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Ab initio calculated gas-phase basicities of polynuclear aromatic hydrocarbons

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Abstract

The gas-phase basicities (GBs) of polynuclear aromatic hydrocarbons (PAHs) have been calculated using the semiempirical Austin model 1 method, ab initio quantum mechanical methods at the HF/3-21G, HF/6-31G(d), MP2/6-31G(d), MP2/6-31+G(d,p) levels, and the B3LYP/6-311G(d,p) density functional method. GBs calculated at these levels of theory are compared to experimentally known GBs measured by equilibrium mass spectrometric methods. Theoretically calculated entropies for PAHs and their protonated carbocations are used to reevaluate original experimental equilibrium data producing a revised set of experimental GBs and proton affinities for PAHs and related hydrocarbons. Experimental GBs for 40 hydrocarbons are found to correlate well with AM1, Hartree–Fock, DFT and MP2 calculated GBs, with regression analyses showing standard errors of 2.12, 1.53, 1.36, and 1.55 kcal mol^{-1} for each of the four methods, respectively. The results permit an evaluation of the reliability of experimental data and suggest a need for new experimental work for some molecules. Predictions are made for GBs for 12 new PAHs whose GBs have not yet been measured. (Int J Mass Spectrom 201 (2000) 283–295) © 2000 Elsevier Science B.V.

Keywords: Polynuclear aromatic hydrocarbons; Proton transfer; Gas-phase basicity; Proton affinity; Ab initio calculations

1. Introduction

Polynuclear aromatic hydrocarbons (PAHs) have played an important role in the development of organic chemistry from aromatic substitution reactions to the properties of buckyball structures, and PAHs were prominent in the earliest attempts to apply theoretical calculations to an understanding of organic chemistry [1]. PAHs are also of practical importance as toxic environmental pollutants [2] and have been implicated as an important component of the interstellar medium [3]. In this article we are using ab initio quantum mechanical methods to calculate the structures and energies of PAHs and the products of their protonation reactions. These calculations permit us to determine the gas-phase basicities (GBs) of PAHs and make comparisons with experimental GBs from gas-phase mass spectrometric measurements.

Protonation of PAHs gives rise to a complex family of allylic/benzylic type cations that play a central role in a variety of processes related to the chemistry of PAHs. Such a protonation reaction is the simplest example of the ubiquitous electrophilic aromatic substitution reaction [4]. Protonated PAHs have

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been proposed to be used as a source of the diffuse interstellar bands observed in the optical spectra of stars [3]. Many PAHs are known to have mutagenic and carcinogenic activity and are subject to regulation by the U.S. Environmental Protection Agency. The mechanism of their biological activity is thought to involve oxidation and epoxide ring opening to carbocations that are related to these protonated PAH structures [5]. Knowledge of the relative stabilities of these carbocations could be very important in understanding the mechanisms of biological activity and can be found in a combination of experimental and theoretical determinations of GBs of PAHs. Analysis of PAHs in the environment is also an important problem, and structure-specific mass spectrometric methods have been proposed to help solve this problem [6]. These methods depend upon a knowledge of the energetics of ionization, such as GBs for the protonation of PAHs in chemical ionization processes. In fact, the experimental determination of GBs for PAHs is a major challenge because of the slow rates of proton transfer to and from many hydrocarbons and the nonvolatility of larger-sized PAHs [6ab,7–9]. Therefore, the reliable calculation of GBs for PAHs could be useful in the evaluation of known experimental measurements and in providing GBs where experimental data are lacking or suspect. Furthermore, experimental gas-phase determinations of these GBs do not distinguish between alternative sites of protonation of the PAHs. Theoretical calculations of known reliability have the potential to solve this problem, provided that comparisons of experimental and theoretical GBs show that the theoretical methods are of sufficient accuracy to distinguish between isomeric structures with relatively small energy differences. Finally, a reliable set of structural and energetic data from experiment and theory can help produce a better understanding of the complex structural factors that contribute to the relative stabilities of PAHs and the carbocations formed as their protonation products.

2. Theoretical methods

Semiempirical AM1 and ab initio calculations were carried out with the Gaussian computational package [10] using the following methods: Austin model 1 (AM1), Hartree–Fock (HF), density functional theory (DFT) with the B3LYP hybrid functionals, second (and higher) order Møller–Plesset perturbation theory (MP2), and coupled-cluster theory with singles, doubles and iterative triples excitations (CCSD(T)). Standard Pople basis sets [3-21G, 6-31G(d) or 6-31G*, 6-311G(d,p) or 6-311G**, 6-31+G(d,p)] and Dunning triple and quadruple zeta correlation-consistent basis sets augmented with diffuse s, p, and polarization functions (aug-cc-pVXZ) were used. The geometries of PAHs and their protonated cations were optimized at AM1, HF/3-21G, HF/6-31G(d), and B3LYP/6-311G(d,p) levels and characterized as minima by analytical frequency calculations in each case at each level of theory. Single point calculations were generally performed at the HF/6-31G(d)//HF/3-21G level, at the MP2-FC/6-31+G(d,p)//HF/6-31G(d) level for several structures of less than 14 carbons, and at the MP2-FC/6-31G(p)//HF/6-31G(d) level. B3LYP/6-311G(d,p)//HF/6-31G(d) single-point calculations were carried out in addition to B3LYP/6-311G(d,p) geometry optimizations. Thermochemical data were calculated with zero-point and thermal energy corrections from scaled HF/6-31G* frequencies using a scaling factor of 0.93 for HF zero-point energies from linear regressions with experimentally known zero-point energies of organic molecules [11]. A scaling factor of 0.900 for HF frequencies was derived from linear regressions of an extensive set of experimental frequencies [11]. Entropies and thermal energy terms were calculated from 0.900 scaled HF/6-31G* frequencies and from hindered-rotor models for molecules and ions containing methyl and ethyl groups [12].

For several reference compounds used on the GB scale to anchor the PAH GBs, gas-phase basicities were calculated using high-level ab initio calculations at the CCSD(T)-FU/aug-cc-pVQZ level for ammonia and phosphine and mainly at the CCSD(T)-FU/aug-cc-pVTZ level using G3(MP2)-like basis set additivity assumptions for larger molecules and ions [13]. Thermochemistries were evaluated as indicated above.

Table 1
Calculated and experimental gas-phase basicities of some reference compounds for PAH basicity measurements. All values in kcal mol^{-1} at 298 K

	G2/E3[a]	CCSD(T)-FU/ aug-cc-pVTZ	CCSD(T)-FU/ aug-cc-pVQZ	Exptl GB NIST[b]
water	157.1	158.1	157.9	157.7
ammonia	195.8	196.3	196.1	195.7
phosphine	179.3	179.0	179.5	179.5
methanol	173.1	174.0[c]	173.6[c]	173.2
methylamine	207.1	207.7[c]	207.4[c]	206.6
dimethyl ether	182.7	183.8[c]		182.7
dimethyl sulfide	191.4	192.4[c]		191.5
dimethylamine	214.8	214.3[c]		214.3
ethylamine	210.3	210.8[c]		209.8
ethylene	156.1	157.0[d]		155.7
propene	170.9	171.9[d]		172.7
iso-butene	185.6	185.4[d]		185.7
1,3-cyclopentadiene		191.1[d]		190.8
benzene		173.5[d]		173.4
toluene		179.7[d]		180.1

[a] Reference 12.
[b] Reference 8.
[c] Estimated using G3-type methods, see 9ab and 13.
[d] CCSD(T)-FC/cc-pVTZ, estimated for iso-butene and larger species, see 9ab.

3. Results and discussion

For each PAH listed in Table 1 and shown in Figs. 1 and 2, calculations at the Huckel level (looking at electronic energies and highest occupied molecular orbital (HOMO) coefficients) and geometry optimizations at the semiempirical AM1 level were carried out for all of the possible isomers from protonation of the PAH at each nonequivalent carbon. From these data, the lowest energy isomers were chosen for further ab initio calculations to determine the structure of the lowest energy isomer. We found, in this process, that no simple rules could be relied upon to make a choice of the preferred site of protonation [6]. In some cases, the energy differences between isomeric ions from competing sites of protonation were close enough that ab initio calculations had to be carried through to the HF/3-21G or HF/6-31G(d), or even the B3LYP and MP2 levels to be sure that a correct choice was made. The structures of the PAHs studied are shown in Fig. 1 with numbering schemes to denote the possible sites of protonation with the preferred site indicated with a bold underline. The rings of all of the PAHs and their protonated cations are planar with C_s symmetry, unless indicated otherwise with the point group symmetry under the structure. The structures of the methyl benzenes are shown in Fig. 2, indicating the conformations of the carbocations formed and their symmetries. For structures not shown, the protonation site in benzocyclobutene is on the four-membered ring, and that on pentalene is in the 2 position. Ethylbenzene has C_s symmetry with the ethyl group perpendicular to the ring plane, and it is protonated in the 4 position with the ethyl group in the ring plane. Cyclopropylbenzene and its 4-protonated ion have C_s symmetry with the aromatic ring plane bisecting the cyclopropane ring. The methyl group hydrogens in the ring planes of 1-methylnaphthalene and 4-protonated-1-methylnaphthalene are both *syn* to C2. The methyl group hydrogens in the ring planes of 2-methylnaphthalene and 4-protonated-2-methylnaphthalene are *syn* and *anti* to C2, respectively. The methyl group hydrogens in the ring planes of 2-methylanthracene and 9-protonated-2-methylanthracene are both *syn* to C1. The methyl group hydrogen is in the ring plane of 9-methylanthracene at the HF/6-31G(d) level and in

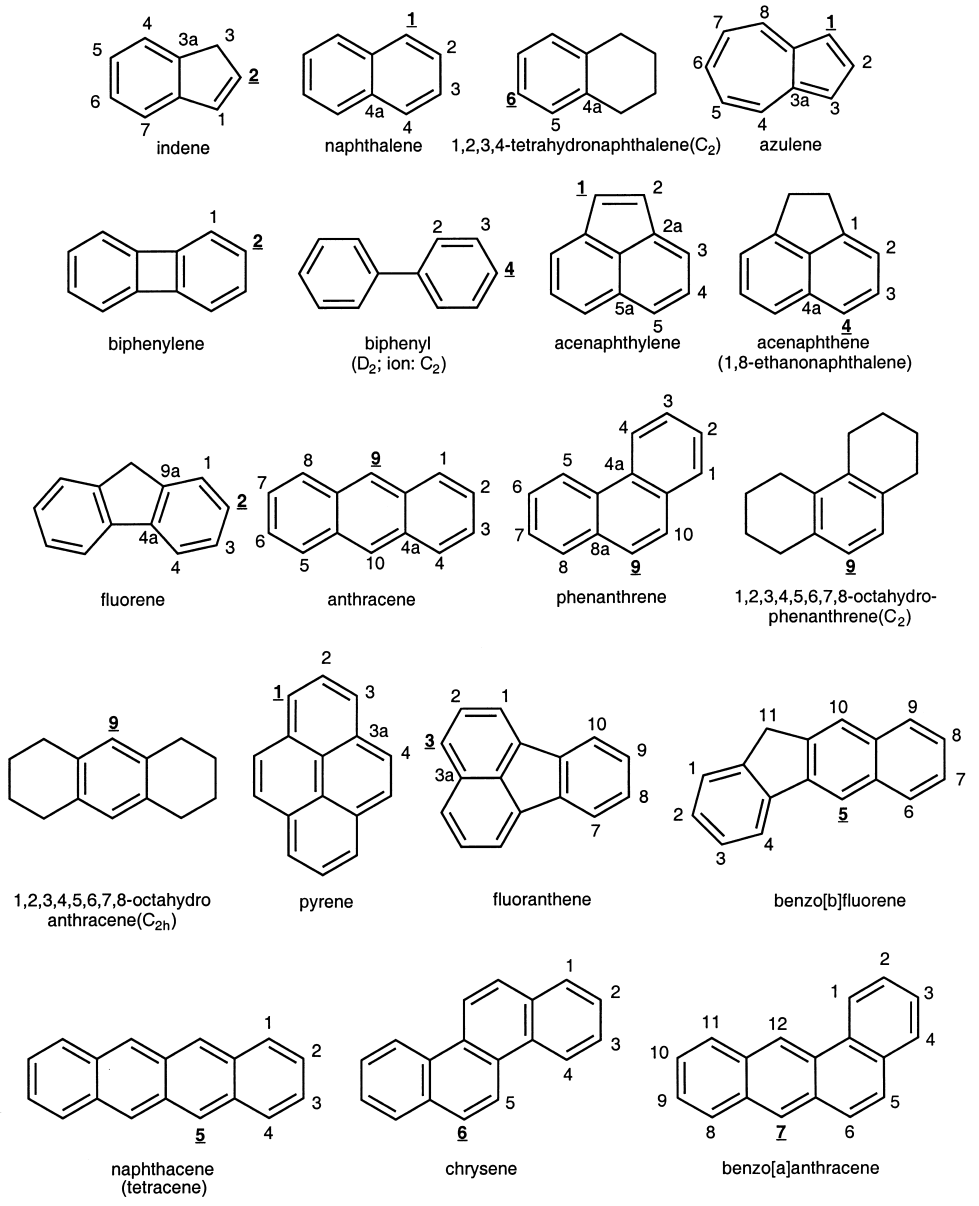

Fig. 1. Structures of PAHs with the number in bold underlined showing the preferred site of protonation.

the DFT ion structure, but perpendicular to the ring plane at the DFT level and in the 10-protonated species at the HF level. The methyl group hydrogen is in the ring plane *syn* to C8 of 7-methylbenzo[a]anthracene at the HF level, but at the DFT level and in the 12-protonated species, the symmetry is C_1. The rings are severely twisted by about 20 ° to give C_1 symmetry for 12-methylbenzo[a]anthracene and 7,12-dimethylbenzo[a]anthracene and their 7-protonated and 5-protonated ions, respectively. Styrene is C_1 symmetry, protonated styrene C_s.

In numerous cases the difference in energy be-

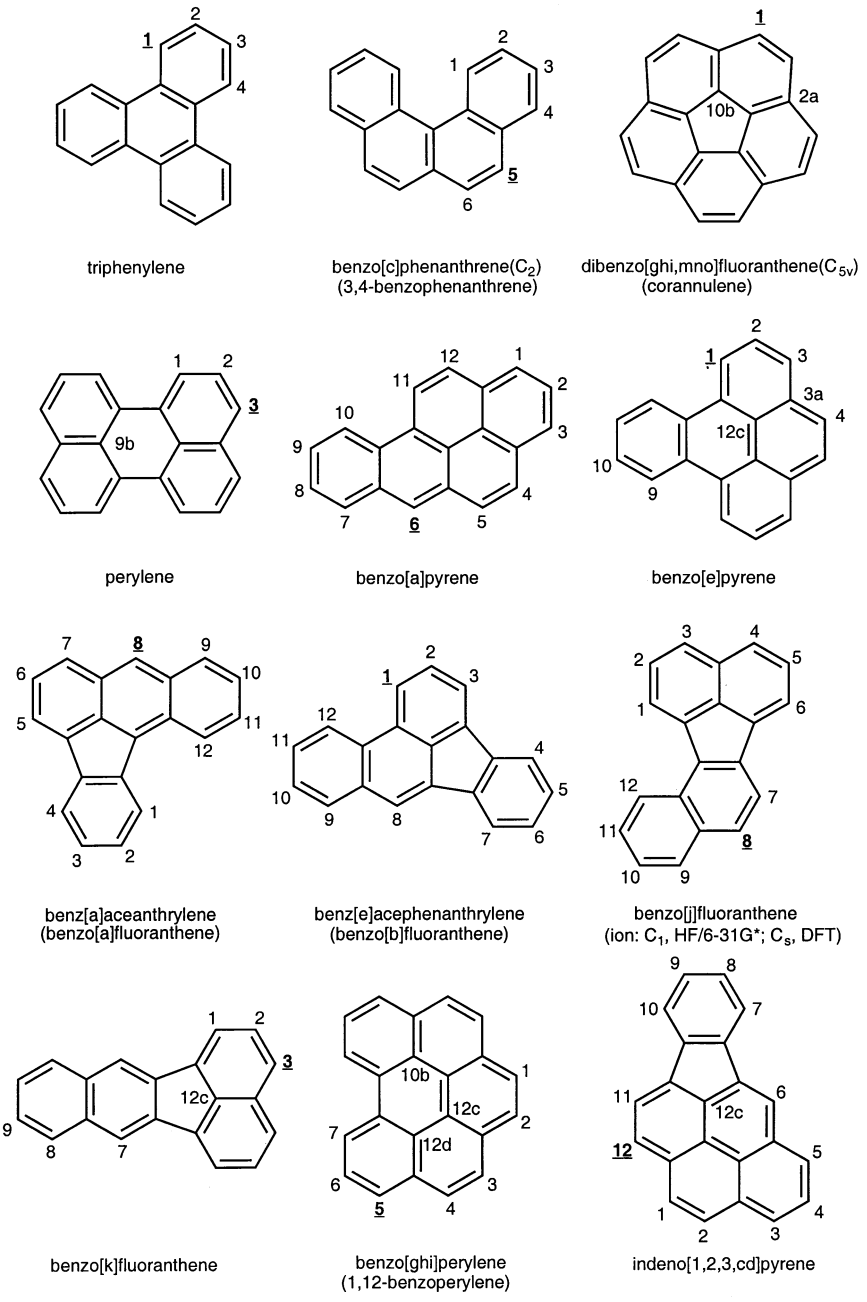

Figure 1. Continued.

tween the preferred carbocation and its closest protonation-site isomer was less than about 2 kcal mol^{-1}, and calculations in these cases were carried out at the HF/6-31G(d)//HF/6-31G(d) and the B3LYP/6-311G(d,p) level at either the HF/6-31G(d) or DFT geometry. These cases include the following molecules with a bold alternate site number for protonation and the HF and DFT energy differences shown,

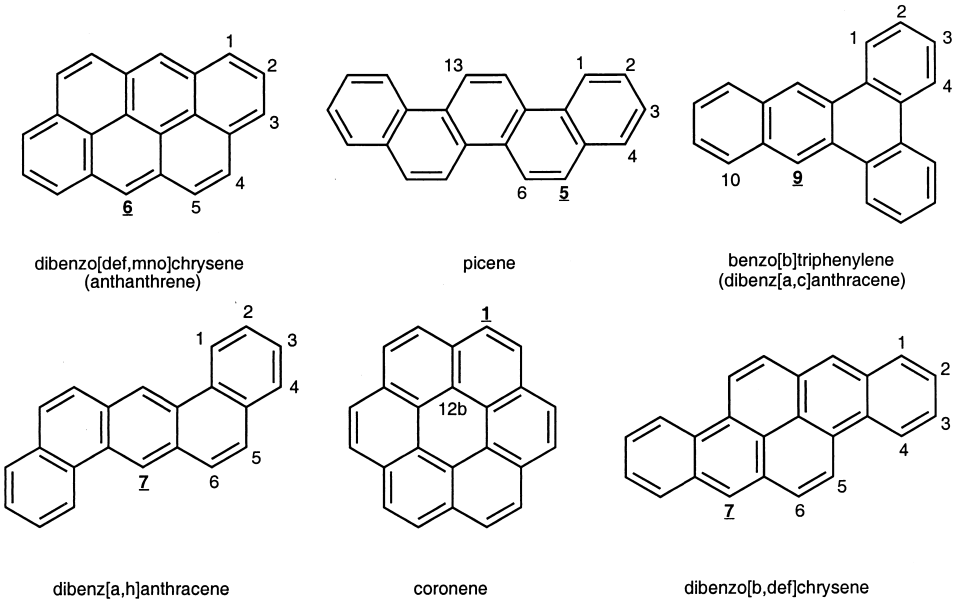

Figure 1. Continued.

respectively, in parentheses in kcal mol^{-1} at each level of theory, where available: 1,3-dimethylbenzene(**2**, 1.8, 1.3), toluene(**2**, 1.7), ethylbenzene(**2**, C_s with CH_3 anti to ring CH_2, 1.5), toluene(**2**, 1.7), tetrahydronaphthalene(**6**, C_1, 1.3), octahydroanthracene(**4a**, C_1, −0.3, 0.9), biphenyl(**2**, 2.5,HF/3-21G), octahydrophenanthrene(alternate stereo isomer for **9**-protonation, C_1, 0.5, 0.4; **4a**, C_1, 0.9, 1.1; **8a**, C_1, 0.7, 1.7), benzo[e]pyrene(**3**, 0.6, 0.2), benz[e]acephenanthrylene(**8**, 2.1, 2.6), cyclopropylbenzene(**2**, C_s with cyclopropyl *anti* to ring CH_2, 3.0, 2.5). Molecules with larger energy differences, 3–12 kcal mol^{-1}, for their closest competitive protonation site are similarly listed as: naphthalene(**2**, 3.8), 1-methylnaphthalene(**5**, 3.9, 3.4), 2-methylnaphthalane(**4**, 4.9, 4.1), biphenylene(**4a**, 3.2, 3.3; **1**, 11.6), acenaphthene(**2**, 4.3, 3.5), fluorene(**4**, 4.6, 2.8), benzo[b]fluorene(**10**, 9.5, 9.8), pyrene(**4**, 11.5, 12.3).

When energy differences are small, the question of whether the correct isomer has been chosen becomes more problematic. Using lower level Huckel energies, HOMO coefficients, and AM1 energies alone are not sufficient to reliably predict the preferred isomer when isomers are nearby in energy. The use of higher level methods generally gives a consistent preference for one isomer that is likely to be reliable, even with energy differences near 1 kcal mol^{-1}. As we shall see, from comparisons of experimental GBs, the HF and correlated methods can be reliable to about 1–2 kcal mol^{-1} and are likely to give some additional error cancellation when the protonation-site isomers are closely related structurally. For very small energy differences, both isomers would be expected to contribute substantially to the overall population.

Experimental and calculated GBs are found in Tables 1 and 2. The entropies for all of the PAHs in this study and all of the reference bases in the primary experimental reference molecules for PAHs and aromatic hydrocarbons [7,14] were determined from scaled HF frequencies using the Pitzer hindered rotor model [12]. For dimethyl species and molecules and ions with more than one internal rotor, no corrections for coupled-rotor effects were made, except to use East and Radom's results, when available [12]. The availability of high-quality entropy data now makes possible a reevaluation of the original gas-phase experimental GB data in a more specific fashion than by the use of generic entropy terms in the most recent NIST compilation. This reevaluation of GB values involves conversion of original high-temperature equilibrium measurements to free energies of proton

Table 2
Experimental and calculated gas-phase basicities at 298 K[a]

	Expt'l GB	Expt'l PA	Expt'l GB NIST	AM1	Res error in *Y*	HF/ 3-21G	Res error in *Y*	HF/ 6-31G*	Res error in *Y*	B3LYP/ 6-311G**//HF	Res error in *Y*	B3LYP/ 6-311G**	Res error in *Y*	MP2/ 6-31G*//HF	Res error in *Y*	MP2/ 6-31+G**//HF
1,3-cyclopentadiene	190.8	197.9	190.8	189.9	−0.6	202.2	−3.9	206.7	−3.1	196.6	0.6	196.7	0.6	192.3	−1.0	190.2
benzene	172.5	178.4	173.4	175.9	−4.5	178.7	−2.5	184.2	−2.1	177.4	−0.8	178.1	−0.6	171.7	−1.8	170.6
toluene	180.1	187.0	180.8	179.9	−1.0	185.9	−0.9	191.2	−0.5	184.6	0.5	185.0	0.6	177.5	0.0	176.4
1,2-dimethylbenzene	182.9	189.1	183.6	182.3	−0.7	189.2	−0.9	194.4	−0.5	189.0	−0.6	189.5	−0.7	181.6	−0.4	180.2
1,3-dimethylbenzene	188.3	195.2	187.9	183.8	3.1	193.2	1.1	198.2	1.7	191.9	2.2	192.2	2.2	184.2	1.7	182.8
1,4-dimethylbenzene	183.3	189.7	183.3	180.3	1.7	187.6	0.8	192.2	1.8	187.5	1.1	188.0	1.0	180.4	0.5	179.0
ethylbenzene	181.7	188.8	181.7	181.0	−0.6	186.1	0.5	191.8	0.6	185.8	1.0	186.1	1.2	178.1	0.7	176.4
1,3,5-trimethylbenzene	193.3	199.6	193.3	188.2	3.5	199.8	0.6	204.5	1.2	198.5	1.4	198.7	1.2	190.3	1.7	189.0
1,2,3,4-tetrahydronaphthalene	185.0	191.4	186.9	183.4	0.3	190.4	0.2	195.6	0.6	190.7	0.0	190.6	0.4	182.4	0.5	
octahydroanthracene	193.6	199.6	194.7	188.4	3.8	199.0	1.6	203.9	2.1	199.8	0.6	200.2	0.2	191.5	1.2	
octahydrophenanthrene	194.1	200.5	194.9	188.9	3.7	198.9	2.2	203.7	2.7	199.4	1.4	199.8	1.0	190.8	1.9	
phenylacetylene	190.9	198.1	191.5	187.3	2.1	198.0	−0.3	204.8	−1.4	200.3	−2.6	200.0	−2.4	191.7	−0.6	190.7
styrene	193.2	200.5	193.4	192.3	−0.7	201.9	−1.2	207.6	−1.5	200.6	−0.6	200.3	−0.3	196.1	−1.5	192.4
indene	195.8	202.8	195.9	195.0	−0.9	205.9	−2.0	210.8	−1.7	202.9	0.0	203.7	−0.8	197.7	−0.6	195.1
naphthalene	185.1	191.2	186.3	187.0	−3.4	193.4	−2.2	198.6	−1.9	192.3	−1.3	192.1	−0.9	186.4	−1.5	184.4
1-methylnaphthalene	192.0	198.7	192.5	191.1	−0.7	199.2	−0.2	203.9	0.5	197.3	1.1	197.2	1.3	190.8	0.6	
2-methylnaphthalene	191.7	198.6	191.8	190.3	−0.2	199.1	−0.5	204.3	−0.2	198.3	−0.1	197.8	0.5	191.5	0.0	
biphenyl	186.6	193.3	187.1	185.2	0.0	190.1	2.0	196.8	1.2	192.2	0.3	192.5	0.3	183.6	0.9	
acenaphthylene	199	205.8		200.1	−2.9	208.6	−1.1	212.4	0.1	206.5	0.0	206.0	0.2	201.1	−0.4	
acenaphthene	196.4	203.1	196.2	192.9	1.9	204.7	−0.5	210.3	−0.7	203.1	0.5	203.1	0.3	196.4	0.4	
fluorene	191.4	197.9	192.1	188.7	1.2	197.1	0.9	203.8	−0.1	198.0	−0.1	198.3	−0.3	189.9	0.7	187.8
anthracene	201.4	207.8	202.3	201.0	−1.4	212.5	−2.0	216.8	−1.3	209.4	−0.1	208.6	0.3	204.8	−0.8	202.6
phenanthrene	189.7	196.0	190.0	188.9	−0.7	195.3	0.8	201.3	0.3	194.4	1.5	195.5	0.6	189.0	0.1	
2-methylanthracene	205.0	211.5	204.4	203.4	−0.3	215.6	−1.0	219.7	−0.2	212.4	0.8	212.0	0.7	207.5	0.1	
9-methylanthracene	206.9	213.6	206.9	204.1	0.8	216.7	0.0	220.8	0.8	212.6	2.5	212.6	2.6	208.0	1.0	
pyrene	201.2	207.4	200.8	198.6	0.9	208.4	1.3	213.8	1.2	207.6	1.3	207.3	1.3	202.0	0.6	
fluoranthene	191.1	197.6	191.4	191.9	−2.4	200.7	−2.3	207.0	−3.1	200.7	−2.8	200.7	−2.8	193.4	−1.4	
naphthacene	211.3	217.1	209.5	208.7	0.6	222.9	−0.8	227.2	−0.3	219.2	1.2	217.9	1.6	214.6	0.4	
chrysene	192.3	198.1	193.6	195.0	−4.4	202.0	−2.3	207.8	−2.7	202.3	−2.9	202.7	−3.5	196.0	−2.0	
benzo[a]anthracene	201	207.7		200.3	−1.1	210.5	−0.7	215.3	−0.3	210.1	−1.2	209.5	−0.9	204.3	−0.8	
triphenylene	189.5	195.5	189.1	189.2	−1.2	194.6	1.2	200.7	0.7	198.0	−2.0	197.1	−1.1	190.1	−0.7	
perylene	205.4	212.1	205.4	201.8	1.7	213.5	1.2	219.3	0.6	213.0	0.7	212.0	0.6	207.2	0.5	
benzo[e]pyrene	201	207.9		197.2	2.0	206.9	2.4	212.9	1.7	208.1	0.6	207.6	0.8	201.7	0.6	
benz[e]acephenanthrylene	195	202.0		192.3	1.1	201.8	0.6	208.3	−0.3	203.7	−1.5	203.8	−1.7	196.3	−0.4	
benzo[j]fluoranthene	199	205.6		200.0	−2.8	207.4	−0.1	212.8	−0.3	208.8	−2.0	208.1	−1.7	201.7	−0.7	
benzo[k]fluoranthene	198	204.5		195.4	0.9	205.2	0.8	211.5	−0.1	207.2	−1.5	206.4	−1.1	199.0	0.1	
benzo[ghi]perylene	203.3	209.8	202.0	199.5	2.0	209.4	2.5	215.5	1.8	210.4	0.9	210.2	0.7	204.3	0.7	
indeno(1,2,3-cd)pyrene	200.0	207.0		199.8	−1.6	209.4	−0.8	215.1	−1.2	209.3	−1.4	209.0	−1.5	203.6	−1.1	
picene	195.5	201.6	196.1	195.2	−1.4	202.0	1.0	208.1	0.4	204.1	−1.3	204.0	−1.4	197.1	−0.5	

Table 2
Continued

	Expt'l GB	Expt'l PA	Expt'l GB NIST	AM1	Res error in *Y*	HF/ 3-21G	Res error in *Y*	HF/ 6-31G*	Res error in *Y*	B3LYP/ 6-311G**//HF	Res error in *Y*	B3LYP/ 6-311G**	Res error in *Y*	MP2/ 6-31G*//HF	Res error in *Y*	MP2/ 6-31+G**//HF
coronene	200.0	205.4	199.6	195.8	2.5	203.2	4.5	209.6	3.5	205.0	2.4	205.8	1.4	198.9	1.4	
benzo[a]pyrene	206	212.6		206.3	−2.3	218.4	−2.4	223.0	−2.0	216.1	−2.1	215.8	−1.8	212.4	−2.9	
benz[a]aceanthrylene	201	206.7		205.9	−6.9	217.5	−6.5	222.5	−6.6	214.6	−5.7	214.0	−5.1	208.6	−4.8	
cyclopropylbenzene	191.8	198.9	191.8	182.9	7.5	193.6	4.3	198.4	5.0	193.5	4.5	193.4	4.6	185.7	4.9	184.1
biphenylene	195.8	202.0	195.8	188.1	6.2	197.8	4.8	206.2	2.3	198.8	3.7	198.8	3.7	191.4	4.2	
azulene	214.3	221.7	214.1	218.2	−6.2	231.5	−5.0	233.8	−3.0	220.0	2.6	218.5	4.1	220.8	−1.6	218.2

	Predicted GBs[b]	
	B3LYP	MP2
pentalene	207.8	209.3
benzocyclobutene	205.3	207.8
benzo[b]fluorene	200.1	199.8
benzo[c]phenanthrene	194.7	195.0
7-Mebenzo[a]anthracene	204.0	204.5
12-Mebenzo[a]anthracene	205.6	205.5
corannulene	193.7	193.5
7,12-diMebenzo[a]anthracene	198.4	198.4
anthanthrene	209.7	211.5
benzo[b]triphenylene	202.0	202.0
dibenz[a,h]anthracene	202.1	202.0
dibenzo[b,def]chrysene	213.7	214.3

[a] All values are in kcal mol^{-1}. The gas-phase basicities (GBs) used in regression analyses are from the reassigned values in the first column using ab initio calculated entropies. Reassigned PAs are in the second column, and the previous NIST assigned values [8]. Calculated GB values are shown under the appropriate levels of theory used followed by a column of the residual errors in the *Y* values in the linear regression analyses. Geometries were optimized at each level of theory, except where HF/6-31G* geometries are indicated by //HF. GBs reported to be ±1 kcal mol^{-1} are from [6ab]. References to all other experimental GBs are in [8].

[b] Predicted GBs from regression lines and B3LYP/6-311G(d,p) and MP2/6-31G(d)//HF calculated GBs.

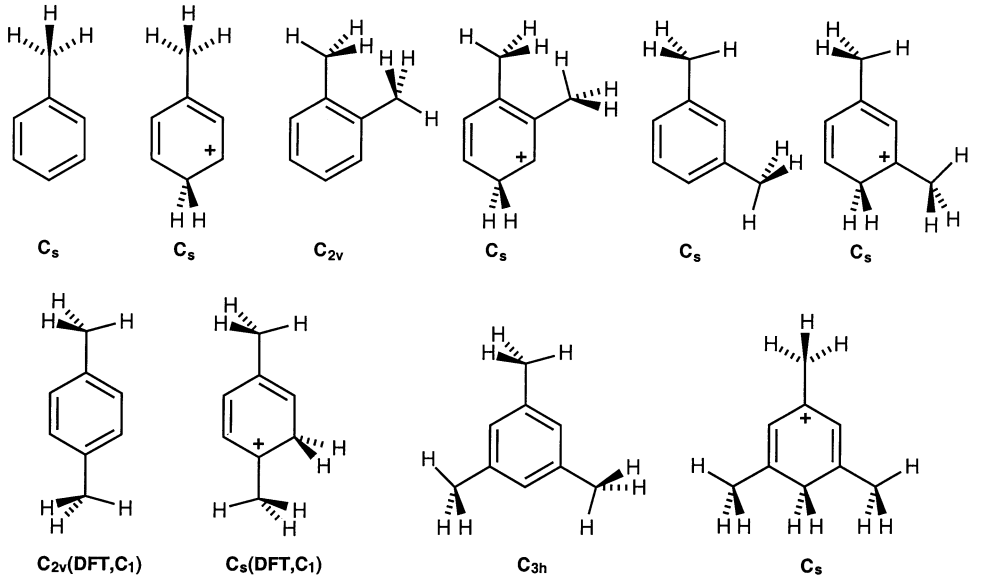

Fig. 2. Preferred conformations of methyl groups in neutral and protonated methylbenzenes.

transfer at room temperature and calculations of GBs from experimentally and theoretically known anchor points for proton affinities (PAs) [12d,15]. The reevaluated GBs and PAs in Table 2 are then calculated using these theoretical entropies.

The GB scale was examined for a large number of reference bases in the region of interest between propene and dimethylamine, using original data from high-pressure mass spectrometry [7,14], and near-room temperature ion cyclotron resonance (ICR) measurements from our laboratory [8,16] and Taft's [8]. In addition, more extensive theoretical models (beyond G2 or G3 methods) have been extended to some key reference molecules on this scale which, together with improved entropies, provide very reliable bases for comparison, with assurance that the theoretical methods have nearly converged. Some of these results are shown in Table 1, where the convergence with respect to basis set can be seen from comparison of the CCSD(T)-FU/aug-cc-pVQZ and CCSD(T)-FU/aug-cc-pVTZ results to be nearly complete [11a]. Such comparisons of MP4-FU and CCSD(T)-FU results also indicate a near convergence with respect to method as well. These calculations now use CCSD(T)(full) calculations which involve the inclusion of core-related correlation, as advocated in the new G3 methodology [13] with some potential improvement over earlier studies [12d,15,17]. Comparisons of these theoretical GBs with the NIST compilation of experimental data shows an excellent correspondence, with the possibility that a small upward adjustment of the NIST scale in the region of methylamine and ethylamine might be considered in evaluation of experimental data. We furthermore found quite good agreement of the overall NIST scale for most key reference molecules with the reevaluated high-pressure mass spectrometric (HPMS) data and the Aue and Taft ICR scales, generally within 1 kcal mol^{-1} or better. The Meot-Ner/Sieck and McMahon HPMS PA data do not always agree very well, but generally their original free energy data are in better agreement. We have therefore taken the HPMS free energies, as our primary data source, rather than the enthalpy data. This HPMS data set, when converted to room temperature, then fits well with that from ICR data over short GB scale segments, and over longer segments of the ICR scales when corrected for artifacts in the ICR data that seem to cause the scale to be artificially compressed. Since this occurs for our ICR data, as well as Taft's, and our measurements were originally

made with nominal temperature control reasonably close to room temperature, we are not sure that this effect is simply the result of heating of the ICR cell. This suggests that the NIST scale is relatively accurate overall. Lacking enough entropy data for a full reevaluation of the entire scale from all sources, we have adopted that scale for all of the common reference molecules used in establishing the GBs of the PAHs and related molecules [7,14].

The most extensive single compilation of PAH data comes from the original article of Meot-Ner and the subsequent papers by Meot-Ner and Sieck. These measurements are especially challenging because of the relative nonvolatility of the higher molecular weight PAHs, requiring indirect pressure measurements with quoted errors of a factor of 2, contributing an error of 0.7 kcal mol^{-1} to the GB measurements at 550 K. Between this and other sources of error, including the possibility of incomplete equilibrium due to side reactions and slow proton transfer [9c], errors as large as 2 kcal mol^{-1} or more would not be impossible and were noted by Meot-Ner in his evaluation of the internal consistency of his measurements. The fit of these data onto the current NIST scale was found again to be imperfect, with errors typically within ± 1 kcal mol^{-1}, but often as large as ± 1–2 kcal mol^{-1}. In some cases (picene and biphenylene), different measurements spanned more than 4 kcal mol^{-1}. In these cases it was expected that theoretical calculations would be sufficiently accurate to guide the interpretation of disparate experimental results and suggest where future experiments might be warranted. Our reassigned GBs for PAHs and related molecules are shown in Table 2 together with derived PAs and the recent NIST assignments based upon generic aromatic entropies and symmetry number changes. Our GBs do not differ by much more than 1 kcal mol^{-1} from the NIST set, except for 1,2,3,4-tetrahydronaphthalene and naphthacene, where the differences are larger.

Some experimental data on the basicities of PAHs come from nonequilibrium qualitative/semiquantitative chemical ionization experiments with ammonia [6ab]. These data are available for eight of the PAHs which are least volatile and some which are carcinogenic. These are reported with GBs in Table 2 to ± 1 kcal mol^{-1} accuracy. Empirical calibration experiments with this technique were carried out on several PAHs with known equilibrium GBs. Molecules with GBs clearly higher or lower than that for ammonia (GB = 195.7 kcal mol^{-1}, PA = 204.0 kcal mol^{-1}; Table 1) can be readily distinguished qualitatively by their MH^+ to M^+ ratios. Those molecules with GBs close to that of ammonia can be empirically assigned a semiquantitative (± 2 kcal mol^{-1}) GB between about 195 and 206 kcal mol^{-1}, but those values near 195 kcal mol^{-1} should be regarded as possible upper limits and those near 206 kcal mol^{-1} lower limits. Again it was expected that theoretical GBs, beyond the AM1 PAs reported in those original articles, might again be helpful in the interpretation of those results. At the bottom of Table 2 are theoretical predictions of GBs and PAs for a series of PAHs and related hydrocarbons for which no experimental basicity measurements are known. Predicted GBs for these 12 molecules are made on the basis of the DFT and MP2 calculated GBs and the regression lines from a linear least-squares analysis of the calculated and experimental GB data.

In Table 3 are statistical data from regression analyses carried out for correlations between the reevaluated GBs in the first column of Table 2 with calculated GBs for the 40 PAHs and related hydrocarbons. GB data for five statistical and chemical outliers below coronene in Table 2 were left out of the analysis for reasons discussed later and to avoid distorting the overall statistical comparisons. The absolute errors in calculated GBs are large for HF values, with the theoretical GBs too high by 11–16 kcal mol^{-1}. AM1 values show smaller absolute errors, but a larger standard error in regression analyses (Table 3). DFT GBs are also high by 4–8 kcal mol^{-1}, while absolute MP2/6-31G(d) GBs are similar to experimental values. The regression statistics in Table 3 show that the DFT(B3LYP) calculations give the smallest standard error of 1.36 kcal mol^{-1}. The standard errors are somewhat higher for the HF and MP2 methods, with the AM1 method exhibiting a standard error over 2 kcal mol^{-1}. The AM1 method performs well for this closely related set of structural

Table 3
Results of regression analyses from correlations of experimental and calculated gas-phase basicities from Table 2 at various levels of theory

	AM1	HF/3-21G	HF/6-31G*	B3LYP/ 6-311G**	MP2/ 6-31G*
R Squared	0.9324	0.9582	0.9651	0.9723	0.9640
Standard error in *Y*	2.12	1.67	1.53	1.36	1.55
Slope	1.0285	0.8399	0.8616	0.9187	0.8251
Y intercept	−3.87	24.90	15.87	9.51	33.67
N	40	40	40	40	40
Standard error in intercept	8.64	5.73	5.49	5.05	5.02
Standard error in slope	0.0449	0.0285	0.0265	0.0251	0.0258

types considering its low computational cost, but might be less reliable as structural types vary more, for example see the larger disagreement of the AM1 and MP2 GBs for pentalene, where higher level calculations are likely required. This can be seen most clearly in comparing the residual errors in *Y* values (experimental GBs) in the columns of Table 2 following the individually calculated GBs. Azulene is the most abnormal case, with the AM1 error suggesting that the experimental GB is too low by 6.2 kcal mol^{-1}, while the DFT error suggests that the experimental value is too high by 4.0 kcal mol^{-1}, a difference of 10.2 kcal mol^{-1}! MP2 and HF calculations fall in between, again with a 5.6 kcal mol^{-1} discrepancy between the MP2 and DFT results! Azulene is clearly a computational challenge and conclusions about its GB must await higher-level calculations that have more nearly converged. We therefore chose to consider azulene as an outlier in the regression analyses. For most molecules the HF, MP2, and DFT residual errors are similar, usually within 1 kcal mol^{-1}. For azulene, pentalene, and benzocyclobutene and, to a lesser extent, cyclopentadiene, phenylacetylene, styrene, and benzene, inconsistencies between calculated GBs at different levels of theory appear to be related to their diverse structural types.

The experimental GBs can now be evaluated in terms of the theoretical calculations, which appear largely consistent with one another and with experimental GBs to within about 1–2 kcal mol^{-1} or better. The columns of *Y* residual values following the individual calculated GBs show maximum standard errors of 2–3 kcal mol^{-1} for the DFT method, but the GBs with the largest errors usually show consistently large errors with the same sign for all methods, suggesting that the source of the discrepancies might possibly result from experimental errors and that reevaluation of experimental results might be considered in these cases. The experimental GBs, then, for 1,3-dimethylbenzene, 9-methylanthracene, and coronene appear to be too high, while those for chrysene, fluoranthene, and benzo[j]fluoranthene appear to be too low by 2–3 kcal mol^{-1}. The residual errors were also calculated from correlation lines for the five outlier molecules tabulated below coronene. Most of these molecules show large and, except for azulene, consistent errors, with the experimental GB too large by 4–5 kcal mol^{-1} for cyclopropylbenzene and biphenylene and too low for benz[a]pyrene by 2–3 kcal mol^{-1} and benz[a]aceanthrylene by 5 kcal mol^{-1}. Numerous other molecules also show consistent but smaller errors, including 1,3,5-trimethylbenzene, octahydrophenanthrene, naphthalene, pyrene, 9-methylanthracene, and picene.

The experimental free energies of proton transfer to biphenylene show experimental inconsistencies up to 4 kcal mol^{-1} and are tied to chrysene and fluorene [7]. Moving the assigned GB of biphenylene lower and that of chrysene higher would be a possibility and would not be entirely inconsistent with the experimental results, but would still leave some large experimental errors, making these candidates for further experimental work. The GBs of naphthalene, 9-methylanthracene, pyrene, and coronene show experimental inconsistencies of about 1–2 kcal mol^{-1}

[7], and might be considered for experimental reevaluation. The GB of picene has experimental uncertainties up to 4.4 kcal mol^{-1}, so some disagreement with theory is not unexpected. The GBs of 1,3-dimethylbenzene and 1,3,5-trimethylbenzene are tied together experimentally with naphthalene [14de] and might both have lower values, but this is not consistent with the fact that naphthalene's calculated GBs might suggest raising its assigned GB.

The 1–2 kcal mol^{-1} residual errors for GBs of PAHs determined from semiquantitative ammonia chemical ionization are not surprising, since the experimental error limits could well be larger than that by this methodology, but the 5 kcal mol^{-1} residual error for benz[a]aceanthrylene is difficult to explain and suggests a need for more experimental work on this outlier molecule. The data for benzo[a]pyrene were considered to be outliers also. Even though the residual error was only 2–3 kcal mol^{-1}, the sign of the error suggests that the assigned GB should be higher than 206 kcal mol^{-1}. Since 206 kcal mol^{-1} is at the far limit of reliability for this experimental technique, as discussed above, this should be considered a lower limit on the GB rather than an assignable value, completely consistent with the calculated GBs.

The most interesting outlier GB chemically, with one of the largest residual errors (~5 kcal mol^{-1}), is for cyclopropylbenzene. This experimental data comes from FT-ICR data, apparently by equilibium methods, although details are not reported [18]. The unusually large GB for this molecule, readjusted to 191.8 kcal mol^{-1} on the NIST scale, is well above the value of 172.6 kcal mol^{-1} for cyclopropane. The measured GB is 5 kcal mol^{-1}, too high to be consistent with protonation on the aromatic ring in the 4 position, which is the structure we assumed in our calculations. In their article, Galli and Speranza [18] suggested that a corner-protonated phenylcyclopropane was formed, whose higher stability by 20 kcal mol^{-1}, with respect to protonated cyclopropane, might be explicable as a result of partial ring opening and delocalization of the charge into the aromatic ring. To test this idea, we attempted to find the protonated cyclopropane as an energy minimum on the MP2 and DFT surfaces, but were unable to find such a minimum with repeated partial optimizations and refined attempts. In all cases the cyclopropane ring opened up to 1-phenylpropyl cation, whose energy is far too low (17.6 kcal mol^{-1} below the ring protonated ion at the B3LYP/6-311G(d,p) level) to explain the observed GB, which then would be about 12–13 kcal mol^{-1} too low. The observation of stabilizations by ring methyl groups is consistent with cyclopropane ring opening, but radiolytic and nuclear decay experiments suggest that the cyclopropane ring should stay intact [18]. Gas-phase protonation with a barrier to ring opening rearrangement to give 1-phenylpropyl cation has some analogy in other gas-phase protonation reactions, for example of cyclopropene or alkynes and allenes [9ab], and could be considered as a possibility in this case. Resolution of this problem will require further theoretical and possibly experimental work.

4. Conclusions

Gas-phase basicities of polynuclear aromatic hydrocarbons calculated using AM1, HF/3-21G, HF/6-31G(d), MP2/6-31G(d), and B3LYP/6-311G(d,p) levels were correlated with experimentally known GBs that have been reevaluated with theoretically calculated entropies and additional theoretical confirmation of the accuracy of the NIST gas-phase basicity scale. Regression analyses on PAHs and related hydrocarbons show standard errors of 2.12, 1.53, 1.36, and 1.55 kcal mol^{-1} for each of the four methods, respectively. The results permit an evaluation of the reliability of experimental data and pinpoint possible experimental problems with literature GBs for biphenylene, chrysene, 1,3-dimethylbenzene, 1,3,5-trimethylbenzene, 9-methylanthracene, coronene, fluoranthene, 1,2,3,4,5,6,7,8-octahydrophenanthrene, naphthalene, pyrene, picene, benz[a]pyrene, and benz[a]aceanthrylene, suggesting a need for reevaluation of experimental data for these molecules. The theoretical methods used here show some inconsistencies with the molecules pentalene, azulene, and benzocyclobutene, calling for higher level theoretical treatments to get convergent results. The GB of cyclopro-

pylbenzene is anomalous in comparison with experiments suggesting that protonation occurs on the cyclopropane ring without ring opening. Such an intermediate was not found theoretically and the energies of the carbocations from protonation at the benzene ring are not consistent with the experimental GB, leaving unresolved the question of how this reaction proceeds. Predictions are made for GBs for 12 new PAHs whose GBs have not yet been measured.

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