.[15] Furthermore, MO theory predicts that the sum of IP and EA for AAH should be equal to a constant (eq 11),[16] and experimental results have been cited to support this relationship.[8] Indeed, if we examine the published calculated values of IP and EA for AAH,[2] we find the sums are indeed constant at 8.68 eV, close to the value predicted from the work function of graphite. Combining eq 10 and 11 allows us to write a common relationship between IP and EA and the orbital energies (eq 12).

$$\text{IP} = \beta m_n + \alpha_1 \quad (8)$$

$$\text{EA} = \beta m_{n+1} + \alpha_2 \quad (9)$$

$$\text{IP} = \text{EA} = \phi = 4.39\text{ eV (for graphite)} \quad (10)$$

$$\text{IP} + \text{EA} = \text{constant} = 2\phi = 8.68\text{ eV (calcd for AAH)} \quad (11)$$

$$\text{IP} - \phi = \phi - \text{EA} = \beta m + \alpha \quad (12)$$

In the previous paper,[1] it was shown that the oxidation and reduction potentials for AAH in acetonitrile are symmetric about a common point. The potentials are related to the orbital energies by (13) and (14) and, if we assume that the solvation energies of the positive and negative ions of a given AAH are equal as predicted by the Born equation, the redox potentials are given by (15)

$$E_O = \text{IP} - \phi + (\Delta G°)_{solv}{}^{+} + \text{constant} \quad (13)$$

$$-E_R = \phi - \text{EA} + (\Delta G°)_{solv}{}^{-} + \text{constant} \quad (14)$$

$$E_M = \text{IP} - \phi + (\Delta G°)_{solv}{}^{\pm} + c \quad (15)$$

where E_M is equal to E_O or $-E_R$ referred to the AAH midpoint potential (M_{AAH}).

According to eq 15, solvation energies of AAH ions could be calculated directly from the corresponding electrode potential measured vs. the AAH midpoint potential and either IP or EA if c were known. In order to determine c in (15), we can approach the calculation of the solvation energies in an independent way. The free energy change for reaction 18 is given by the sum of the free energy changes for the half cells (16) and (17) and is equal to $-(E_O - E_R)$, the potential span between oxidation and reduction of an AAH. The relationship between solvation energies, electrode potentials, and IP or EA is then given by (19). If we once again assume that the solvation energies of the positive and negative ions are equal, we arrive at (20). It should be noted that calculation of the sum of the solvation energies according to (19) can be carried out without implicating a reference potential.

$$\text{AAH}^+ + e \rightarrow \text{AAH} \quad (16)$$

$$\text{AAH}^- \rightarrow \text{AAH} + e \quad (17)$$

$$\text{AAH}^+ + \text{AAH}^- \rightarrow 2\text{AAH} \quad (18)$$

$$-(E_O - E_R) = -E_{sum} = \text{EA} - \text{IP} - (\Delta G_{solv}{}^{+} + \Delta G_{solv}{}^{-}) \quad (19)$$

$$-E_{sum} = \text{EA} - \text{IP} - 2(\Delta G°)_{solv}{}^{\pm} \quad (20)$$

Substitution of $(\Delta G°)_{solv}{}^{\pm}$ obtained from (20) into (15) allows for the evaluation of c in (15) which proved to be 0.

Redox Data and Solvation Energies. Redox potentials of several AAH in acetonitrile were measured in the presence of suspended neutral alumina[9] at a platinum electrode. The reduction potentials for all of the compounds investigated were reversible while only some of the oxidation potentials were independent of voltage sweep rate. The potentials are

Table II. Sweep Rate Dependence of AAH Oxidation Potentials in Acetonitrile

	$(E_p - 30\text{ mV})^a$						
mV/sec	0	I	II	VI	IX	XVI	V
100	2.61	88	1.31	1.39	1.78	1.60	1.72
200	2.65	1.71	1.33	1.41	1.80	1.61	1.75
400	2.69	1.73	1.35	1.44	1.84	1.62	1.77
800	2.72	1.76	1.37	1.44	1.86	1.63	1.81
1500	2.79	1.84	1.37	1.44	1.88	1.64	1.83

[a] Potentials measured vs. the reversible couple of perylene and are referred to the saturated aqueous calomel electrode (SCE). Measurements were made on solutions containing n-Bu_4NBF_4 (0.2 *M*) and suspended neutral alumina.

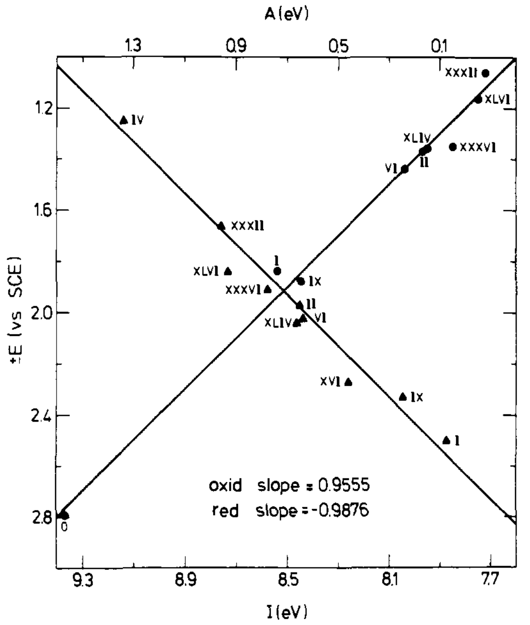


Figure 1. Oxidation and reduction potentials of AAH in acetonitrile (vs. SCE) vs. *I* and *A*. The point for compound IV is for reduction in dimethylformamide; the solubility in acetonitrile was too low. ●, oxidations; ▲, reductions.

listed in Table I. Potentials measured from reversible cyclic voltammograms are referred to as R. Those measured from voltammograms, on which reduction peaks were not observed for the cation radicals and the peak potentials were sweep rate dependent, are designated by r if the peak potential was observed to reach a limiting value with increasing sweep rate and if not the potentials are designated by i. Data for compounds not showing reversible behavior are summarized in Table II. Redox potentials (E_M) referred to the midpoint potential are given and solvation energies $(\Delta G°)_{solv}^{\pm}$ calculated from (21) are listed.

$$-(\Delta G°)_{solv}^{\pm} = \text{IP} - \phi - E_M \qquad (21)$$

The near constancy of $(-\Delta G°)_{solv}^{\pm}$ (average = 1.94 eV) is the most striking feature of these data which indicates that plots of E_M vs. IP $- \phi$ or $\phi -$ EA should be linear with unit slope. Plots of the measured potentials (vs. SCE) vs. these quantities are shown in Figure 1, and in Figure 2 E_M is plotted vs. IP $- \phi$. The plots are indeed linear with unit slope. It is of interest to note that two of the compounds giving the largest deviations (Figure 2 and Table I) are structurally related, perylene (XXXII) gave a positive deviation while benzoperylene (XXXVI) showed a negative deviation in $(-\Delta G°)_{solv}^{\pm}$. Thus, the deviations that do occur do not appear to be related to molecular size. For purpose of comparison, Figure 3 shows a plot of IP for the same compounds vs. the energy coefficients of the highest occupied MO's.[2] The deviations from the correlation line of Figure 2 are not so great as those of Figure 3. The latter supports the contention that the variations that do occur should not be attributed to solvation energy changes.

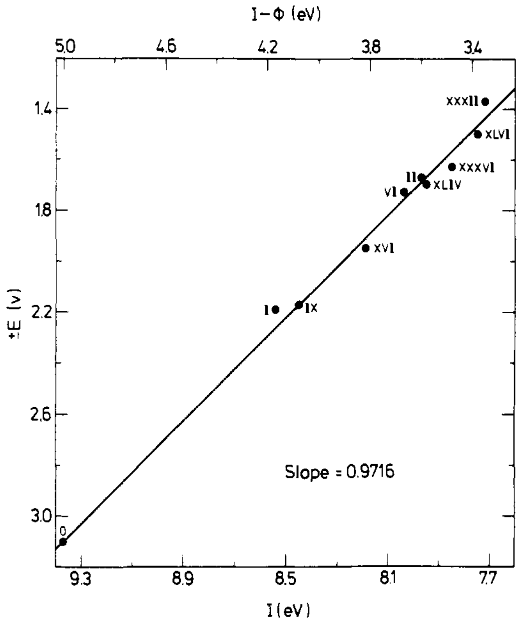


Figure 2. Redox potentials of AAH in acetonitrile (vs. midpoint potential) as a function of $I - \phi$.

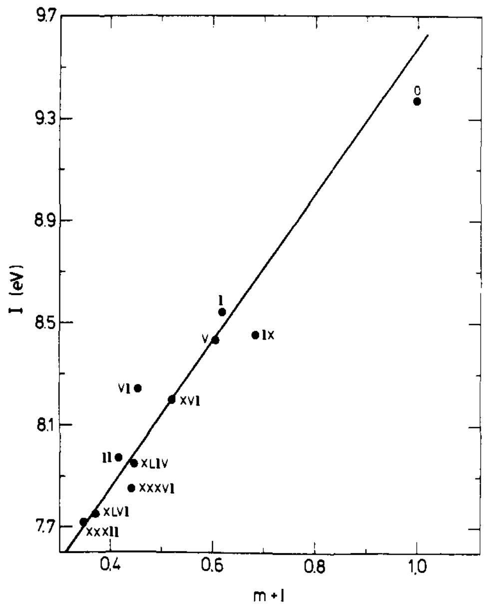
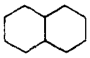
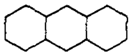
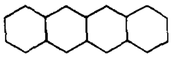
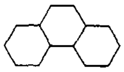
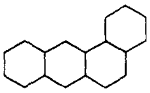
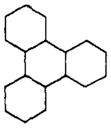
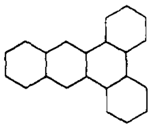
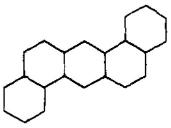
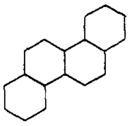
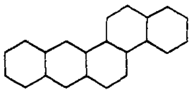
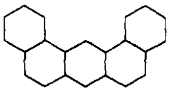
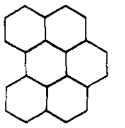
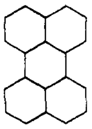
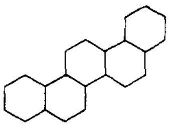
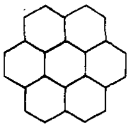
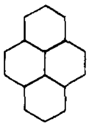
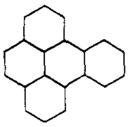
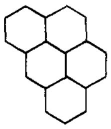
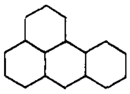
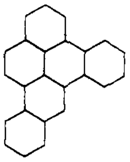
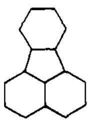


Figure 3. Ionization potentials (ref 2) vs. energies of the highest occupied MO.

Oxidation potential data of Pysh and Yang[17] have recently been correlated with calculated values of IP, and the slope of the correlation line was found to be equal to 0.87.[2] Using the compounds which show reversible oxidation behavior as standards, the published potentials were adjusted to the AAH midpoint potential (Table III). Potentials were calculated from (15) with $(\Delta G°)_{solv}^{\pm}$ taken as −1.94 eV, the average value in Table I. The differences in observed and calculated potentials are listed, and the average deviation was found to be ±0.08 V. The compounds known to give very reactive cation radicals, benzene, naphthalene, and phenanthrene, gave the largest deviations (+0.13 −

Table III. Observed and Calculated Electrode Potentials of AAH

	Compd[a]	E_{calcd}[b]	$E_{1/2}$[c]	Δ_1[d]	$\pm E_{\text{M}}$[e]	Δ_2[f]
	C	3.09	2.82	+0.25	3.10	−0.01
	I	2.26	2.06	+0.20	2.19	+0.07
	II	1.69	1.61	+0.08	1.67	+0.02
	III	1.32	1.29	+0.03		
	V	2.15	2.02	+0.13	2.16	−0.01
	VI	1.76	1.70	+0.06	1.73	+0.03
	IX	2.17	2.07	+0.10	2.17	0.00
	X	1.82	1.77	+0.05		
	XIII	1.79	1.71	+0.08		
	XVI	1.91	1.87	+0.04	1.95	−0.04
	XVII	1.60	1.53	+0.07		
	XX	1.82	1.78	+0.04		
	XXXVI	1.67	1.53	+0.14	1.63	+0.03
	XXXII*	1.44	1.37	+0.07	1.37	+0.07
	XXVI	1.88	1.85	+0.03		
	XXXIV	1.70	1.75	−0.05		
	XLIV*	1.67	1.68	−0.01	1.70	−0.03
	XLV	1.75	1.79	−0.04		
	XLVI*	1.47	1.46	+0.01	1.50	−0.03
	XLVII	1.50	1.67	−0.17		
	XLVIII	1.56	1.53	+0.03		
	LXII	2.06	1.97	+0.09		
			Av:	±0.08		±0.03

[a] Numbering is that used in ref 2. [b] Calculated from: E = IP − 6.28 V. [c] Values in ref 17 + 0.52 V (referred to midpoint potential using compounds marked with * as standards). [d] $E_{\text{calcd}} - E_{1/2}$. [e] This work. [f] $E_{\text{calcd}} - E_{\text{M}}$.

+0.25 V), suggesting that deviation from unit slope in the correlation line could indeed be due to kinetic behavior of the cation radicals. For comparison, the difference between potentials measured in this work and the calculated values are listed. In this case the average deviation was found to be ±0.03 V and the largest observed deviation was +0.07 V.

Discussion

The symmetry of the ionization energies of AAH in the gas phase is shown by (12). How is this relationship to be interpreted? Consider the respective ionization reactions (22) and (23) and the corresponding free energy expressions (24) and (25), where the $\Delta G°$'s are the free energies of formation of the ions from the AAH and the ϕ's are the differences in energies of the electrons in the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) of the AAH and in the gas phase. Combining the latter two equations results in (26) for IP + EA. For graphite, (27) holds.

$$(\text{AAH})_{\text{gas}} \rightarrow (\text{AAH}^+)_{\text{gas}} + \text{e} \quad (22)$$

$$(\text{AAH})_{\text{gas}} + \text{e} \rightarrow (\text{AAH}^-)_{\text{gas}} \quad (23)$$

$$\text{IP} = (\Delta G°_{\text{AAH}^+})_{\text{gas}} + \phi_{\text{HOMO}} \quad (24)$$

$$-\text{EA} = (\Delta G°_{\text{AAH}^-})_{\text{gas}} - \phi_{\text{LUMO}} \quad (25)$$

$$\text{IP} + \text{EA} = (\Delta G°_{\text{AAH}^+})_{\text{gas}} - (\Delta G°_{\text{AAH}^-})_{\text{gas}} + \phi_{\text{HOMO}} + \phi_{\text{LUMO}} \quad (26)$$

$$(\Delta G°_{\text{AAH}^+})_{\text{gas}} = (\Delta G°_{\text{AAH}^-})_{\text{gas}} = \phi_{\text{HOMO}} + \phi_{\text{LUMO}} \quad (27)$$

In going from the infinitely large AAH, graphite, to smaller AAH, $(\Delta G°_{\text{AAH}^+})_{\text{gas}}$ and $(\Delta G°_{\text{AAH}^-})_{\text{gas}}$ go from zero to finite values, the former becoming more positive and the latter more negative. If (IP + EA) is constant (eq 11), the changes in free energies of formation of the ions must be accompanied by comparable changes in ϕ_{HOMO} and ϕ_{LUMO}. ϕ_{HOMO} must become less positive and ϕ_{LUMO} less negative. If we assume that $(\Delta G°_{\text{AAH}^+})_{\text{gas}}$ is equal but opposite in sign to that for the negative ion (eq 28), we are led to the conclusion that changes in ϕ_{HOMO} ($\Delta\phi_{\mathrm{HOMO}}$) in going through the series of AAH are accompanied by comparable changes in ϕ_{LUMO} (eq 29). That is, the energy changes experienced by the electrons in going from and to the HOMO and LUMO of AAH vary in exactly the same way as the structure of the AAH is changed. In fact the latter is true even though recent work[18] has revealed that (11) is a result of approximations in the MO calculations and does not hold for the AAH series. The changes observed in the sums of IP and EA when real values are used instead of calculated values are systematic and the symmetry implied by (12) is preserved.[18]

$$(\Delta G^\circ{}_{\mathrm{AAH^+}})_{\mathrm{gas}} = -(\Delta G^\circ{}_{\mathrm{AAH^-}})_{\mathrm{gas}} \qquad (28)$$

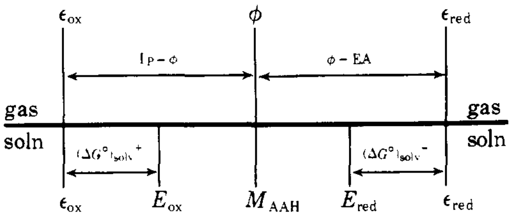
$$\Delta\phi_{\mathrm{HOMO}} = -\Delta\phi_{\mathrm{LUMO}} \qquad (29)$$

A similar symmetry is also observed for the redox reactions of AAH in solution. Oxidation and reduction potentials are equally disposed about a common point, M_{AAH}.[1] Solvation energies of the ions calculated from (21) were found to be equal to one-half of the sums of the solvation energies of the positive and negative ions calculated according to (20). Therefore, the constant (c) in (15) is equal to zero. Thus, we arrive at the result that E_{M} differs from the gas phase energies (IP − ϕ and ϕ − EA) by the solvation energies of the respective ions (eq 30).

$$E_{\mathrm{M}} - (\Delta G^\circ)_{\mathrm{solv}}{}^{\pm} = \mathrm{IP} - \phi = \phi - \mathrm{EA} \qquad (30)$$

The significance of (30) is that solvation energies can be calculated without knowing the "absolute" potential of a reference electrode. Thus, if the solvation energies of positive and negative ions of AAH are equal, the "absolute" potential for an electrode reaction is the sum of E_{M} and ϕ (eq 31).

Scheme I



$$E_{\text{"absolute"}} = E_{\mathrm{M}} + \phi \qquad (31)$$

The observation that the solvation energies of AAH ions in acetonitrile are invariant throughout the series requires further comment. The fact that plots (Figure 1) of reversible oxidation potentials vs. IP and reversible reduction potentials vs. EA are linear with slopes very close to 1.0 indicates that $(\Delta G^\circ)_{\mathrm{solv}}{}^{+}$ and $(\Delta G^\circ)_{\mathrm{solv}}{}^{-}$ are constants independent of the structure of the AAH. Deviations from unit slope in previous studies were most likely due to the use of potentials measured under conditions where kinetic processes affected the measured values. The constancy of the solvation energies is also shown by the plots of the sums of the oxidation and reduction potentials vs. IP (Figure 4) and EA (Figure 5). Slopes very close to the expected value, 0.50, were observed in both the latter cases. Obviously, the Born equation (32)

$$(-\Delta G^\circ)_{\mathrm{solv}} = (1 - 1/D)\mathrm{N}e^2/2r_{\mathrm{e}} \qquad (32)$$

where the symbols have their usual meaning, does not apply to the solvation energies of AAH ions. The latter predicts that $(\Delta G^\circ)_{\mathrm{solv}}$ should vary inversely with the radius of the ion (r_{e}) approximated to resemble a sphere.

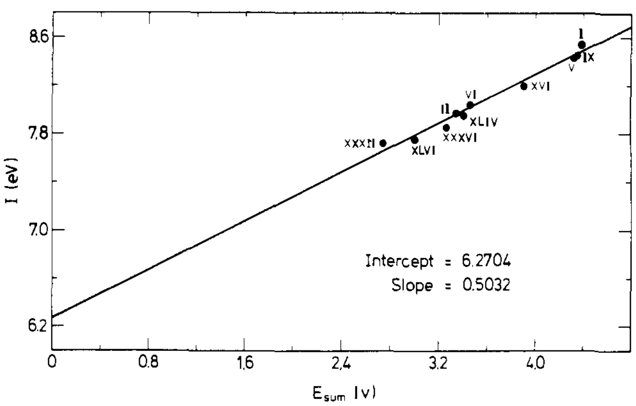


Figure 4. Numerical sum of redox potentials of AAH in acetonitrile vs. I.

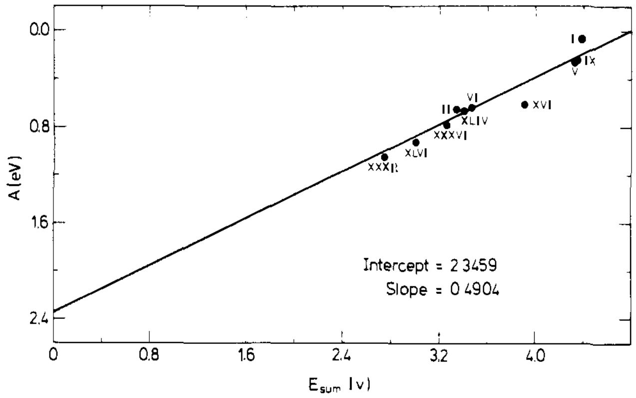


Figure 5. Numerical sum of redox potentials of AAH in acetonitrile vs. A.

As mentioned earlier, the span of the oxidation and reduction potentials of an AAH, i.e., $E_{\mathrm{sum}} = E_{\mathrm{O}} + (-E_{\mathrm{R}})$, is independent of the reference point. The numerical sums of the oxidation and reduction potentials for the AAH are listed in Table IV along with the calculated values[2] of IP and EA. The intercepts (Figures 4 and 5) indicate that E_{sum} should be equal to zero when IP = 6.27 and EA = 2.35. Under conditions where E_{sum} is zero, (19) reduces to (33); i.e., the orbital energies are compensated by the solvation energies and the equilibrium constant for reaction 34 is equal to 1.0.

$$\mathrm{IP} - \mathrm{EA} = (-\Delta G^\circ)_{\mathrm{solv}}{}^{+} + (-\Delta G^\circ)_{\mathrm{solv}}{}^{-} \qquad (33)$$

$$2\mathrm{AAH} \rightleftarrows \mathrm{AAH^+} + \mathrm{AAH^-} \qquad (34)$$

Thus, for the hypothetical AAH having an IP of 6.27 and EA of 2.35, E_{sum} would be equal to zero and a solution of the compound in acetonitrile would be 50% ionized according to equation 34.

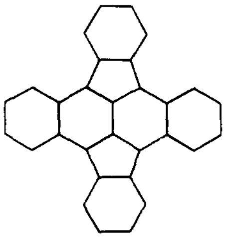
Furthermore, it can readily be shown that K_{34} changes by a factor of 10 for every 60-mV change in E_{sum}. Thus, for a compound showing an E_{sum} equal to −0.12 V, K_{34} would be equal to 100 and the compound would be 99% ionized.[21] The largest value of EA given in ref 2 was 2.04 for LXXII. If one examines the trend in EA with structural change for an AAH, it is apparent that the most effective ring fusion to increase EA is a benzene ring fused to the AAH structure through a five-membered ring. It should be pointed out that fusion through a five-membered ring forms an aromatic hydrocarbon which is no longer alternant. For example in the series, I, LXII, and LXX, the electron affinity increases from 0.07 to 0.840 to 1.371 as the number of fused benzene rings is increased. A similar trend is found in the anthracene series. For the tetracenes, LXXII has EA = 2.04, the

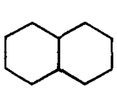
Table IV. The Sum of Oxidation and Reduction Potentials of AAH

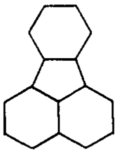
Compd	E_{sum}[a]	Ip[b]	EA[b]	IP + EA
I	4.38	8.54	0.074	8.61
II	3.34	7.97	0.653	8.62
V	4.32	8.43	0.273	8.70
VI	3.46	8.04	0.640	8.68
IX	4.34	8.45	0.251	8.60
XVI	3.90	8.19	0.516	8.71
XXXII	2.74	7.72	0.956	8.68
XXXVI	3.26	7.85	0.779	8.63
XLIV	3.40	7.95	0.664	8.61
XLVI	3.00	7.75	0.930	8.68
				Av: 8.68

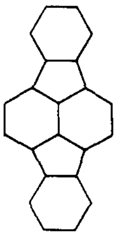
[a] The numerical sum of the oxidation and reduction potentials of AAH in acetonitrile. [b] Values from ref 2.

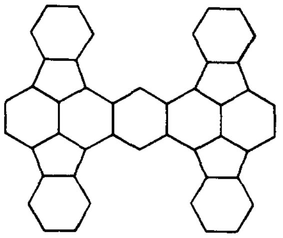
compound with only one fused ring, LXIV,[2] has EA = 1.60, and EA is equal to 1.06 for the parent in the series, III. We can crudely estimate the effect of benzene ring fusion to the pentacenes to be about 0.5 increase in EA for the first fused ring, 0.4 for the second, 0.3 for the third, and 0.2 increase in EA for the fourth fused benzene ring. The EA value for pentacene is 1.34[2] and adding the predicted changes we estimate that compound **1** should have an EA of the order of 2.75 eV. The latter leads to the prediction that K_{34} for compound **1** in acetonitrile should be of the order of 10^7. The driving force for ionization of AAH with E_{sum} less than 0 is the solvation energy of the ions. None of the series could be conductors in the solid phase until IP = EA, i.e., graphite.


LXXII


I


LXII


LXX


1

The IP and EA values used in this study were calculated[2] rather than experimental because they represent the largest internally consistent set of data available. The calculated values compare remarkably closely with observed values where data are available.[2] A detailed comparison of calculated and experimental values has recently been made, and systematic trends in the data were observed.[18] The observed differences[18] in calculated and experimental values do not affect the conclusions of this study.

Experimental Section

The apparatus used for the voltammetric measurements was standard and has been described.[19] Acetonitrile was purified by a literature procedure[20] and passed over neutral alumina before use. Potential measurements were made in the manner previously described.[9] Reagent grade hydrocarbons were used as obtained. The slopes and intercepts of the correlation times (Figures 1-5) were obtained by standard least-squares procedures.

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(21) The AAH for which E_{sum} = −0.12 V would have an *I* equal to 6.26 and an *A* equal to 2.36 eV.