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Ionic Probes of Aromaticity in Annelated Rings

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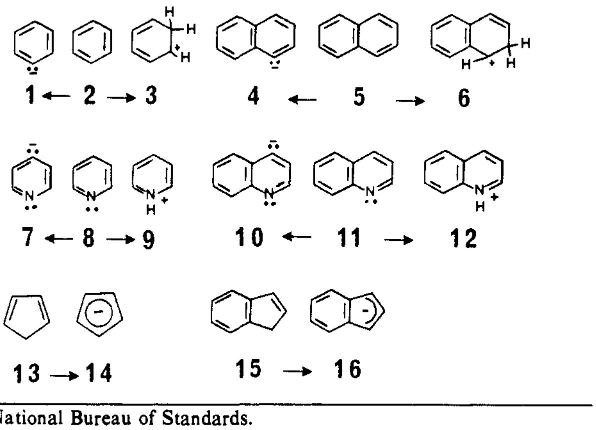
Abstract: Ionization by the deprotonation of benzene and pyridine, and by the protonation of pyridine, involves lone pairs in the σ plane without significant π effects. In these cases annelation by a benzene ring increases the acidity or proton affinty by a constant 6 ± 1 kcal/mol, ascribed to increased polarizability. In comparison, protonation of benzene and deprotonation of cyclopentadiene disrupts or creates a 6-electron aromatic system, respectively, and in their annelated derivatives, naphthalene and indene, a secondary 4-electron conjugated π system. These cases involving π electrons show annelation effects that are substantially larger (13.4 kcal/mol) or smaller (1.0 kcal/mol), respectively, than just the electrostatic effect. Analysis of these data suggests that the stability of secondary 4-electron systems in the annelated rings is smaller by 6 ± 1 kcal/mol than the aromatic 6-electron systems, in fair agreement with Herndon's structure–resonance values for these species. Annelation effects are reproduced well by Dewar's AM1 semiempirical method.

Aromaticity is a primary concept in the understanding of the structure and energetics of organic compounds. Extensive literature exists on the subject,[1,2] and many experimental and theoretical approaches have been offered to evaluate the magnitude and origin of this phenomenon. We will not attempt to review what is known, but rather present a simple and suggestive application of gas-phase ion energetics to this problem based mostly on the present measurements. We offer below a measure of resonance stabilization in annelated compounds as applies to the present data.

This paper exploits the observation that, in some aromatic compounds and their annelated derivatives, protonation or deprotonation involves lone pairs in the σ plane of the molecule, without significant direct π interactions. In contrast, there are cases where protonation or deprotonation destroys or creates the aromatic 6-electron system (i.e. Clar's "aromatic sextet"[1] in the parent compound or a 4-electron system, conjugated to a 6-electron one, in the annelated derivatives. These points are illustrated by structures **1**–**12**. It may be expected that increasing the molecule's size by annelation has mostly electrostatic effects in the first group but also an additional electronic effect in the second.



We will present measurements of deprotonation energies of the annelated compounds. When these data are examined, the following questions can be addressed: (1) What is the effect of annelation on the ion thermochemistry? (2) What is the added aromatic stability due to a second ring annelated to a 6-electron system and how does this reflect in the ion thermochemistry when electrons are added or removed from the π system? Can the ionic data provide a consistent quantitative measure of aromatic stabilization?

As to the first question, no previous gas-phase data on anions exist. However, the proton affinities of polycyclic hydrocarbons[3a] and annelated nitrogen heterocyclics[3b] have been measured. In both cases, the proton affinity increases with annelation, due in part to the electrostatic stabilization of the larger ions and, in the hydrocarbons, also aromaticity effects.

As to the second question, a second 4-electron π system is expected to be less resonance stabilized than a first fully aromatic 6-electron system to which it is annelated. Therefore, in protonating or deprotonating the single-ring compounds, a fully stabilized π system is perturbed or created, while the analogous processes on the annelated compound perturb or create a system of less stabilized four π electrons. This should affect the ionic properties, i.e. protonation and deprotonation energy, of the second vs the first ring. The question is then whether the ionic data are consistent with lesser aromatic stabilization of the second ring.

In the present paper, we provide experimental and theoretical, AM1, gas-phase acidities of annelated compounds and compare these with the parent single-ring compounds reported in the preceding paper.[4] We examine the thermochemistry and the

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(1) Clar, E. *Polycyclic Hydrocarbons*; Academic: New York, 1964; Vol. 1, Chapter 6.

(2) Garratt, P. J. *Aromaticity*, 2nd ed.; Wiley: New York, 1986.

(3) (a) Meot-Ner (Mautner), M. *J. Phys. Chem.* **1980**, *84*, 2716. (b) Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1979**, *101*, 2396.

0002-7863/88/1510-5937$01.50/0

Table I. Thermochemistry of Proton-Transfer Reactions $B^- + AH \rightarrow A^- + BH$

AH	B	$\Delta H^{\circ\,a}$	$\Delta S^{\circ\,b}$	ΔG°(T)	$\Delta H^\circ_{acid}(BH)^c$	ΔH°_{acid}
naphthalene	benzene	−6.8	1.6		400.7	393.9
	1,4-diazine	1.7	2.0		392.6	394.3
	H_2O	3.1	11.1		390.8	393.9
						394.0[d]
quinoline	C_6H_5F	−1.4	(0)	−1.4 (579)	387.3	385.9
	CH_3OH	3.7	7.0		381.6	385.3
						385.6[d]
1-methylnaphthalene	C_6H_5CCH	−0.4	(2.2)	−1.7 (601)	371.1	370.7
	$C_6H_5NH_2$	3.4	3.4		367.3	370.7
						370.7[d]
indene	CF_3COCH_3	2.4	0.4		351.9	354.3
	CH_3COOH	5.5	2.6		348.8	354.3
						354.3[d]
indole	$C_6H_5NO_2$	−2.2	(0)	−2.2 (600)	354.2	352.0
	CF_3COCH_3	0.0	2.0		351.9	351.9
	CH_3COOH	2.9	2.4		348.8	351.7
						351.9[d]
azulene	$C_6H_5NH_2$	2.4	(0)	2.4 (600)	367.3	369.7
	$CH_3CONHCH_3$	5.2	(0)	5.2 (605)	362.3	367.5
	pyrrole	6.3	(0)	6.3 (614)	359.6	365.9
						367.7[d]

[a] In kcal/mol. Where ΔG° values are indicated and ΔS° is in parentheses, ΔH° is derived from ΔG° measured at the indicated temperature and ΔS° is estimated from $\Delta S^\circ_{rot\,sym}$. [b] In cal/mol·K. [c] Acidities of reference compounds from ref 7. [d] Average values of ΔH°_{acid} from the ladder in ref 4.

species wave functions, as obtained from AM1 computations, to identify the annelation effects. The anionic data, and previous cation data on proton affinities, are then used as ionic probes for the aromatic stabilization of annelated rings.

Experimental and Computational Methods

The measurements were performed on the NBS pulsed high-pressure mass spectrometer. The method was described previously and is identical with that employed in the measurement of the gas-phase acidities of single-ring aromatic compounds.[4]

The theoretical calculations using the AM1 method and the computational details are also identical with those of the preceding paper.[4] However, the sizes of annelated compounds prevented us from performing meaningful ab initio calculations.

Results

The measurements entail proton-transfer equilibria between the compounds of interest and reference compounds whose gas-phase acidities are known.

$$B^- + AH \rightleftharpoons A^- + BH$$

Temperature studies yield the van't Hoff plots shown in Figure 1. The plots give ΔH_1° and ΔS_1°, as reported in Table I, with estimated errors of ±1 kcal/mol and ±2 cal/mol.K, respectively. The results were incorporated into an interlocking ladder of ΔH°_{acid} values including other aromatic carbon acids.[4] The ladder provides multiple alternative paths between compounds and more accurate averaged ΔH°_{acid} values for the compounds of interest. The values obtained from the ladder are assigned to the compounds AH.

The deprotonation enthalpies (DPE) obtained from AM1 are compared to the experimental values in Table II. In Table II, the position of the negative charge as shown denotes the deprotonated site. The necessary corrections to the AM1-DPEs[4] are taken into account. Namely, the heats of formation of the anions having nearest-neighbor lone pairs are increased by 10.7 kcal/mol and by 5 kcal/mol for those derived from methyl-substituted species.

The effects of annelation on the experimentally determined gas-phase acidities and proton affinities are given in Table III. Also shown are the corresponding values derived from the AM1-DPEs for the species of interest.

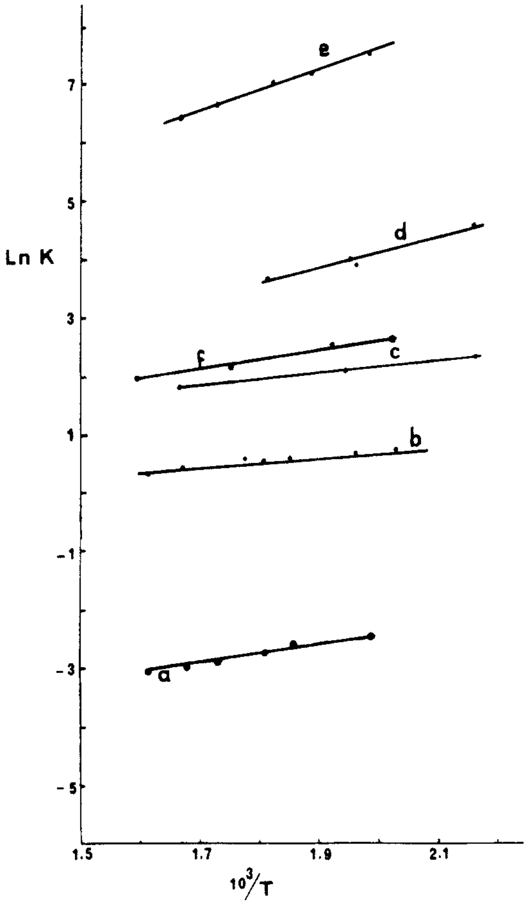

Figure 1. van't Hoff plots for proton-transfer equilibria $A^- + BH = B^- + AH$, for A^- and BH as follows: (a) $C_{10}H_7^-$ (naphthalene-H)$^-$ + H_2O, (b) (naphthalene-H)$^-$ + 1,2-diazine, (c) (indene-H)$^-$ + CF_3COCH_3, (d) (indene-H)$^-$ + CH_3COOH. (e) $C_6H_5^-$ + naphthalene, (f) (azulene-H)$^-$ + $C_6H_5NH_2$.

Discussion

1. Unsubstituted Two-Ring Systems. Table III shows the decrease in acid dissociation energies $\Delta H^\circ_{acid} = \Delta H^\circ_D(A^- - H^+)$, i.e., increase in gas-phase acidity upon annelation for several cyclic

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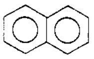
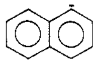
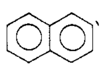
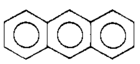
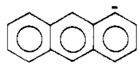
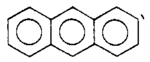
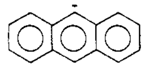
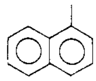
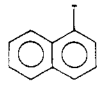
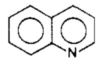
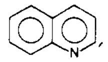
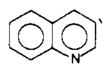
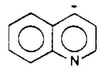
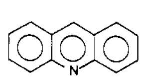
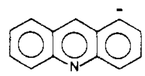
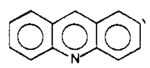
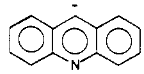
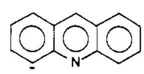
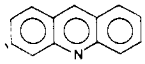
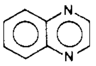
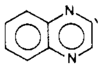
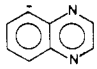
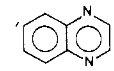
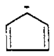
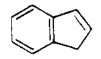
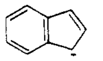
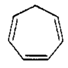
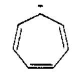
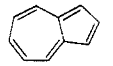
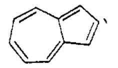
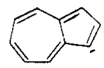
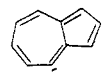
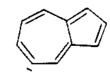
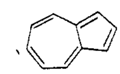
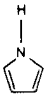
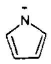
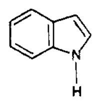
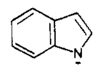
[4] Meot-Ner (Mautner), M.; Kafafi, S. A. *J. Am. Chem. Soc.*, in press.

Table II. Comparison between Experimental and Theoretical, AM1, Deprotonation Enthalpies (DPE)[a]

	molecule	anion	deprotonation enthalpy exptl	deprotonation enthalpy AM1	error
1			394.2	395.3	1.1
2				396.0	
3				391.6	
4				392.5	
5				387.1	
6			370.7	368.1	−2.6
7				393.4	
8				390.0	
9			385.6	388.5	2.9
10				387.4	
11				389.1	
12				380.5	
13				389.1	
14				389.1	
15				386.2	
16				390.5	
17				388.4	
18			355.1	355.3	0.2
19			354.3	358.1	3.8
20			373.9	368.5	−5.4
21				399.1	
22				399.0	
23				384.0	
24				384.5	
25			367.7	381.0	13.4
26			360.8	355.4	−5.4
27			351.9	346.3	−5.5

[a] All values are in kcal/mol. $\Delta H_f(H^+)$ = 367.2 kcal/mol.

Table III. Annelation Effects on Gas-Phase Acidities and Proton Affinities (PA)

species	$\Delta\Delta H^\circ_{acid}$[a]	ΔDPE-(AM1)	effect[b]	ΔPA[a]	effect[b]
benzene/naphthalene	6.5	6.7	σ	13.4	$\sigma + \pi$
naphthalene/anthracene		8.2	σ	12.3	$\sigma + \pi$
pyridine/quinoline	5.4	7.2	σ	5.7	σ
1,4-diazine/quinoxaline		6.4	σ	5.4	σ
cyclopentadiene/indene	1.0	−2.8	$\sigma - \pi$	3.6[c]	σ
indene/fluorene	1.4		$\sigma - \pi$	−3.2[c]	$\sigma - \pi$
quinoline/acridine		8.0	σ	5.4	σ
toluene/1-methylnaphthalene	8.6	10.6	$\sigma + \pi$	10.9	$\sigma + \pi$
pyrrole/indole	9.0	9.1	$\sigma + \pi$		

[a] In kcal/mol. PA and ΔH°_{acid} values from this work and ref 7 and 9. Positive $\Delta\Delta H^\circ_{acid}$ and ΔPA denotes greater acidity or basicity, respectively, of the annelated compound. [b] σ effects (polarization) and π effects as assigned in the text. [c] Based on PA(indene) = 203.2 kcal/mol.[8]

carbon acids. We denote this difference as ΔH°_{anneln} = ΔH°_{acid}(parent) − ΔH°_{acid}(annelated).

When we begin with the benzene/naphthalene system, the AM1 charge densities pattern on the various carbon atoms of naphthalene show that the 1-position should be slightly easier to deprotonate than the 2-position. The charge densities at these two carbons are −0.120 and −0.130, respectively. This is an indication that the DPEs of these positions in naphthalene should not differ appreciably. This is shown to be the case in Table II where the difference in DPEs of these positions is 0.7 kcal/mol. Deprotonation of benzene and naphthalene yields the corresponding anions where the carbon lone pairs are localized at the deprotonation site. Examination of the highest occupied molecular orbital (HOMO) of phenyl and naphthalenyl anions shows that nearly 75% of the HOMO wave function is concentrated at the deprotonation sites. Symmetry considerations and substituent effects[4] show that the lone pair is affected by σ-withdrawing substituents but should not be coupled effectively to the π system. This is due to the fact that, for planar systems, the σ and π networks are orthogonal. The stability of the ion and therefore the acidity of the conjugate neutral acid should be affected by the polarizability of the added ring but not by resonance effects. The observed annelation effect of 5–6 kcal/mol is therefore assigned to polarization. Similarly, increased polarization by annelation should increase the stability of cations when protonation involves lone pairs in the plane of the ring. This occurs in the cases of pyridine/quinoline, 1,4-diazine/quinoxaline, and quinoline/acridine, and we note that the increase of 5–6 kcal/mol upon annelation are in fact similar in magnitude to the polarization effect assigned to the anions. The two anionic and three cationic values assigned to polarization are very close, in fact identical within experimental accuracy, and we assign the average value, $\Delta H^\circ_{polarizn}$ = 6 kcal/mol, to this effect. The average AM1 value for polarization is 6.7 kcal/mol.

In comparison, we may examine molecules with two fused rings where deprotonation (or protonation) of the second ring contributes (or eliminates) π electrons. These systems are cyclopentadiene/indene and benzene/naphthalene, respectively, as illustrated in structures **1–16** above. The data show that the annelation effects on the acidity (or basicity) are significantly different from the 6 kcal/mol assigned to $\Delta H°_{\text{polarizn}}$.

Specifically, in cyclopentadiene, deprotonation creates a stable 6-electron aromatic ring, which increases the ion stability by $\Delta H°_{\text{res},6}$. However, in indene only a 4-electron system is created by deprotonation (AM1 results show that deprotonation of indene takes place from the five-membered ring; see Table II), and this should be favored energetically only by $\Delta H°_{\text{res},4}$, less than in the aromatic 6-electron system, by the difference $\Delta H°_{\text{res},6\text{-}4} = \Delta H°_{\text{res},6} - \Delta H°_{\text{res},4}$. In other words, the resonance effect alone should cause annelation to decrease the resulting system stability, and therefore also decrease the acidity, by an amount $\Delta H°_{\text{res},6\text{-}4}$. On the other hand, ionization is favored in indene by $\Delta H°_{\text{polarizn}}$. Assuming that the two effects are additive, eq 1 can be used.

$$\Delta H°_{\text{anneln}} = \Delta H°_{\text{polarizn}} + \Delta H°_{\text{res}.6\text{-}4} \qquad (1)$$

Applied to cyclopentadiene/indene, eq 1 yields $\Delta H°_{\text{res},6\text{-}4} = 5$ kcal/mol. Here, the sum of the two effects almost cancels, leading to the observed small annelation effect of only 1 kcal/mol.

An effect with reverse sign occurs in the protonation of benzene and naphthalene. Here, protonation on benzene destroys a 6-electron aromatic system, while in naphthalene only a second, 4-electron system. This should make the protonation of naphthalene less unfavorable and, therefore, increase the proton affinity by $\Delta H°_{\text{res}}$. Here, eq 1 yields $\Delta H°_{\text{res},6\text{-}4} = 7$ kcal/mol. In other words, here, the polarization and resonance effects add, yielding a large annelation effect of 13 kcal/mol.

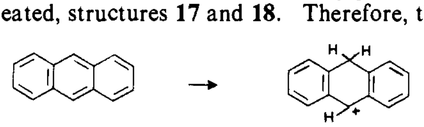
The difference in resonance stabilization of the aromatic 6-electron and the annelated 4-electron systems found in the anionic and cationic systems from eq 1 are therefore similar in magnitude. Here, the polarization effects in the anion and cation were assumed similar. The fact that $\Delta H°_{\text{res},6\text{-}4}$ is also similar to then not an assumption but derived from the data. However, it must be noted that this does not mean that the total resonance energies in benzene vs those in cyclopentadienide are equal, but only the *differences* between $\Delta H°_{\text{res},6}$ and $\Delta H°_{\text{res},4}$ in the two cases are similar. Therefore, we may assign the average difference as $\Delta H°_{\text{res},6\text{-}4} = 6 \pm 1$ kcal/mol.

Our value for $\Delta H°_{\text{res},6\text{-}4}$ can be compared with the resonance energies ascribed by Herndon to neutrals and cations.[5] For the benzene/naphthalene pair, the appropriate comparison with (RE (naphthalene-H$^+$) − RE(naphthalene)) − (RE(benzene-H$^+$) − RE(benzene)). Herndon's value, based on the number of resonance structures, is 8.5 kcal/mol, in reasonable agreement with our $\Delta H°_{\text{res},6\text{-}4} = 7$ kcal/mol for this pair. Another interesting comparison is with H atom addition enthalpies,[6] which affect resonance structures similarly to protonation. The experimental difference between benzene and naphthalene is 10 kcal/mol, and in the absence of charge it can be attributed completely to resonance. This value is somewhat higher than our 7 kcal/mol.

Table III shows that AM1 predicts the annelation effects within better than ±2 kcal/mol in all cases except cyclopentadiene/indene, where electron repulsion between the new 4-electron system in the anion and the 6-electron ring may be underestimated, similar to the underestimation of lone-pair repulsion.[4]

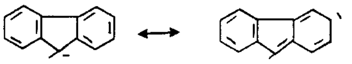
2. Three-Ring Compounds. The ring carbon acidities of benzene and naphthalene are predicted accurately by AM1 (see Table II), and therefore the result for anthracene should also be reliable. When this result is used, the further annelation in naphthalene/anthracene is also stabilizing by 8 kcal/mol and may be assigned to $\Delta H°_{\text{polarizn}}$. A similar value is obtained from AM1 for the acidities of quinoline/acridine and also from the experimental proton affinities of the quinoline/acridine pair, all being σ-polarization effects.

In comparison, the proton affinity of anthracene is increased over naphthalene by 12.3 kcal/mol, a large value indicative of an additional π effect. In this case, when the above reasoning is used, a 4-electron π system is destroyed by protonation but a sextet is created, structures **17** and **18**. Therefore, the π effect is again $\Delta H°_{\text{res},6\text{-}4}$, and eq 1 gives 4 kcal/mol, a somewhat smaller value than in the one-ring/two-ring pairs, as may be expected.


17 **18**

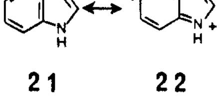
In comparison, Herndon's resonance energies[5] give 13 kcal/mol and the H atom addition energies 12 kcal/mol, both higher than our present estimate.

Another system of interest is indene/fluorene. Here, the deprotonation of indene produces a 4-electron π system conjugated to a 6-electron ring and has some π stabilizing effect. In contrast, deprotonation of fluorene produces the carbanion **19** without delocalizaiton or, should there be delocalization, it requires destruction of a six-membered ring as in **20**. Either way, the electronic effect is destabilizing, and, as a consequence, despite the favorable polarization effect, the acidity of fluorene is greater than indene only by 1.4 kcal/mol. A similar effect of the destruction of a 6-electron ring in fluorene is noted also in protonation. The protonation of indene destroys only a double bond weakly conjugated to the benzenoid π system, while in fluorene protonation destroys a 6-membered benzenoid π system. Consequently, despite increased polarization, the proton affinity of fluorene is *lower* than that of indene by 3.2 kcal/mol. We note that the above π effects are in nature different from the combination of factors assigned to $\Delta H°_{\text{res},6\text{-}4}$ above.

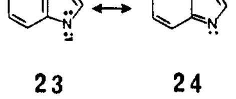

19 **20**

3. Indole, 1-Methylnaphthalene, and Azulene. These compounds possess annelated rings, but they constitute special cases in having a nitrogen or an external acid site or lacking an aromatic sextet, respectively. Compared with the 6 kcal/mol polarization effects, they all show larger annelation effects, indicating a π contribution. Some qualitative justification can be made, special to each case.

In pyrrole/indole, it may be expected that $\Delta H°_{\text{aneln}}$ will be mostly a polarization effect since removing the proton leaves a σ lone pair. However, the observed $\Delta H°_{\text{anneln}}$ is large, 9 kcal/mol. In the indolide anion, the conjugation of the 4-electron π system of the five-membered ring with the benzene aromatic sextet is enhanced compared with the neutral molecule. In terms of resonance structures, in the neutral, conjugation requires charge separation and is unfavorable (structures **21** and **22**), while in the anion analogous additional resonance structures are allowed (structures **23** and **24**), in addition to those possible in the neutral or in the one-ring pyrrolide anion. Therefore, the π effect is favorable to the deprotonation of indole and contributes to the increased annelation effect.



21 **22**



23 **24**

A large annelation effect, though somewhat smaller than naphthalene, is also found in the protonation of toluene/1-methylnaphthalene. In protonated toluene, the charge is already stabilized by the methyl group, and therefore the further polarization energy upon annelation is smaller than in benzene. Using

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$\Delta H^\circ_{\text{polarizn}}$ = 4 kcal/mol, a reasonable value for this system, in eq 1 again yields $\Delta H^\circ_{\text{res},6-4}$ = 6 kcal/mol. In comparison, Herndon's resonance value is 8 kcal/mol, in good agreement.[5]

Deprotonation of toluene/1-methylnaphthalene occurs on the methyl group and therefore does not involve the ring directly. However, the resulting sp^2 lone pair in the anion perturbs the ring π system. This should be more unfavorable when the perturbed system is the stable aromatic 6-electron system and less destabilizing when it is a 4-membered conjugated system. Therefore, here again the π effect of annelation is favorable and adds to polarization, leading to a fairly large $\Delta H^\circ_{\text{anneln}}$ = 8.6 kcal/mol.

Finally, azulene cannot be directly compared to any one ring system, since it does not have an sp^3 carbon as the five-membered or seven-membered "constituents", cyclopentadiene and cycloheptatriene.[10] However, it is noted that its acidity is greatly increased, by 26 kcal/mol, over that of naphthalene. The increased acidity suggests a special stabilization of the azulenide anion. We note that the five-membered ring in azulene formally possess 5 π electrons. The AM1 charge densities pattern in azulene and its most stable anion, see Table II, show that deprotonation of the seven-membered ring creates a lone pair and adds a negative-charge center that helps in pushing extra electron density to the five-membered ring and forming a "quasi"-aromatic sextet. In this respect, deprotonation is analogous with protonation on the seven-membered ring that forms a tropylium-like sextet. The analogy is enhanced by the observation that the proton affinity of azulene is also larger than that of naphthalene by 25 kcal/mol, similar to the acidity difference.

Summary

In summary, compounds where deprotonation or protonation does not involve π effects give a consistent 6 ± 1 kcal/mol for charge stabilization by polarization of an annelated ring. This adds to electronic effects when deprotonation or protonation also contributes or removes π electrons. Specifically, we observe cases where annelation transfers the effects from involving a 6-electron π system to involving an annelated 4-electron system. These results, involving anions and cations, give a consistent 6 ± 1 kcal/mol for the difference between the aromatic stabilization of a first 6-electron or a second, annelated 4-electron system.

Registry No. 1, 91-20-3; **3**, 120-12-7; **6**, 90-12-0; **7**, 91-22-5; **10**, 260-94-6; **15**, 91-19-0; **18**, 542-92-7; **19**, 95-13-6; **20**, 544-25-2; **21**, 275-51-4; **27**, 120-72-9.

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[10] AM1 overestimated the heat of formation of neutral azulene by 12 kcal/mol.

Circular Dichroism of Oxiranes: An Independent Systems/Perturbation Approach

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Abstract: The circular dichroism (CD) spectra of the first two Rydberg transitions of alkyl-substituted oxiranes are interpreted by an independent systems/perturbation approach. When alkyloxirane compounds are treated as an achiral oxirane ring perturbed by alkyl substituents, quantitative relationships between CD and oxirane structure are obtained. The dipolar coupled-oscillator model of Kirkwood and Kuhn proves to be the only significant mechanism for both the n(0) → 3s and n(0) → 3p transitions. The static coupling model suggested by Gedanken et al. to account for the sign of the n(0) → 3s transition does not account for the variation in CD magnitudes that is observed.

I. Introduction

Chiral oxiranes have excited much interest in recent times because of their potential as building blocks for asymmetric synthesis.[1] They can be synthesized with high stereoselectivity from naturally occurring chiral compounds such as diethyl tartrate,[2] amino acids,[1,3] and diols,[4] or alternatively racemic mixtures can be synthesized from prochiral systems and then separated (e.g. by chromatography[5]). The stereochemistry of an oxirane can often be determined from knowledge of the synthetic route or on the basis of packing arguments. An independent verification of the assignment is desirable, especially for systems with similar substituents on C2 and C3 in Figure 1. The circular dichroism (CD) experiments of Gedanken et al.[6-8] potentially fill this role since the sign and magnitude of a CD band is directly related to its stereochemistry. If the mechanism giving rise to the CD is understood, then the stereochemistry of the system can be determined from the observed spectrum.

Gedanken et al.[6-8] have measured the CD of a number of oxiranes in the region of 185-155 nm. Two of the low-lying transitions have been assigned as Rydberg transitions from a nonbonding 2p_x-type orbital largely localized on the oxygen of the oxirane ring to the oxygen 3s and 3p states.[9] In accord with ref 9, we shall denote these transitions as n(0) → 3s and 3p, respectively. The n(0) → 3s transition is separated from its neighboring transitions, and the CD band signs reflect the positions of the substituents according to a quadrant rule,[7] showing a positive CD for substituents with $y > 0$ and $x > 0$ or with $y < 0$ and $x < 0$ (cf. Figure 1) and a negative CD in the other two quadrants. This behavior is precisely what is expected on symmetry grounds (without any reference to mechanism) for an approximately C_{2v} oxirane in the presence of substituents on C2 and C3 oriented as in Figure 1. In order to understand more complicated CD variations as a function of substituent, it is necessary to determine what mechanism is the dominant contributor to the CD. Gedanken et al.[7] have suggested that the sign variations can be rationalized with Schellman's symmetry analysis[10] of the one-

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