Thermochemical study of arenecarboxylic acids

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Dedicated to Professor José Elguero – a great colleague and a good friend – on the occasion of his 70th birthday

(received 08 Feb 05; accepted 22 Apr 05; published on the web 20 Jun 05)

Abstract

We analyze and compare the energetics of arenoic acids from studies of thermodynamic data such as the enthalpy of formation, $\Delta_f H°_m$. This quantity offers a powerful procedure for the understanding of the contrasting structural, conformational, and reactivity trends exhibited by compounds.

Keywords: Arenoic acids, enthalpies of formation, proton affinities

Introduction

The structure and energetics of molecules are fundamental concepts in chemistry, the energy associated with a particular structure being related to the constituent atoms and to the corresponding interatomic bonds and angles that form the molecular framework.[1] Thermochemical data, such as the enthalpy of formation, are often helpful for the understanding of the contrasting structural, conformational, and reactivity trends exhibited by isomeric compounds. On the other hand, contemporary quantum chemistry is generally interested in the *ab initio* prediction of the molecular structure and the energy of the isolated molecules.[2]

If benzene and its substituted derivatives are the paradigm of aromatic molecules,[3] furans and thiophenes are the simplest representatives of stable aromatic structures bearing oxygen and sulfur.[4] Their structures can be assumed to be derived from benzene by the replacement of two annular CH groups by oxygen or sulfur respectively. Furan and thiophene also obey Hückel's $(4n + 2)\pi$- electron rule and they are thus considered to be aromatic compounds. Mulliken population analysis of the π-electron distribution in furan and thiophene points to a greater aromaticity of thiophene relative to furan.[3] This has been attributed to the size of the heteroatom, which determines the degree of delocalization of electron density in the ring. The commonly accepted (textbook) order of aromaticity is benzene > thiophene > furan.

Benzoic acid has been a key substance for the concepts of aromaticity and substituent effects in organic chemistry. Benzene is the archetypal aromatic hydrocarbon, and carboxyl groups were among the first functional groups to be introduced into a hydrocarbon—the Grignard reagent and its reaction with CO_2 being among the simplest reactions to form new C–C bonds. Once formed, the newly affixed carbon of the carboxyl group can be modified to give a plethora of other substituents. Hammett's σρ analysis was among the first quantitative correlations in organic chemistry to quantify substituent effects on both equilibria and rates, and benzoic acid provided a key molecular framework for the disentangling of σ- and inductive effects from π- and resonance substituent effects. While the vast majority of chemical experiments were – and are – made in the condensed phase, the diagrams drawn by organic chemists, usually refer to isolated molecules. Only more recently have there been corresponding experiments in the gas phase, accompanied by quantum chemical calculations on isolated molecules. Although benzoic acid clearly acts as an acid, although in the absence of solvation, *i.e.*, in the gas phase, benzoic acid is both a stronger acid and a stronger base than water. Benzoic acid has been a key substance for all of these concepts in organic chemistry: as an easily purified, easily obtained substance it very early became an important experimental standard, "benchmark" and calibration material for the calibration of experimental calorimetric measurements of all organic compounds.

Naphthalene is another important standard. Like benzoic acid, this easily obtained and easily purified species became an experimental standard for measurements and an archetype for concepts. With its two rings it became a stepping-stone for the understanding of general polynuclear aromatic hydrocarbons. It became a paradigm (much more important than its isomer azulene—a later paradigm in its own right—and even more so than its largely ignored 8:4-fused- isomers bicyclo[6.2.0.0^{1,8}]decapentaene and the all-but-forgotten 9:3 fused bicyclo[7.1.0.0^{1,9}]decapentaene. Naphthalene is also important for studies of steric interactions with its so-called *peri*-1- and 8-positions which are structurally but not electronically nearby, and for electronic phenomena such as the site-specificity for electrophilic attack [1-(α-) *vs* 2-(β-)] and bond fixation (the Mills–Nixon effect).

In general, it can be considered that the –COOH group in thiophenecarboxylic (thenoic) acids and furancarboxylic (furoic) acids is much the same as in any organic compound. Substituted naphthalene, furan and thiophene derivatives have been investigated, albeit with much less intensity and interest than benzoic acid derivatives. In this article we analyze and compare the energetics of the so-derived arenoic acids from the results of a combination of experimental determinations and high-level *ab initio* calculations of enthalpies of formation, $\Delta_f H^\circ_m$ which we have recently reported.[5–7]

Results and Discussion

Experimental determination of enthalpies of formation

The experimental enthalpies of formation in the condensed state of 1- and 2- naphthoic acids[7] and 2- and 3- furan carboxylic acids,[6] were determined with a combustion calorimeter equipped with a static bomb. For the 2- and 3- thiophene carboxylic acids[5] a combustion calorimeter equipped with a rotary bomb was used.

The standard enthalpy of formation of an organic compound in the condensed state, $\Delta_f H^\circ_m$(cd), depends both on the chemical binding forces within the molecules and the forces between molecules. For a discussion of the chemical binding forces alone, it is necessary to remove the intermolecular forces from consideration. This can be achieved by conversion of the value of the enthalpy of formation to the ideal theoretical gas state, $\Delta_f H^\circ_m$(g), wherein the effect of the intermolecular forces is zero. To derive the value of the enthalpy of formation in the gas state of solid compounds the knowledge of the enthalpy of sublimation is required. The experimental methods used to determine sublimation enthalpies for these compounds were Knudsen effusion, transpiration (transference), and combined correlation-gas chromatography-fusion enthalpy.

All the results obtained for 2- and 3-thiophenecarboxylic acids,[5] 2- and 3- furancarboxylic acids,[6] and 1- and 2- naphthoic acids,[7] are given in the respective references.

Table 1 gives the results obtained for the enthalpies of formation in both condensed and gas states, and the sublimation enthalpies for these compounds.

Table 1. Standard molar enthalpies at T = 298.15 K

Compound	$\Delta_f H^o_m$(cr) kJ mol^{-1}	$\Delta_{sub} H^o_m$ kJ mol^{-1}	$\Delta_f H^o_m$(g) kJ mol^{-1}
1-Naphthoic acid[a]	-333.5 ± 1.0	110.8 ± 0.8	-222.7 ± 1.3
2-Naphthoic acid[a]	-346.1 ± 1.5	115.0 ± 0.9	-231.1 ± 1.7
2-Furancarboxylic acid[b]	-498.5 ± 1.4	88.2 ± 1.5	-410.3 ± 2.1
3-Furancarboxylic acid[b]	-502.4 ± 1.6	86.6 ± 0.5	-415.8 ± 1.7
2-Thiophenecarboxylic acid[c]	-350.4 ± 1.4	91.2 ± 1.3	-259.2 ± 1.9
3-Thiophenecarboxylic acid[c]	-353.7 ± 1.4	91.9 ± 0.9	-261.8 ± 1.7

[a] Values taken from ref. 7. [b] Values taken from ref. 6. [c] Values taken from ref. 5.

Theoretical determination of enthalpies of formation

The energies of furan- and thiophene- carboxylic acids were calculated using Gaussian-2 theory, at the G2(MP2)[8] and G2[9] levels. G2(MP2) and G2 correspond effectively to calculations at the QCISD(T)/6-311+G(3df,2p) level on MP2(full)/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point vibrational energies and a so-called higher-level correction to accommodate remaining deficiencies.

In standard Gaussian-n theories, the theoretical enthalpies of formation are calculated through the atomization reactions, (1) for furancarboxylic acids, and (2) for thiophenecarboxylic acids.

$$C_5H_4O_3(g) \rightarrow 5\ C(g) + 4\ H(g) + 3\ O(g) \qquad (1)$$

$$C_5H_4O_2S(g) \rightarrow 5\ C(g) + 4\ H(g) + 2\ O(g) + S(g). \qquad (2)$$

Another method is to derive the theoretical enthalpies of formation using a standard set of isodesmic reactions, the "bond separation reactions".[10] This method has been detailed in previous studies.[11,12] In the case of furan- and thiophene- carboxylic acids, the bond separation reactions using their classic (localized, uncharged) valence bond structures are, respectively:

$$C_5H_4O_3\ (g) + 7CH_4\ (g) + H_2O\ (g) \rightarrow 2\ C_2H_6\ (g) + 2\ C_2H_4\ (g) + 3CH_3OH\ (g) + H_2CO\ (g) \qquad (3)$$

$$C_5H_4O_2S\ (g) + 7\ CH_4\ (g) + H_2S\ (g) \rightarrow 2\ C_2H_6\ (g) + 2\ C_2H_4\ (g) + +2\ CH_3SH\ (g) + CH_3OH\ (g) + H_2CO\ (g) \qquad (4)$$

The calculated enthalpies of formation are collected in Table 2.

Table 2. G2(MP2) and G2-calculated enthalpies of formation of furan- and thiophenecarboxylic acids, from atomization and from bond separation isodesmic reactions. Values in kJmol^{-1}

Compound	G2(MP2)		G2		Experiment
	Atomization	Bond separation	Atomization	Bond separation	
2-Furan-carboxylic acid[a]	-409.6	-404.2	-411.9	-408.1	-410.3 ± 2.1
3-Furan-carboxylic acid[a]	-414.5	-409.2	-416.8	-413.0	-415.8 ± 1.7
2-Thiophene-carboxylic acid[b]	-271.4	-263.5	-262.0	-266.1	-259.2 ± 1.9
3-Thiophene-carboxylic acid[b]	-273.5	-265.6	-264.1	-268.2	-261.8 ± 1.7

[a] Values taken from ref. 6. [b] Values taken from ref. 5.

Owing to the size of naphthoic acids, Gaussian-2 calculations are very expensive. In this case, full geometry optimizations were carried out at the HF/6-31G(d) level, and the corresponding harmonic vibrational frequencies evaluated at the same level of theory, to confirm that the optimized structures found correspond to minima of the potential energy surface, and to evaluate the corresponding zero-point vibrational energies and the thermal corrections at 298 K. All the minima found at the HF/6-31G(d) level were again fully re-optimized at the MP2(FULL)/6-31G(d) level.

The enthalpies of formation of the isomeric naphthoic acids have been calculated using the simple and direct homodesmotic reaction (5)

$$\text{naphthalene} + \text{benzoic acid} \rightarrow \text{naphthoic acid} + \text{benzene} \qquad (5)$$

The calculated enthalpies of formation are collected in Table 3.

Table 3. MP2(FULL)/6-31G(d)-calculated enthalpies of formation of naphthoic acids, from homodesmotic reaction (5). All values in kJ mol^{-1}

	MP2(full)/6-31G(d)	Experimental
1-Naphthoic acid[a]	-217.2 ± 1.8	-222.7 ± 1.3
2-Naphthoic acid[a]	-228.8 ± 1.8	-231.1 ± 1.7

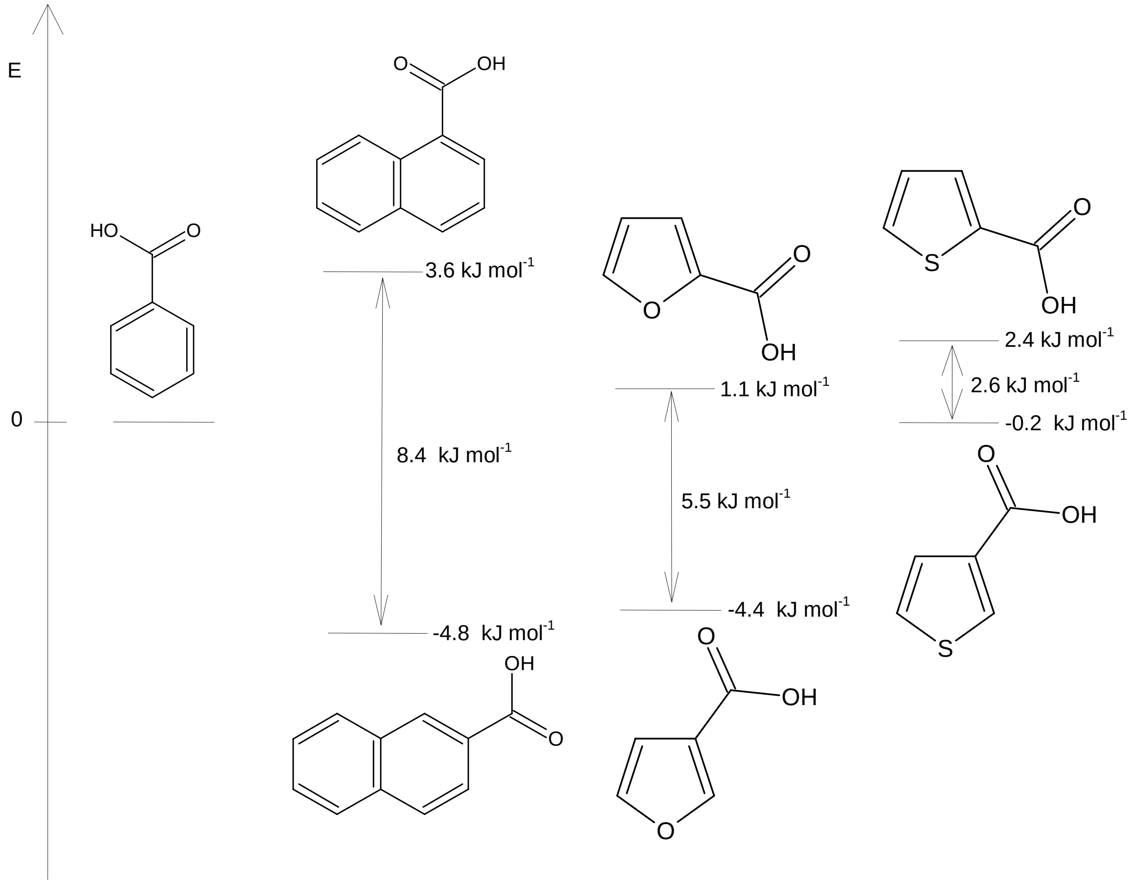
[a] Values taken from ref. 7.

Scheme 1 gives the differences found between the experimental enthalpies of formation of the arenoic acids studied and given in Table 1 and the reference compound, benzoic acid. Comparison of our experimental and theoretical results for the enthalpies of formation of the isomers of naphthoic acids, furancarboxylic acids and thiophene carboxylic acids shows that 2-naphthoic acid, 3-furancarboxylic acid and 3-thiophenecarboxylic acid are thermodynamically more stable, than 1-naphthoic acid, 2-furancarboxylic acid, and 2-thiophenecarboxylic acid, respectively. The isomerization enthalpies obtained from reactions (6), (7), and (8) give the values for this magnitude for the naphthoic, furancarboxylic, and thiophenecarboxylic acids as -8.4 ± 1.3, -5.5 ± 1.6, and -2.6 ± 1.7 kJ mol^{-1}. Since the procedure for the combustion experiments and the methodology to determine the enthalpy of formation in condensed state are the same for each pair of isomers like the equivalent of the calorimeter, calibration, auxiliary substances used, $\Delta_f H^o_m(H_2O, 298.15\ K)$, $\Delta_f H^o_m(CO_2, 298.15\ K)$, etc. we expect that the errors associated with these variables are largely cancelled when isomers are compared. As such, we consider the isomer differences to be real.

$$1\text{-}C_{10}H_7\text{-}COOH\ (g) \rightleftharpoons 2\text{-}C_{10}H_7\text{-}COOH\ (g) \qquad (6)$$

$$2\text{-}C_4H_3O\text{-}COOH\ (g) \rightleftharpoons 3\text{-}C_4H_3O\text{-}COOH\ (g) \qquad (7)$$

$$2\text{-}C_4H_3S\text{-}COOH\ (g) \rightleftharpoons 3\text{-}C_4H_3S\text{-}COOH\ (g) \qquad (8)$$



Scheme 1

How should we compare arenoic acids? A thermochemical analysis

Consider the unsubstituted arenoic (arenecarboxylic) acids. As noted above, there are measured values of the gas phase enthalpies of formation of those of benzene, naphthalene (the 1- and 2-isomers), furan (both the 2- and 3- isomers) and thiophene (the 2- and 3- isomers). Table 4 presents these values and compares them with those for the corresponding hydrocarbon: the enthalpies of formation of the arenoic acid and the parent ring system, and their difference are given.

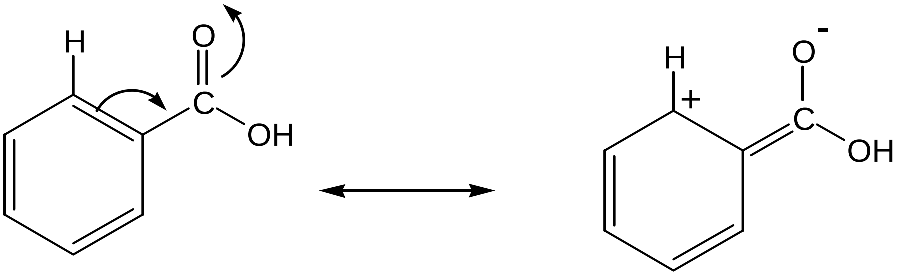
Interestingly, all of these difference- values are roughly the same suggesting a very similar interaction of the carboxyl group with the ring systems. It would be useful to make a similar comparison with compounds containing the same ring systems and other substituents containing carbonyl groups, such as the aldehyde, the methyl ketone, or even the methyl carboxylate ester. However, the desired thermochemical data are generally absent for many such groups, and in no case are they available for the derivatives of all four of our ring systems.

Table 4. Enthalpies of formation in the gas state, $\Delta_f H^o_m(g)$, at $T = 298.15$ K, of arenoic acids and their parent ring systems

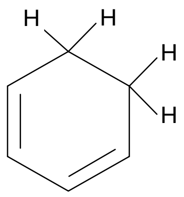
Arenoic acids	$\Delta_f H^o_m(g)$	Parent ring	$\Delta_f H^o_m(g)$	Difference
Benzoic acid[a]	-294.0 ± 2.2	Benzene[a]	82.6 ± 0.7	376.6 ± 2.3
1-Naphthoic acid	-222.7 ± 1.3	Naphthalene[a]	150.3 ± 1.4	373.0 ± 1.9
2-Naphthoic acid	-231.1 ± 1.7			381.4 ± 2.2
2-Furancarboxylic acid	-410.3 ± 2.1	Furan[a]	-34.8 ± 0.7	375.5 ± 2.2
3-Furancarboxylic acid	-415.8 ± 1.7			381.0 ± 1.8
2-Thiophenecarboxylic acid	-259.2 ± 1.9	Thiophene[a]	115.0 ± 1.0	374.2 ± 2.1
3-Thiophenecarboxylic acid	-261.8 ± 1.7			376.8 ± 2.0

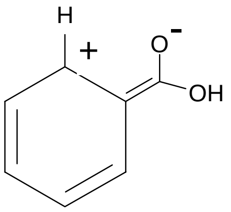
[a] Enthalpies of formation of benzoic acid and of the parent ring systems are all taken from ref. 13.

The electronic structures of these arenoic acids include dipolar resonance contributions, *i.e.*, there are ionic resonance structures.



These are formally derivatives of the dihydrogenated parent ring system, where two endocyclic methine (=CH-) groups in the aromatic species have been changed into endocyclic methylenes ($-CH_2-$) but now one of these methylenes has an appended exocyclic anionic $=C(O^-)OH$ group and the other is now the cationic $–CH^+-$.





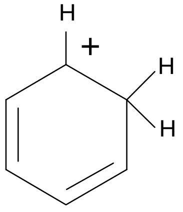


Table 5 gives the difference of the gas phase enthalpies of formation of the arenoic acid and the simple dehydrogenated ring system, *e.g.*, benzene is compared with 1,3-cyclohexadiene, furan with its 2,3-dihydro derivative.

Table 5. Enthalpies of formation in the gas state, $\Delta_f H^o_m$(g), at T = 298.15 K, of arenoic acids and their dihydrogenated parent ring systems

Arenoic acids	$\Delta_f H^o_m$(g)	Dihydrogenated parent ring system	$\Delta_f H^o_m$(g)	Difference
Benzoic acid[a]	-294.0 ± 2.2	1,3-cyclohexadiene[b]	104.6 ± 0.6	398.6 ± 2.3
1-Naphthoic acid	-222.7 ± 1.3	1,2-dihydronaphthalene[c]	[126.8 ± 2.4]	349.5 ± 2.7
2-Naphthoic acid	-231.1 ± 1.7			357.9 ± 2.9
2-Furancarboxylic acid	-410.3 ± 2.1	2,3-dihydrofuran[b]	-72.3 ± 0.4	338.0 ± 2.1
3-Furancarboxylic acid	-415.8 ± 1.7			343.5 ± 1.7
2-Thiophenecarboxylic acid	-259.2 ± 1.9	2,3-dihydrothiophene[a]	90.7 ± 1.8	349.9 ± 2.6
3-Thiophenecarboxylic acid	-261.8 ± 1.7			352.5 ± 2.5

[a] Enthalpies of formation of benzoic acid and 2,3-dihydrothiophene from ref. 13.

[b] Enthalpies of formation of 1,3-cyclohexadiene and of 2,3-dihydrofuran are from ref. 14. For 1,3-cyclohexadiene, see also the analysis by Liebman in ref. 15.

[c] The enthalpy of formation of 1,2-dihydronaphthalene was estimated by summing the liquid-phase enthalpy of formation given in Pedley,[13] and equating its enthalpy of vaporization with that of 1,2,3,4-tetrahydronaphthalene (difference of recommended enthalpies of formation in liquid and gaseous phases), a hydrocarbon of similar molecular weight, volume and shape.

Perhaps not surprisingly, the difference in enthalpy of formation for benzene is considerably larger than that of furan. We are, of course, used to saying that the ring in benzene is considerably more aromatic than that in furan. Perhaps more surprising is the closeness of the difference values we find for furan, naphthalene and thiophene.

The final comparison acknowledges the positive charge in the ring system, and so compares the enthalpy of formation of the arenoic acid with that of the protonated ring system; see Table 6.

We are considering the most stable protonated species, as determined by measurements of the gas-phase proton affinity.) Again, the enthalpy-of-formation- difference from benzene is considerably larger than that of furan. As above, we are surprised by the closeness of the difference values we find for furan, naphthalene and thiophene.

Enthalpies of formation of benzoic acid and of hydrocarbons all taken from Pedley.[13]It would appear that the arenoic acids are related by a roughly constant difference from the parent ring system more than they are to the corresponding dihydrogenated or protonated species. Perhaps this is not surprising, in that we do not expect substituents to strongly disrupt aromatic systems, whilst hydrogenation and protonation most assuredly do.

Table 6. Enthalpies of formation in the gas state, $\Delta_f H^o{}_m(g)$, at T = 298.15 K, of arenoic acids and their protonated parent ring systems

Arenoic acids	$\Delta_f H^o{}_m(g)$	Protonated parent ring system	$\Delta_f H^o{}_m(g)$[a]	Difference
Benzoic acid[b]	-294.0 ± 2.2	Benzene	908.4	1202
1-Naphthoic acid	-222.7 ± 1.3	Naphthalene	883.6	1106
2-Naphthoic acid	-231.1 ± 1.7			1115
2-Furancarboxylic acid	-410.3 ± 2.1	Furan	698.0	1108
3-Furancarboxylic acid	-415.8 ± 1.7			1113
2-Thiophenecarboxylic acid	-259.2 ± 1.9	Thiophene	836.2	1095
3-Thiophenecarboxylic acid	-261.8 ± 1.7			1098

[a] These values were estimated by summing the enthalpies of formation of the gaseous hydrocarbons, from Pedley, ref. 13, that of H^+ from Wagman *et al*. in ref. 16, and the proton affinity (with a negative sign) from Hunter and Lias, ref. 17.

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María Victoria Roux was born in Madrid (Spain). She received her Master´s degree (1968) and her PhD (summa cum laude) in Chemistry (1972) at the Complutense University with Professor M. Colomina. In 1972 she was appointed as researcher in the Department of Thermochemistry of the Institute of Physical Chemistry "Rocasolano", where she is Head of the Department of Dynamic and Molecular Structure. She is also the chairperson of the Thermochemistry Working Group of the International Confederation for Thermal Analysis and Calorimetry. Her interest concerns the relation structure-energy in organic molecules. She is author of ca. 100 scientific publications, patents and review articles.

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Joel F. Liebman received his B.S. degree at Brooklyn College and his Ph.D. degree (with Leland C. Allen) at Princeton University. His postdoctoral experience was first with A. David Buckingham and John W. Linnett at Cambridge University as a NATO Postdoctoral Fellow, and then with Thomas D. Coyle at the U.S. National Institute of Standards and Technology as an NRC-NBS Postdoctoral Associate. He subsequently joined the Department of Chemistry and Biochemistry of the University of Maryland, Baltimore County, where he is a Professor of Chemistry. His research is heavily collaborative with numerous ongoing projects with friends and coworkers, both experimentalists and fellow theorists. Besides his interests in the energetics of organic molecules and related ions, his studies include the chemistry of compounds containing boron, fluorine, and the noble gases. His responsibilities also include editorial activities for journals and book series. He teaches introductory courses for both scientists and nonscientists, and also undergraduate and graduate electives in chemical bonding. He is also an enthusiastic punner, poet, and piano player.