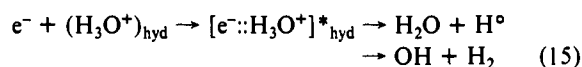


particular the reorientational relaxation of water molecules close to the hydronium seems to be faster than in bulk water. This means that the monoexponential stabilization of this encounter pair is in agreement with a deactivation process inside a potential well involving molecules bounded to hydronium ion. In the specific case of aqueous solutions, the solvent reorganization would include the hydrogen bond restructuring in the vicinity of hydrated proton without the intervention of a significant diffusion process. We can wonder whether in concentrated aqueous acid solutions the radical ion pair deactivation occurs through two deprotonation processes of the hydrated hydronium ion. These processes would include either an early deprotonation of H_3O^+ with a subsequent neutralization of H^+ by the electron or an electron-induced OH bond cleavage leading to the generation of the hydroxyl radical (eq 15)



It is interesting to notice that the cleavage rate constant of the encounter pair occurs at a similar time scale as the H-bond mean lifetime (0.58 ps at 293 K)⁵¹ or average lifetime of the hydronium ion in liquid water.^{52–54} This means that the relaxation of the encounter pair can be dependent either on the H bond dynamics between H_3O^+ and water molecules or on proton migration from hydronium to neighboring water molecules. We suggest that the limiting factor of the deactivation dynamics of the encounter pair corresponds to the activation energy of the radical-ion bond cleavage reaction including either a proton migration from hydronium ion to neighbor water molecules or a local polarization

effect on H bonds. In this way, the initial reactivity of excess electron with hydrated hydronium ion ($\text{H}_3\text{O}^+ + e^-$)_{hyd} would depend on the local structure of this cation in the vicinity of water molecules. Recent computer simulations of hydrated hydronium ion performed at 300 K have shown that the relaxation of water molecules around a new hydronium ion is a process that is faster than the lifetime of this ion.⁴⁸ In this hypothesis, the relaxation of the encounter pair can be compatible with ultrafast local reorganization of water molecules including a few vibrational periods of OH bonds or librational and translational movements of the hydronium ion.

In conclusion, transient spectra observed in the visible and near-infrared have permitted us to identify the formation of hydrated electron and encounter pair populations. In comparison with the spectrum of the stabilized hydrated electron ($E_{\text{max}} = 1.7$ eV), the maximum of the band assigned to the radical pair is red shifted ($E_{\text{max}} = 1.35$ eV). We have shown that a photochemical single electron transfer performed in concentrated acid aqueous solution induces the formation of an encounter pair involving an epithermal electron and a hydronium ion. This encounter pair formation occurs earlier than the electron hydration step. The deactivation dynamics of this radical pair (850 fs) is comparable to the estimate of the mean lifetime of the hydronium ion or H-bond. The present femtosecond spectroscopic data strongly suggest that the monoexponential relaxation of this encounter pair toward an equilibrium configuration can be triggered by a rearrangement of the hydrogen bonding to hydronium ion or an electron-proton transfer involving an hydronium ion and neighboring water molecules. Further experimental works are in progress to investigate the role of water molecules surrounding encounter pair during the deactivation step.

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Tautomerization Energetics of Benzoannelated Toluenes

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Abstract: The energy of tautomerization of some isotoluene structures has been measured by gas-phase ion/molecule reactions and by solution calorimetry. Benzoannellation appreciably destabilizes the aromatic tautomer, relative to the isotoluene form. An inverse saturation effect on the acidities of toluene, 1-methylnaphthalene, and 9-methylantracene is observed. The *p*-isotoluene 3-methylene-1,4-cyclohexadiene appears to have the weakest C–H bond dissociation energy known, 64 ± 3 kcal/mol. Molecular orbital calculations bear out these results.

The extra stability of aromatic compounds is such a well-documented concept in organic chemistry that there is a tendency to assume that species that can become aromatic will do so. In this light, the kinetic stability of prismane² and Dewar benzene, bicyclo[2.2.0]hexa-2,5-diene,³ seems surprising at first, until the rationale of orbital symmetry forbiddenness is considered. It would be useful, however, to have some method of turning aromaticity on and off in a given structure, so that the energy difference could be determined. One possibility for this involves tautomerization,

a type of isomerism involving minimal perturbation of the structure. Tautomers have the same heavy-atom connectivity, and only the attachment of the hydrogen atoms is varied. This in general allows interconversion of tautomers by Brønsted acid/base catalysis.

Such tautomers involving aromatic structures were originally not considered to be isolable, save for the case of phenol derivatives.⁴ The first semiquantitative report of tautomerism as a measure of aromaticity in hydrocarbons was in 1949 by Clar and Wright,⁵ for the reversible interconversion of 6-methylpentacene

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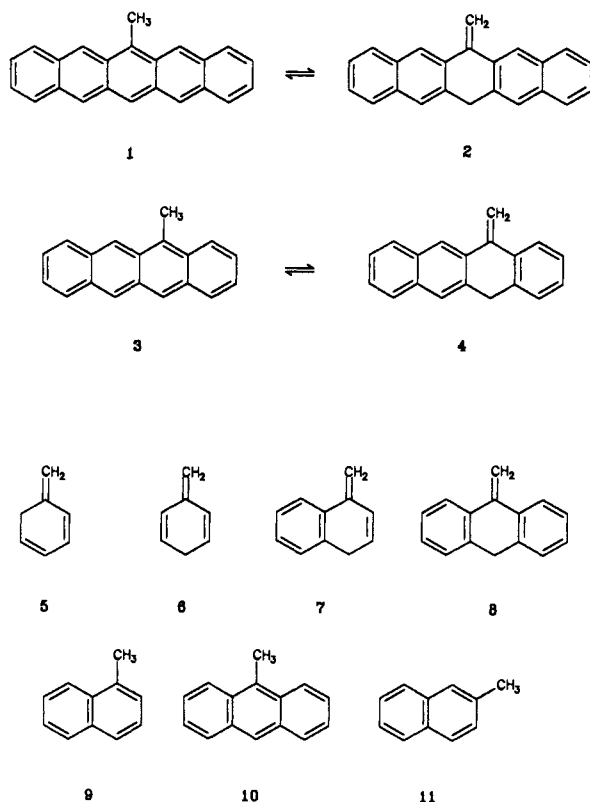
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(1) and 6-methylene-6,13-dihydropentacene (2). Methylene form



2 is favored at room temperature, but fully aromatic 1 is predominant at 200 °C. By UV spectroscopy, 5-methyltetracene (3) appears to contain a small amount of the tautomer 4 but 9-methylanthracene (10) contains no detectable tautomer 8. The corresponding nonannelated system (toluene versus 3-methylene-1,4-cyclohexadiene (6)) was postulated as having an equilibrium lying completely toward the aromatic tautomer.⁵ On the basis of resonance energies derived from the UV spectra, Clar⁶ predicted that for the series 6–8 the equilibrium should favor the aromatic tautomer by 39, 34, and 25 kcal/mol minus the (unknown) cross-conjugative resonance energy of the isotoluene form in each case.

There have been several recent syntheses of isotoluene-type structures,⁷ some stabilized by benzoannulation.⁸ We have previously reported⁹ thermochemical data and gas-phase ion chemistry for the parent cases of such a tautomeric system, 5-methylene-1,3-cyclohexadiene (*o*-isotoluene, 5) and 3-methylene-1,4-cyclohexadiene (*p*-isotoluene, 6). These were both found to have a ΔH_f 24 ± 3 kcal/mol greater than that of toluene,¹⁰ yet they are surprisingly stable with respect to tautomerization reactions,¹² in that they can be handled at room temperature for up to 1 h. In spite of their similarity of structure, however, their gas-phase ion chemistry takes different pathways. The $C_7H_7^+$ ion formed from 5 on electron ionization is ca. 60%

tropylium and 40% benzylum cation, while that from 6 is >90% benzylum.⁹

As shown in the original investigation by Clar and Wright,⁵ benzoannulation¹³ can reduce the aromaticity of adjacent rings. For example, one can take as a measure of aromatic character the heat of hydrogenation of one double bond in a nominally aromatic π system, to give a nonconjugated 1,4-diene. The enthalpy of reaction for benzene plus hydrogen to give 1,4-cyclohexadiene is +6 kcal/mol, naphthalene to 1,4-dihydronaphthalene is ca. -3 kcal/mol, and anthracene to 9,10-dihydroanthracene is -17 kcal/mol.¹⁴ For a nominally nonaromatic 1,3,5-cyclohexatriene, a heat of single hydrogenation of -25 kcal/mol can be estimated,¹⁵ indicating a great deal of reduction of aromatic character in naphthalene and anthracene with benzoannulation. This is consistent with the increased reactivity in these rings.¹³

The use of gas-phase ion/molecule chemistry allows us to obtain quantitative data for the equilibria between aromatic structures like toluene and the conjugated but nonaromatic tautomers such as 6 (referred to hereafter as the isotoluene form). It would be instructive to examine the energies of the fused analogues, benzo-*p*-isotoluene (7) and dibenzo-*p*-isotoluene (8), relative to their aromatic tautomers 9 and 10, to see if the trend of reduced aromatic character with increased benzoannulation holds. The thermal chemistry of these has recently been reported.¹⁶ We report here the energetics of these structures versus their aromatic tautomers, plus some ion/molecule chemistry related to the benzyl/tropyl problem. Semiempirical molecular orbital calculations on these, and several other isomers, are reported.

Experimental Section

Ion/Molecule Chemistry. The ICR spectrometer used in this work has been previously described.¹⁷ All ICR experiments were done in the rapid-scan¹⁸ mode by signal averaging 10–50 scans. Acidity equilibria were measured by the usual techniques,¹⁹ with the following exception. Tricyclic compounds 8 and 10 are not sufficiently volatile at room temperature to obtain stable pressures in the desired 10^{-6} Torr range. A few milligrams of one of these is placed on the tip of a solid insertion probe, adapted from an AEI MS-7 mass spectrometer. This is inserted into the ICR vacuum system so that the sample is ca. 3 cm away from the ICR cell in the vacuum chamber. This gives intense ion signals from the species involved. Because of pressure gradients within the vacuum system, however, we believe that the pressure reported by the ionization gauge during this experiment is considerably lower than the pressure in the cell, even with the usual correction for ionization cross-section dependence of the ionization gauge reading.²⁰ To measure the actual neutral pressure in the cell, the relaxation transient¹⁸ for the radical cation of 8 or 10, under ionizing electron beam energy conditions just above the ionization energy of the compound, is recorded. The exponentially decaying envelope of the transient is a measure of the rate of ion/molecule collisions in the cell. The low electron energy is necessary so that the radical cation of the species of interest is the only ionic mass present in the cell. When this rate is divided by the rate constant for momentum transfer, obtained from the Barker–Ridge theory,²¹ a value for the pressure in the cell is obtained. We find that, for the low-volatility compounds in this work, the cell pressure is ca. 5 times higher than that

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Table I. Experimental Results

compound	ΔG_{acid}^a	ΔS_{acid}^b	ΔH_{acid}^a	ΔH_{taut}^c	ΔH_{soln}^d	$\Delta H_{\text{taut}}^{d,e}$
toluene	373.7 ± 2.0^f	23.8	380.8		-0.04 ± 0.02	
<i>o</i> -isotoluene (5)	349.0 ± 3.0^h	26.0	356.8	24.0		
<i>p</i> -isotoluene (6)	349.0 ± 3.0^h	26.0	356.8	24.0		
1-methylnaphthalene (9)	365.8 ± 2.0^f	23.8	372.9		0.3 ± 0.1	
1-methylene-1,4-dihydronaphthalene (7)	349.0 ± 2.0^h	27.0	357.1	15.8	-14.7 ± 1.6	15.0 ± 2.0
9-methylanthracene (10)	355.1 ± 2.0^f	23.8	362.2		3.1 ± 0.5	
9-methylene-9,10-dihydroanthracene (8)	349.0 ± 3.0^h	27.0	357.1	5.1	-0.3 ± 0.3	3.4 ± 4.0

^aUnits: kcal/mol. ^bUnits: cal/mol·K. ^cDifference in enthalpy between aromatic and isotoluene forms ($\delta \Delta H_{\text{acid}}$, kcal/mol), ± 1.8 kcal/mol. ^dFrom calorimetric measurements, solution/reaction into CCl_4 , (kcal/mol). ^eNot corrected for differences in heat of vaporization of tautomeric forms (error bounds reflect this, see text). ^fReference 11. ^gEquilibrium acidity measurements. ^hBracketted acidity measurement.

measured at the ion gauge. The ion gauge is halfway from the leak to the turbomolecular pump, while the cell is next to the leak. The ion gauge sensitivity factors for **8** and **10** were calculated from their polarizabilities.²⁰ Variations in ion gauge pressure and that from the relaxation method due to changes in pumping speed were found to be proportional, so that a constant ion gauge reading was taken as evidence for a constant true pressure in the cell. This "single-ion relaxation" technique was checked by comparing the pressure obtained this way for benzene in the vacuum system, where volatility should not be a problem, against the ion gauge pressure, corrected by the capacitance manometer method. The agreement between the two methods at several pumping speeds was within 10%. The pressures obtained from this single-ion relaxation method were used in the calculation of equilibrium constants. The standard acids against which **8** and **10** were measured were admitted to the system by the normal method of leak valves, after a stable pressure of the tricyclic compound was obtained.

For the isotoluene tautomers **8** and **9**, the equilibrium method for measuring the gas-phase acidity will not work, since reprotonation of the anion will result in the more stable aromatic form. The acidities of **8** and **9** were determined by a bracketing method,⁹ by measuring how strong an anionic base is needed to deprotonate the tautomers. The anions were generated by electron ionization of appropriate precursors. The conjugate acid of the anionic base so generated was also admitted into the vacuum system at ca. $(2-4) \times 10^{-6}$ Torr, to allow for thermalization of the primary anion by proton transfer.²²

Calorimetry. The solution calorimeter is similar in construction to the one described by Arnett and co-workers.²³ Details will be reported elsewhere. Liquid samples are injected into the calorimeter with a Hamilton 50- or 25- μL syringe; solid samples are injected with a 5-mL disposable syringe, modified by cutting the tip off and sealing it with a Teflon disk that pops out on depressing the plunger. The solid sample is placed in a small well in this disk.

The accuracy of the calorimeter was tested by measuring the heats of solution or reaction for a number of compounds. For the heat of solution of potassium chloride into water, repeated runs give 4.1 ± 0.1 kcal/mol, compared to the literature value of 4.11 ± 0.02 kcal/mol.²⁴ The solution volume in the calorimeter Dewar is 250–300 mL; the temperature of the solution was 24 ± 2 °C (ambient).

Aromatic compounds **9** and **10** were obtained commercially and purified by recrystallization [**10**, mp 80–81 °C (lit.²⁵ mp 81.5 °C)] or distillation [**9**, bp 116–118 °C (20 mm) [lit.²⁵ bp 107 °C (10 mm)]]; The tautomers **7** and **8** were obtained from J. J. Gajewski and A. Gortva.¹⁶ MNDO calculations were done with QCPE program 455 (MOPAC 4.0),²⁶ modified to run on an IBM RT computer.²⁷ Molecular mechanics calculations were done with the PCMODEL program from Serena Software,²⁸ on an IBM PS/2 Model 70.

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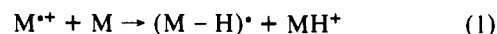
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Results

The relative free energy of a pair of tautomers in the gas phase can be determined by measuring the difference in gas-phase acidity of the two tautomeric forms. From established equilibrium methods,¹⁹ 1-methylnaphthalene is found to be 0.2 kcal/mol more acidic than neopentyl alcohol and 0.9 kcal/mol less acidic than benzyl alcohol, placing ΔG_{acid} at 362.5 ± 2.0 kcal/mol. For 9-methylanthracene, a ΔG_{acid} of 355.1 ± 2.0 kcal/mol is found, 1.0 kcal/mol less acidic than trifluoroethanol. With the use of the same entropy of acidity as for toluene, 23.9 ± 0.8 eu,¹¹ $\Delta H_{\text{acid}}(\mathbf{9}) = 369.7 \pm 2.3$ kcal/mol and $\Delta H_{\text{acid}}(\mathbf{10}) = 362.2 \pm 2.3$ kcal/mol. Compounds **7** and **8** are both deprotonated by methanethiolate, but not by 2-propanethiolate. Both thiolates were generated by electron ionization of the respective RSSR disulfide precursors.²⁹ This bracketing technique yields ΔG_{acid} for both **7** and **8** as 349.0 ± 3.0 kcal/mol and $\Delta H_{\text{acid}} = 357.1 \pm 3.3$ kcal/mol. The larger error bounds of the bracketed acidities represent the discrete step size of the method. The data are summarized in Table I to give the difference in tautomeric enthalpies. The entropy of acidity for **5** and **6** is calculated to be that of the free proton plus the loss of the methyl rotor, as is done for toluene.¹¹ For the isotoluene tautomers **7** and **8**, no rotor is lost on proton removal. The isotoluene ring is slightly floppy (see below) and should stiffen on ionization to the aromatic benzyl anion. We thus assign an entropy of 27 eu to the acidity reaction, representing 1 eu for ring stiffening beyond the free proton's entropy of 26.0 eu. The uncertainties quoted for the acidities are for the absolute values; the acidities relative to one another, which is the quantity pertinent to the tautomerization enthalpy, are probably known to ± 1.2 kcal/mol in ΔG and ± 1.8 kcal/mol in ΔH .

In parallel with the reactivity pattern noted earlier⁹ for **5** and **6** versus the aromatic tautomer toluene, in the gas phase the radical cations formed upon electron ionization of **7** and **8** are reactive with their own neutrals in an autoprotection reaction (1). The



aromatic tautomers **9** and **10** do not undergo such a reaction. On the basis of known thermochemistry, reaction 1 is 10 kcal/mol endothermic for toluene and 22 kcal/mol exothermic for **6**.³⁰ This is an important observation in that if the neutral gas in the ICR spectrometer undergoes the tautomerization reaction on the stainless steel walls of the vacuum system, then the reactions observed for **7** and **8** should be the same as those for **9** and **10**.

The ionization energy of **7** measured in the ICR spectrometer is 8.4 ± 0.5 eV, and the appearance energy of the $(\text{M} - \text{H})^{\bullet}$ ion is 4.0 eV higher at 12.4 eV. The uncertainty represents the axial trapping well in the ICR cell. For comparison, 2-phenyl-1,3-butadiene, with a π system isoelectronic to that of **7**, has an ionization energy of 8.15 ± 0.2 eV.¹¹ For **8**, the ionization energy is 7.6 ± 0.5 eV and the appearance energy of the $(\text{M} - \text{H})^{\bullet}$ ion is 12.6 eV. The comparable π system of 1,1-diphenylethene has a literature ionization energy of 8.0 ± 0.02 eV.¹¹ The relative accuracy of the values obtained in the ICR spectrometer under

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identical conditions are probably better than their absolute accuracy.

We previously found that **6** gives <10% of the tropylium form of $C_7H_7^+$ and >90% benzylium on electron ionization at energies within a few electronvolts of threshold, in contrast to 60% tropylium for toluene.⁹ This is based on the argument that the reactive part of the $(M-H)^+$ population is in the benzylium form, while the unreactive part is tropylium. For toluene, **5**, and **6**, the $(M-H)^+$ ions are reactive with their own neutrals in the ICR.⁹ Using the same criteria, we find here that the $(M-H)^+$ ion from **9** is ca. 60% tropylium near threshold, decreasing to $34 \pm 5\%$ tropylium at electron ionization energies of 20–30 eV. Its non-aromatic tautomer **7** behaves in an essentially similar fashion. The products in both cases are $(M+13)^+$ ions, presumably via an electrophilic substitution reaction. For **7**, these latter ions react further with the neutral to yield higher masses corresponding to neutral addition plus loss of H_2 or $C_{10}H_8$. No further reactivity is seen for $(M+13)^+$ ions from **9**.

For the dibenzo tautomers **8** and **10**, in contrast, no reaction is observed for any part of the $(M-H)^+$ population in its own neutral gas. At face value this would seem to indicate that the $(M-H)^+$ ions are all tropylium; however, it may also indicate that the benzylium ion has become so stable due to delocalization of charge back into the rings that it is now too poor an electrophile to react with the neutral π system. It would be expected that neutral **10** would be a better nucleophile in this reaction than toluene, because of the reduced aromatic character of the central ring. In order to find a suitable probe for this structure, we have reacted the $(M-H)^+$ from **10** with a wide variety of nucleophiles, including alcohols, ethers, amines, amides, and nitriles, but have not found any nucleophile that gives a diagnostic reaction. It is possible that the carbenium ion from **10** is all tropylium, but at present we reserve judgement on this point.

Calorimetry. The various hydrocarbon compounds were injected into 250 mL of carbon tetrachloride in the calorimeter Dewar flask. Originally, this was done with and without several equivalents of trifluoroacetic acid present in the solvent; this acid is known to catalyze the rearrangement of the isotoluene forms **7** and **8** to their aromatic tautomers in the condensed phase.¹⁶ It was found that the heats of solution for **7** and **8** were independent of the presence of the acid, and adding trifluoroacetic acid to CCl_4 containing **7** or **8** gave the same heat evolution as adding CF_3CO_2H to pure CCl_4 . Analysis of more concentrated solutions of **7** or **8** in CCl_4 by NMR shows only the aromatic tautomers being present, within 1 min of addition of the hydrocarbon, although NMR spectra in benzene- d_6 are obtainable for the tautomers.¹⁶ Rearrangement of these substances on gas chromatographic analysis¹⁶ prevents direct analysis of the calorimetric solution. We thus believe that trace impurities in the CCl_4 catalyze the rearrangement. The data for **7** are corrected for the presence of 5% of **9** in the original material.¹⁶

A problem arises in data analysis, because the heats of vaporization of these species are not known for any of the nonaromatic tautomers or for 1-methylnaphthalene.¹⁴ These data are required to complete the thermochemical cycle, to obtain gas-phase heats of formation of the tautomers. For the tautomeric hydrocarbons that are liquids (**7** and **9**), we assume that heats of vaporization are the same to within 1 kcal/mol. This appears to be reasonable, on the basis of other hydrocarbons.¹⁴ For solids such as **8** and **10**, it is unlikely that heats of sublimation are similarly transferable, due to differences in crystal packing forces. We thus assign larger error bounds to the calorimetric measurement, and we point out that the value agrees well with the gas-phase heat of tautomerization, implying that the heats of sublimation must be similar.

The relative enthalpies and gas-phase free energies of dibenzo tautomers **8** and **10** imply that there could be some observable amount of isotoluene form **8** in a sample of **10**. The proton NMR spectrum of a 5% solution of **10** in $CDCl_3$, with a trace of CF_3CO_2H present to catalyze the tautomerization, was obtained by averaging 10632 transients (9 h) on a Nicolet NT-200 spectrometer. Although there were several signals that grew into the

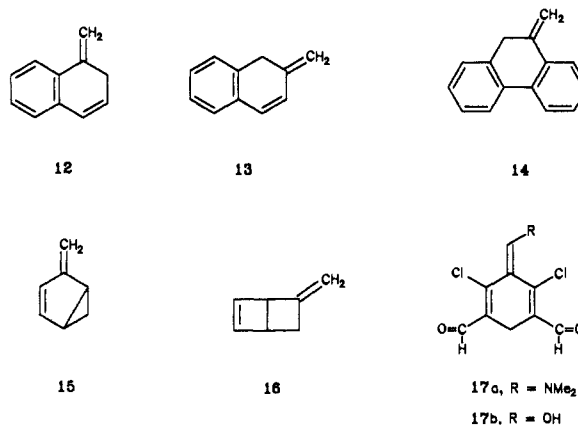
spectrum in the region of the expected¹⁶ sp^3 methylene signal at δ 3.70, none could be unequivocally assigned to isotoluene form **8**; most were obviously multiplets. We place an upper limit of 0.2% ($\Delta G^\circ = 3.7$ kcal/mol) on the presence of **8** in **10** in this solvent.

Calculations. In order to understand the features of the structures that give rise to the energetic and reactivity differences observed here, we have carried out a variety of molecular mechanics and semiempirical molecular orbital calculations. These prove to be more amenable to reproducing the experimental results than previous calculations involving only π SCF methods.³¹ Comparison of the experimental data with such calculations also provides information on how well each method can handle the small structural differences in the present set of molecules. The results of these calculations are given in Table II. All geometries were completely optimized.

It is apparent from the values in Table II that both MNDO²⁶ and molecular mechanics²⁸ calculations reproduce the experimental tautomerization enthalpies almost within the experimental uncertainty, though molecular mechanics tends to give slightly larger values. The latter may be due to molecular mechanics giving aromatic structures slightly too stable. We chose to use the MNDO Hamiltonian rather than the more recent AM1³² version because MNDO appears to deal more accurately with aromatic structures.³³

The charges on the benzylic $-CH_2^+$ groups in the $(M-H)^+$ cations of toluene, 2-methylnaphthalene, and 9-methylantracene, as calculated by the MNDO method, are +0.50, +0.37, and +0.27, respectively. This is consistent with the decrease in electrophilic reactivity postulated here, to explain the reduced reactivity of the largest member of this series. MNDO calculations of the relative energies of the benzylium versus tropylium cations in this series also reveal a stability trend: while tropylium ($\Delta H_f = 207.5$ kcal/mol) is calculated to be more stable than the benzylium cation ($\Delta H_f = 217.9$ kcal/mol) by 10.2 kcal/mol, benzotropylium ($\Delta H_f = 223.1$ kcal/mol) is only 5.8 kcal/mol more stable than the benzylium cation from 1-methylnaphthalene ($\Delta H_f = 228.9$ kcal/mol), and dibenzotropylium ($\Delta H_f = 239.9$ kcal/mol) is 2.2 kcal/mol more stable than the benzylium cation from 9-methylantracene ($\Delta H_f = 242.2$ kcal/mol).

Several other isomers have been investigated by MNDO calculations, since it appears that this calculational method reproduces the experimental data fairly well. The *o*-isotoluene form of 1-methylnaphthalene (**12**) is comparable in energy to the para form,



at 16 kcal/mol higher in energy than the aromatic tautomer. For 2-methylnaphthalene, a similar energy difference is seen for the tautomer **13**. For 9-methylphenanthrene, however, tautomer **14** is 16 kcal/mol higher in enthalpy, by molecular mechanics, in contrast to 9-methylantracene where the calculated tautomeric energy difference is 8 kcal/mol.

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Table II. Results of Computational Methods: MNDO and Molecular Mechanics

compound	ΔH_f (MNDO)	ΔH_{taut}	ΔH_f (MM) ^c	ΔH_{taut}	$\Delta H_f(M-H)^{+a}$ (MNDO)	$\Delta H_f(M-H)^{+b}$ (MNDO)
toluene	13.5		11.4		218.0	208.0
<i>o</i> -isotoluene (5)	35.4	21.9	38.5			
<i>p</i> -isotoluene (6)	35.4	21.9	38.5	27.1		
<i>m</i> -isotoluene (15)	55.6	42.1	55.6	44.2		
1-methylnaphthalene (9)	33.1		28.4		228.9	223.1
1-methylene-1,2-dihydronaphthalene (12)	49.0	15.9	47.6	19.2		
1-methylene-1,4-dihydronaphthalene (7)	49.0	15.9	49.5	21.1		
2-methylnaphthalene (11)	30.7		27.2			
2-methylene-1,2-dihydronaphthalene (13)	46.0	15.3	45.3	18.1		
9-methylanthracene (10)	58.5		52.0		242.1	239.9
9-methylene-6,10-dihydroanthracene (8)	59.7	1.2	60.3	7.7		
9-methylphenanthrene			59.5			
9-methylene-9,10-dihydrophenanthrene (14)			43.2	16.2		
5-methyltetracene (3)			75.2			
5-methylene-5,11-dihydrotetracene (4)			75.8	0.6		
6-methylpentacene (1)	104.0		99.0			
6-methylene-6,13-dihdropentacene (2)	95.1	-8.9	91.7	-7.3		
phenol	-26.3		-22.3			
<i>p</i> -isophenol	-10.8	15.5	1.8	24.1		
1-naphthol	-8.3		-8.0			
1-naphthone	0.0	8.3	9.6	17.6		
9-anthrol	15.3		9.6			
9-anthrone	11.5	-3.8	17.2	7.6		

^a Benzylium cation. ^b Tropylium cation. ^c Molecular mechanics.²⁸

Two other isomers of toluene are in the energetic range under consideration here, 4-methylenebicyclo[3.1.0]hex-2-ene (15) and 5-methylenebicyclo[2.2.0]hex-2-ene (16). These are calculated to be 42.1 and 55.1 kcal/mol higher in enthalpy than toluene, respectively, by the MNDO method.

Discussion

There is one other report of the gas-phase acidity of 9. Using high-pressure pulsed mass spectrometry at 500–600 K, Meot-ner and co-workers³⁴ find 9 to be 1.7 kcal/mol more acidic (ΔG) than phenylacetylene, in contrast to our results here that place it at 2.3 kcal/mol less acidic than phenylacetylene. There are a few cases known where relative acidities change by 2–3 kcal/mol over a 300 K range,¹¹ but such cases usually involve the loss of large rotors on deprotonation, e.g., diphenylmethane and acetanilide. We cannot explain the present discrepancy, save that we have checked the acidity of 9 in the ICR spectrometry several times with consistent results.

Successive benzoannellation increases the acidity of toluene by 7.9 kcal/mol for the first benzo group and 10.7 kcal/mol for the second. The size of the effect is not surprising, considering (a) the increase in formal resonance structures for the anion and (b) the increase in polarizability.³⁵ It is unusual, however, that the second group has a greater effect than the first. Saturation effects³⁶ commonly result in successive substituents being less effective in stabilization of structures. The origin of the inverse saturation effect here may be due not to increased stabilization of the anion but to destabilization of the conjugate neutral acids. Experimental gas-phase ΔH_f values are not available for 9 and 10, but for the nonmethylated series benzene, naphthalene, and anthracene, successive benzoannellation increases ΔH_f by 16.1 and 19.0 kcal/mol, respectively.¹⁴ The nonlinear increase is consistent with the weakening of resonance stabilization in the central ring of anthracene. MNDO calculations reproduce this effect and, for the methylated series toluene, 9, and 10, give increases of ΔH_f

on benzoannellation of 19.6 and 26.0 kcal/mol. The larger increase for the second benzoannellation is due to steric interaction of the methyl group with the peri-hydrogens. This is evidenced by the conformation of the methyl group: in toluene and 1-methylnaphthalene, the optimized geometry has one of the methyl hydrogens coplanar with the ring, but in 9-methylanthracene, the odd hydrogen is perpendicular to the ring. Molecular mechanics yields similar trends in heats of formation and conformation. For the anionic conjugate bases of these species, an equal increase of 10 kcal/mol in the heat of formation is observed for each benzoannellation, as expected from the increase in polarizability and resonance stabilization. The AM1 method,³² reputedly better at calculating anion stabilities, yields essentially similar numbers. Both methods calculate the absolute acidities to be 10–15 kcal/mol too acidic.³² Thus, it is the relative energetics of the neutral acids that dictate the inverse saturation effect observed for the acidities.

In contrast, benzoannellation has essentially no effect on the acidity of the isotoluene forms, 6–8 being equal in acidity within the uncertainty of the bracketing method. If the *exo*-methylene group is ignored, however, this acidity series represents a comparison between acids that are, respectively, doubly allylic, benzylic-allylic, and doubly benzylic. Diphenylmethane and 1,4-pentadiene are within 5 kcal/mol of each other in acidity¹¹ so that the carbanion stabilizing effect of trading an adjacent vinyl group for a phenyl is relatively small.

From literature homolytic bond strengths,³⁷ electron affinities for the benzyl-type radicals may be derived from the experimental acidities.³⁸ For benzyl anion, a value of 20.8 ± 3.8 kcal/mol is obtained, in good agreement with the directly measured value of 19.9 ± 0.3 kcal/mol.³⁹ For the benzyl anion from 1-methylnaphthalene, an EA of 25.8 ± 3.8 kcal/mol is derived, and for the corresponding species from 9-methylanthracene, an EA of 33.2 ± 3.8 kcal/mol is found. The homolytic C–H bond strengths at the sp^3 methylene of the isotoluene forms yielding the benzylic radicals can also be calculated as the bond strength of the aromatic tautomer³⁷ minus the enthalpy difference of the two tautomers. This gives $DH^\circ(8) = 77 \pm 3$, $DH^\circ(7) = 69 \pm 3$, and $DH^\circ(6)$

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= 64 ± 3 kcal/mol. We believe that the C–H bond in **6** is the weakest C–H bond strength known for a closed-shell species.

If the tautomerization enthalpies for **6–8** are compared with the heats of 1,4-hydrogenation of benzene, naphthalene, and anthracene to the nonconjugated arenes, a linear correlation ($r = 0.999$) is observed. The tautomerization enthalpies are ca. 80% of the hydrogenation enthalpies, consistent with some cross-conjugative stabilization between the two π systems on either side of the central ring in the isotoluene case. This is not possible in the hydrogenation series, due to the presence of insulating sp^3 carbons joining the rings.

We have also examined the naphtho-fused tautomeric pairs **1–2** and **3–4** using molecular mechanics. For the pentacene system, the isotoluene tautomer **2** is favored by 7 kcal/mol in enthalpy, while for the tetracenes the tautomeric pair is calculated to be essentially thermoneutral. Such calculations are probably only good to a few kilocalories per mole but are consistent with the experimental observations,⁵ if entropic factors are taken into account. The aromatic tautomer has a methyl group that acts as a nearly free rotor,⁴⁰ while the ring moiety is fairly rigid. The isotoluene tautomer has lost the methyl rotor but has a somewhat more floppy ring. Both molecular mechanics and MNDO calculations indicate that the parent *p*-isotoluene (**6**) is planar but that the benzo- and naphtho-fused structures are bent into a boatlike form at the nonaromatic ring, by torsion angles of 150–159°. This is presumably due to repulsion of the hydrogens on the *exo*-methylene group by the peri-hydrogens in the fused aromatic rings. Our estimate of the tradeoff here is that the isotoluene forms are ca. 3 eu lower in entropy than the aromatic tautomers, largely due to loss of the methyl rotor. Thus, higher temperatures should favor the aromatic form, as is observed experimentally for **1–2**.⁵ For the tetracene, at room temperature and above, entropy always wins; at low temperature in the NMR, it may be possible to observe the isotoluene tautomer.

An analogous system is phenol and its keto form. Shiner and co-workers⁴¹ have shown by ion/molecule experiments comparable to those here that the keto tautomer of phenol with the shifted hydrogen on the para carbon is 10 kcal/mol above phenol in enthalpy, while the ortho form is 6 kcal/mol higher in enthalpy than phenol. Thus, the tautomerism in this case for the para form is ca. 14 kcal/mol more favorable than for toluene, at 24 kcal/mol. If dibenzoannulation has the same effect on phenol as on toluene, a prediction of $10 - 8 - 11$ kcal/mol = -9 kcal/mol for the relative enthalpies of anthrol and anthrone is obtained, with the keto form favored. Experimentally, both compounds are isolable, and the

equilibrium in absolute ethanol favors the keto form by 89:11 (-1.2 kcal/mol).⁴² MNDO calculations (Table II) agree with this, placing the gas-phase anthrone as -3.8 kcal/mol more stable than the anthrol. Molecular mechanics does not adequately describe these energies.

Isotoluene **17**, synthesized by Katritzky and co-workers,⁴³ is relatively stable even to acid. It could be possible that the "push-pull" nature of the substitution, with a good donor group at one end of the π system and a good acceptor at the other, might stabilize the isotoluene form to the point where it is favored at equilibrium. MNDO calculations do not bear this out, however. While the substituents do have some effects on the equilibrium, compared to the parent case of **6**, the isotoluene form is still 16 kcal/mol higher in energy than the aromatic tautomer, compared to 22 kcal/mol for the parent case. Therefore, any persistence of **17** must be due to kinetic factors. A reasonable mechanism for acid-catalyzed tautomerization would be protonation at the α -carbon, followed by proton removal from the *p*-carbon. The amino group in **17a** may preferentially attach the catalytic proton, slowing the tautomerization.

We have explored numerous other combinations of substituents on the rings by molecular mechanics calculations. Perfluorination, save for the tautomeric hydrogen, of *p*-isotoluene **6** shifts the equilibrium toward the isotoluene, but only to its' still being 17.2 kcal/mol less stable than $C_6F_5CF_2H$. Other combinations of donor and acceptor substituents on **6** affect the enthalpy difference between it and toluene, but none come near shifting the isotoluene to the more stable form. A *p*-fluoro substituent shifts the **8–10** equilibrium to 3.3 kcal/mol, with the aromatic tautomer still the most stable. The best case so far found by molecular mechanics is 2,3,4,5,6,7,10-heptafluoro-9-methylanthracene: it is thermoneutral with respect to the isotoluene tautomer. Further fluorination of the 1- and 8-positions in this molecule raises the isotoluene form in energy to 3.3 kcal/mol above the aromatic case, due to steric interactions with the *exo*-methylene group. The isomer of the pentacene **1** with the naphthyl groups fused to the central isotoluene ring at the 1,2-face rather than the 2,3-face is destabilized to 17 kcal/mol *higher* in enthalpy than the aromatic case, compared to -7 kcal/mol for **1**.

Conclusions. It is evident that isotoluene structures are best stabilized, relative to the aromatic form, by benzoannulation and that polar effects on the relative tautomer stabilities are relatively small. These species exhibit unique ion/molecule chemistry and extremely low homolytic C–H bond strengths.

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