Pure Appl. Chem., Vol. 79, No. 6, pp. 1003–1021, 2007.
doi:10.1351/pac200779061003

Physical origin of chemical phenomena: Interpretation of acidity, basicity, and hydride affinity by trichotomy paradigm*

Zvonimir B. Maksić[1,2,‡] and Robert Vianello[1]

[1]Quantum Organic Chemistry Group, Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, POB 180, 10002 Zagreb, Croatia; [2]Faculty of Science, The University of Zagreb, Horvatovac 102a, 10002 Zagreb, Croatia

Abstract: Some of the most important aspects of modeling in chemistry are discussed in detail. It is argued that the interpretive side of (quantum) chemistry is indispensable, since it gives sense to a myriad of experimental and computational results. The usefulness of some physical modeling is illustrated by the trichotomy approach in rationalizing acidity, basicity, and hydride affinities of neutral organic compounds. According to trichotomy paradigm, the simple chemical reaction of protonation and H^- attachment can be decomposed into three separate sequential steps, which in turn mirror the initial-, intermediate-, and final-state effects. Ample evidence is given, which convincingly shows that the trichotomy approach has some distinct advantages in interpreting aforementioned properties that belong to the most important ones in chemistry and biochemistry.

Keywords: proton affinity; basicity; acidity; hydride affinity; superbases; superacids.

INTRODUCTION

Quantum theory, developed at the beginning of the 20th century, is the greatest scientific revolution in the history of mankind. P. A. M. Dirac [1] in 1929 writes: "The general theory of quantum mechanics is now almost complete…. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble". It is gratifying that the latter stumbling block has been overcome by now. We have witnessed, namely, tremendous advances in natural science due to remarkable development of theoretical methods and their implementation in computers with ever increasing power over a few last decades. It gave rise to a quiet, but permanent scientific (r)evolution, which has dramatically changed modern physics and chemistry. It also increasingly penetrates contemporary molecular biology. It is fitting to say that computational quantum theory tears down boundaries between these three traditional disciplines, unifying them in a unique and universal natural science. Undoubtedly, computational natural science will have important impact on the development of molecular medicine in this century. It is probably not exaggerated to say that computational chemistry is one of the major avenues of research in computational natural science. Indeed, the accuracy of the modern computational chemistry, based on the first principles only, is competitive with many experimental techniques being usually faster and cheaper at the same time [2–7]. The rigorous ab initio procedures provide nowadays an invaluable tool for studying systems not easily

*Paper based on a presentation at the 18th International Conference on Physical Organic Chemistry (ICPOC-18), 20–25 August 2006, Warsaw, Poland. Other presentations are published in this issue, pp. 955–1151.

‡Corresponding author: Tel.: +385 1 4561117; Fax: +385 1 4561118; E-mail: zmaksic@spider.irb.hr

amenable to measurements, to mention only short-lived species, very reactive intermediates, chemical reactions and transition states, interstellar molecules, hazardous materials, etc. Moreover, ab initio and some density functional theory (DFT) methods can be used for predictive purposes in designing new compounds exhibiting desired properties, thus aiding the experimental research leading to industrial applications.

Rigorous theory and accurate calculations, however, do not exhaust the role of theoretical chemistry. Numbers provided by experiments or computations have not much meaning unless interpreted by models obtained by pruning unnecessary details and focusing on the quintessence of the problem. This was nicely put forward by theoretical physicist V. F. Weisskopf: "A real understanding of natural phenomena implies a clear distinction between the essential and peripheral." Thus, modeling is extremely important ingredient of any scientific method. In fact, its role is impossible to overestimate [8–13]. This point deserves some more comments. A salient feature of models is that they represent an approximate description of complex systems called objects or originals. In the modeling process, we deliberately sacrifice perfect truth(fulness), because the object is chipped by neglecting less relevant details. In contrast, a strong emphasis is laid on the most important facets. Hence, the model reflects dominant physical effect(s) and ignores details immaterial for the feature of phenomenon under scrutiny. It follows that good models based on sound physical concepts satisfy Occam's razor criterion [14]. Albert Einstein issued an important warning, however, about the danger of oversimplification by saying "As simple as possible, but not simpler", which should always be kept in mind. It should also be strongly pointed out that the omission of numerous details does not necessarily mean a weakness of the models, since it is overcompensated by a gain in clarity and generality. This pivotal feature enables classification and order for a myriad of experimental and/or computational data. One of the current authors emphasized that "Models (as well as the underlying concepts) provide pervasive physical insight and extract the key features of very complex phenomena thus revealing their essence, simplicity and beauty…. Metaphorically speaking, models extend the range of our senses. They make possible one to mentally 'see' what cannot be seen" [15]. In other words, modeling reduces perplexed problems of the structure of matter to concepts, which are intellectually manageable. It is useful to bear in mind that quantum models provide an important and meaningful link between meticulous and intricate computations on one side and empirical concepts on the other as illustrated by a diagram

rigorous calculations ↔ models ↔ phenomenological concepts

which in turn works reversibly in both directions. The situation in chemistry is particularly favorable, because one is usually more interested in understanding the trend of changes of a particular property in a family of related compounds. In these cases, even a simple model like, e.g., hybridization of atomic orbitals, can offer semiquantitative information on a number of properties of the local covalent bonds [16,17].

An important question arises about the relationship between models and reality. Clearly, models provide an incomplete description of the natural phenomena, but are they only theoretical constructs and artifacts? In our view, a reliable model has a grain of truth. It is true within the limits of the approximation(s) involved in the model and, importantly, it is valid within a carefully established range of applicability of the model—no more than that, but also not less than that at the same time [15].

It is of utmost importance to recall that simple conceptual models have led to great discoveries in molecular science, which cracked some important codes of Nature, more frequently than very detailed accurate calculations, to mention only Pauling's model of the peptide bond and the structure of α-helix and β-pleated sheets [18].

Building on extensive previous results, we felt it is worthwhile to present an interpretation of three elementary, but nevertheless extremely important, chemical reactions in chemistry and biochemistry—protonation, deprotonation, and hydride ion addition reactions—based on the trichotomy paradigm. In each case, the reaction is decomposed into three stages, which is a consequence of idealization, i.e., modeling. In spite of that, three contributions add up to a rigorous formula, which is, in principle, exact.

It is important to point out that each of the three steps corresponds to a simple and intuitively appealing picture of the aforementioned chemical reactions.

PROTON AFFINITIES AND BASICITIES OF NEUTRAL ORGANIC BASES AND SUPERBASES

Basicity and its counterpart acidity belong to the most fundamental notions of chemistry and biochemistry. According to Brønsted, basicity is defined as affinity of the base toward a proton. Let us imagine that the proton is very far from a base. Since quantum mechanics is a holistic theory, it considers the system containing interacting subunits in its entirety. Consequently, the physical picture of the protonation process occurring in the gas phase can be divided into three distinct sequential steps [19]: (a) removal of an electron from the base in question to give a radical cation, (b) attachment of the ejected electron to the incoming proton to form the hydrogen atom, and (c) creation of the chemical bond between the newly formed radical cation and the hydrogen atom. Notice that the first act requires a price, which should be paid for protonation. It is given by the ionization energy of a base. This is, however, generously rewarded by the electron affinity of the proton with 313.6 kcal mol^{-1}, which greatly contributes to the overall exothermicity of the process. It is taken for granted here that the proton donor is not a part of the process, which is justified if genuine basicity of a compound in question is considered. Trichotomy approach (a)–(c) has a high cognitive value, enabling classification of the studied compounds into three categories depending on whether the initial-, intermediate-, or final-state effect is predominant. Initial-state effects on the gas-phase basicities of neutral Brønsted bases are reflected in Koopmans' ionization energies [19] calculated in the frozen electron density and clamped atomic nuclei approximation within the one-electron picture. The latter implies ejection of an electron from the Hartree–Fock (HF) *n*-th molecular orbital (MO). Thus, the ionization is assumed to be an instantaneous event at the moment $t_0 = 0$. In this case, Koopmans' ionization energies depend exclusively on the electron distribution of the neutral base under scrutiny and mirror genuine properties of the initial state. The second or intermediate stage of the protonation process takes into account that ionization is not a sudden event, but occurs in a real time $t_0 + \Delta t$ instead. Hence, both electrons and nuclei relax in the radical cation, giving rise to the stabilizing relaxation energy. Finally, the bond formation between created radical cation of the base and hydrogen atom is given by the homolytic bond association energy term, which represents properties of the protonated conjugate acid—the final-state effect. This simple physical picture is easily put in mathematical garments [19] as follows. The intrinsic gas-phase absolute proton affinity (APA) is obtained in a standard way

$$B + H^+ \rightarrow (B_\alpha H)^+ - APA(B_\alpha) \tag{1}$$

as a negative value of the enthalpy for the reaction 1, where B stands for a base in question and subscript α denotes the atomic site of the proton attack. It has two components: $APA(B_\alpha) = \Delta E + \Delta(pV)$, where ΔE denotes the change in the total molecular energy between the base B and its conjugate acid BH^+, including both the zero-point vibrational energy and the finite temperature (298.15 K) correction. The second component $\Delta(pV)$ represents the pressure-volume work contribution. Ionization is given by

$$B - e^- \rightarrow B_\alpha^{\bullet +} - IE(B)_1^{ad} \tag{2}$$

Here, $IE(B)_1^{ad}$ signifies the first adiabatic ionization energy describing ejection of the least bound electron and simultaneous formation of the base radical cation denoted by $B_\alpha^{+\bullet}$. The electron is captured by the incoming proton

$$H^+ + e^- \rightarrow H^\bullet + EA(H^+) \tag{3}$$

where $EA(H^+)$ is the electron affinity of the proton being 313.6 kcal mol^{-1} [21]. The bond association energy $(BAE)_\alpha^+$ is given by eq. 4

$$B_\alpha^{\bullet+} + H^\bullet \rightarrow (B_\alpha H^+) + (BAE)_\alpha^+ \quad (4)$$

Finally, the relaxation energy upon ejection of an electron is described by

$$E(ei)^{(n)}_{rex} = IE(B)_n^{Koop} - IE(B)_1^{ad} \quad (5)$$

Combining eqs. 1–5, one obtains

$$APA(B_\alpha) = -IE(B)_n^{Koop} + E(ei)^{(n)}_{rex} + (BAE)_\alpha^+ + 313.6 \text{ kcal mol}^{-1} \quad (6)$$

It should be pointed out that eqs. 1–4 represent a customary thermodynamic cycle. However, inclusion of the Koopmans' ionization term is crucial, since it mirrors genuine properties of the initial state, enabling delineation of the latter from the final-state effect exhibited by the created protonated form. Formula 6 is, in principle, exact, and the only approximations involved are those introduced by computations of single terms. Two points deserve a comment. Firstly, it should be emphasized that Koopmans' ionization is calculated in the HF approximation. We discussed its performance in some detail [22]. It turned out that Koopmans' model of calculation of the ionization energies is good, since the relaxation and correlation energy contributions cancel to a great deal. Rich experimental evidence corroborates this conclusion. It was found that the one-electron HF picture is very useful in rationalizing the photoelectron spectra [23–25]. Moreover, there is growing evidence that the MO concept itself has a touch of reality, particularly for peripheral orbitals [26–29]. Having said that, however, it should be kept in mind that the initial-state effect is described in an approximate way. If this is so, then the relaxation term $E(ei)^{(n)}_{rex}$ is given approximately too. This is not a serious drawback, because we shall mostly consider relative values measured against a gauge compound within a set of closely related molecules (vide infra). Secondly, a very important part of the trichotomy analysis is the fact that the frontier highest occupied molecular orbital (HOMO) is not necessarily the most important orbital in the protonation. Generally, the MO playing the leading role in the attachment of a proton is called PRIMO (principal molecular orbital). It is the MO that participates most directly in the creation of a new chemical bond with the incoming proton such as, e.g., the MO describing a sigma lone pair of the basic nitrogen atom.

In order to interpret the trend of changes in the APAs along a series of compounds possessing the same functional group or atom to be protonated, it is convenient to select a standard (parent) compound, abbreviated as **st**, serving as a reference. Then the variation in the APAs obtained by $\Delta[APA(\mathbf{B}_\alpha)]$ is measured relative to APA(**st**). The difference can be resolved into three contributions according to triadic formula

$$\Delta[APA(\mathbf{B}_\alpha)] = APA(\mathbf{B}_\alpha) - APA(\mathbf{st}) = [-\Delta(IE)_{\alpha,n}^{Koop}; \Delta E(ei)^{(n)}_{\alpha,rex}; \Delta(BAE)_\alpha^+] \quad (7)$$

where the square brackets denote summation of the three bordered terms and the differences Δ explicitly read as follows:

$$\Delta(IE)_{\alpha,n}^{Koop} = IE(\mathbf{B}_\alpha)_{\alpha,n}^{Koop} - IE(\mathbf{st})_{\beta,m}^{Koop} \quad (8a)$$

$$\Delta E(ei)^{(n)}_{\alpha,rex} = E(ei)(\mathbf{B}_\alpha)^{(n)}_{\alpha,rex} - E(ei)(\mathbf{st})^{(m)}_{\beta,rex} \quad (8b)$$

$$\Delta(BAE)_\alpha^+ = BAE(\mathbf{B}_\alpha)_\alpha^{\bullet+} - BAE(\mathbf{st})_\beta^{\bullet+} \quad (8c)$$

It should be noted that indices β and *m* could be different in principle from α and *n*, respectively, implying that the sites of protonation in **B** and **st** could differ in principle. Triadic analysis embodied in eqs. 6 and 7 proved useful in rationalizing proton affinities of neutral bases, and according to Deakyne [30] it has some advantages over alternative interpretive schemes.

We shall analyze the intrinsic basicity of non-ionic organic bases and superbases as reflected in their gas-phase proton affinities by using several theoretical methods depending on the families of molecules to be examined. The nitrogen, phosphorus, and carbon atoms as the basic sites will be discussed. We shall commence with the $NH_{3-m}(Me)_m$ (m = 0–3) family of compounds and continue with the sys-

tems depicted in Fig. 1. Their proton affinities and triadic components are presented in Table 1. Methylamines have been studied by the MP2(fc)/6–311+G(d,p)//B3LYP/6–31G(d) [19], thereafter denoted as MP2. Perusal of the data reveals a good agreement with the experiment for the first adiabatic ionization energy and the gas-phase proton affinities. One observes a sharp decrease in the $(IE)_1^{Koop}$ term with every additional methyl group, which implies a smaller price to be paid in terms of energy in ejecting one electron from the nitrogen unshared electron pair placed in the HOMO. Hence, Koopmans' ionization strongly enhances basicity in this group of molecules. The relaxation energy is practically constant, whereas the bond association term decreases with the number of methyl groups. The latter feature diminishes basicity, but Koopmans' term prevails. Consequently, the amplified basicity along the series is a result of the initial-state effect [19]. In order to test the DFT methods, which are more practical in large systems, some B3LYP/6–311+G(2df,p)//B3LYP/6–31G(d) calculations (thereafter denoted as B3LYP) were also carried out. The corresponding results are given within squared brackets in Table 1. The overall agreement between the MP2 and DFT results is good. However, there are also some discrepancies, which imply that results should be taken with due care. Generally, accordance with the available experimental data, which are unfortunately scarce, is reasonable for all molecules examined (Table 1). Comparison of APAs of NH_3 and methanimine **1** shows that these two widely different types of nitrogen atoms possess practically the same intrinsic basicity as evidenced by the MP2 results and

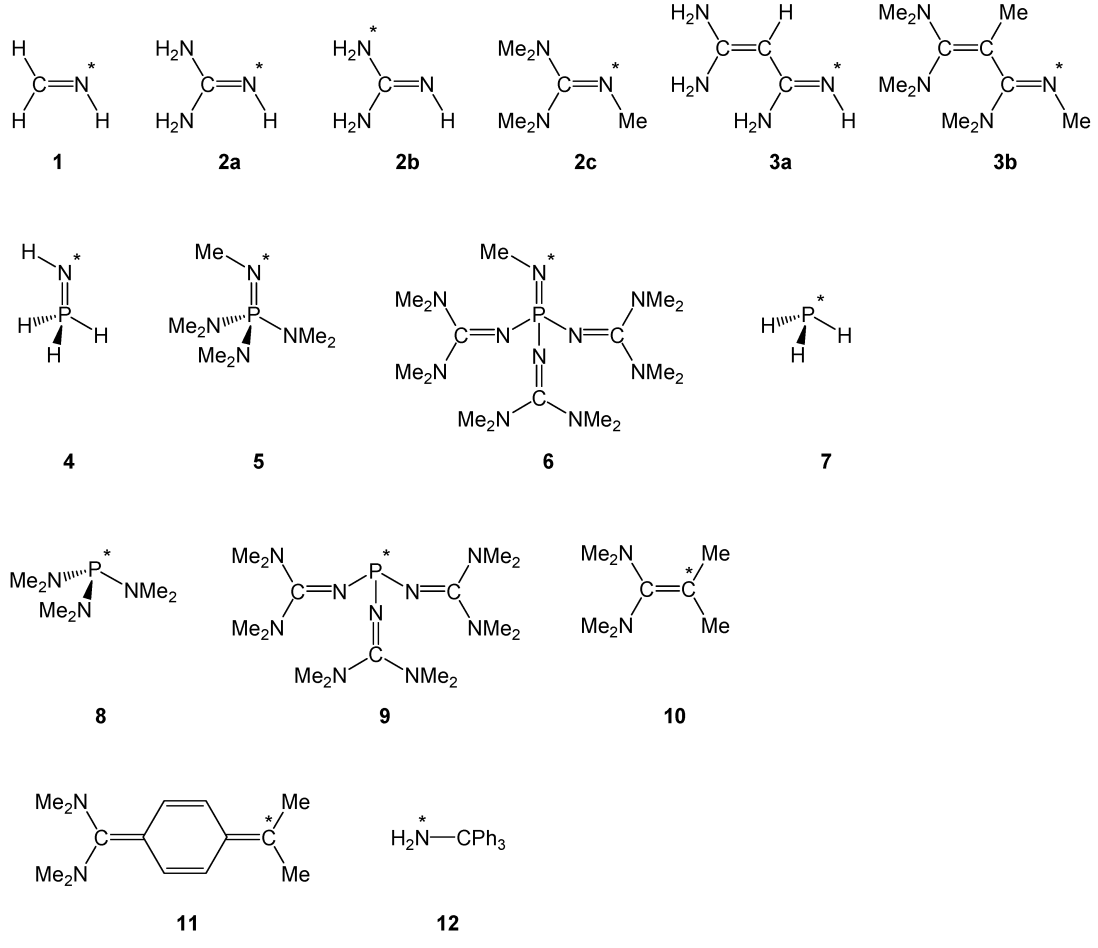


Fig. 1 Schematic representation of bases and superbases investigated in this work. The protonation center is denoted by an asterisk.

Table 1 Theoretical proton affinities of some selected neutral bases and superbases and their decomposition according to triadic analysis. The experimental data are given when available (in kcal mol^{-1}). Theoretical methods employed are cited in the footnote.

Molecule	$(IE)_{n,\alpha}^{Koop}$	$E(ei)^{(n)}_{rex}$	$(IE)_1^{ad}$	$(BAE)_\alpha^{\bullet+}$	APA
NH_3	$(270.3)_1^a$	41.8	228.5 (232.2 ± 0.5)[c]	120.2	205.3 (204.0)[c]
	$[271.2]_1^b$	[36.7]	[234.5]	[121.5]	[200.6]
NH_2Me	$(246.3)_1^a$	40.6	205.7 (205.2 ± 2.3)[c]	107.8	215.7 (214.9)[c]
$NHMe_2$	$(231.4)_1^a$	41.5	189.9 (190.0 ± 1.8)[c]	98.9	222.6 (222.2)[c]
NMe_3	$(221.2)_1^a$	41.2	180.0 (181.0 ± 1.2)[c]	93.3	226.9 (226.8)[c]
	$[222.0]_1^b$	[45.2]	[176.8]	[88.3]	[225.1]
1	$(271.1)_1^a$	43.1	228.6 (229.8)[c]	121.8	206.8 (203.8)[c]
	$[271.9]_1^b$	[45.1]	[226.8]	[120.4]	[207.2]
2a	$(267.7)_2^a$	70.5	197.2	117.4	233.8 (235.7)[c]
2b	$(231.6)_1^a$	34.4	197.2	85.2	$201.6\ (200.7)_{G2(MP2)}$
2c	$[240.5]_3^b$	[74.3]	[166.2]	[104.8]	[252.2]
3a	$(259.7)_3^b$	98.3	161.4	104.5	256.7
3b	$[234.0]_4^b$	91.5	142.5	94.8	265.9
4	$(256.0)_2^a$	57.9	198.1	116.7	$232.2\ (225.8)_{G2}$
	$[258.2]_2^b$	55.1	203.1	116.7	227.2
5	$[215.9]_1^b$	[63.9]	[152.0]	[99.0]	[260.7]
6	$[197.3]_1^b$	[75.6]	[121.7]	[95.3]	[287.3]
7	$[243.9]_1^b$	[17.3]	[226.6]	[100.0]	[187.0] (188.0)[c]
8	$[198.2]_1^b$	[46.6]	[151.6]	[80.5]	[242.6] (242.5)[c]
9	$[165.8]_1^b$	[49.6]	[116.2]	[81.3]	[278.8]
10	$[172.8]_1$	[30.1]	[142.7]	[79.6]	[250.5]
11	$[131.6]_1$	[12.1]	[119.5]	[79.4]	[273.5]
12	$(259.8)_7^a$	72.2	187.6	101.1	227.1
13	$[243.5]_5^b$	116.4	127.1	95.8	282.3
14	$[234.3]_5^b$	112.7	121.6	95.1	287.1
15	$[228.1]_5^b$	113.1	115.0	94.7	293.3

[a]MP2(fc)/6–311+G(d,p)//B3LYP/6–31G(d) results.
[b]Results of B3LYP/6–311+G(2df,p)//B3LYP/6–31G(d) method used in the present work are given within square brackets.
[c]The experimental data are taken from ref. [21]. The G2(MP2) and G2 computational results are given for **2b** and **4**, respectively.

experimental measurements. Interestingly, all three terms are also very close, if MP2 results are considered. More specifically, APA(**1**) – APA(NH_3) = [–1.4; 1.3; 1.6] = 1.5 kcal mol^{-1}, implying that methanimine is slightly more basic as a result of the favorable contributions from the relaxation energy and the bond association energy. Interestingly, Koopmans' term predicts this molecule to be less basic than NH_3 if only the properties of the initial neutral molecule are taken into account. However, the methanimine framework is more flexible in accommodating NH_2 substituents as in guanidine **2a**. This has important consequences for the properties of the latter compound, which is substantially more basic than NH_3 and **1** for two reasons. First, the σ-lone par of the imine nitrogen is placed in the PRIMO, which is HOMO-1 (Scheme 1). In spite of the fact that it is not the outermost orbital, its orbital energy is higher than HOMOs in NH_3 and methanimine **1**. More importantly, the relaxation energy in guanidine is considerably larger, being 70.5 kcal mol^{-1}. If we choose NH_3 as a gauge molecule, then one can safely state that high basicity of **2a** is a consequence of the reorganization energy in the **2a**$^{\bullet+}$ radical cation, APA(**2a**) – APA(NH_3) = [2.6; 28.7; –2.8] = 28.5 kcal mol^{-1}, thus proving the point. In this connection, it is interesting to make a digression and take a look at the protonation of guanidine from a different angle, which is offered by homodesmotic reactions [31]. Let us try to estimate the cationic resonance stabilization in conjugate acid $(H_2N)_2C{=}NH_2^+$ in the following way [32]:

molecule	HOMO	HOMO–1	HOMO–2	HOMO–3	HOMO–4	HOMO–5	HOMO-6
NH_3	(-0.43220)						
2a/**2b**	$(-0.36949)_{2b}$	$(-0.42604)_{2a}$					
4	-0.36524	(-0.41145)					
12	-0.31158	-0.32598	-0.32719	-0.33820	-0.34110	-0.34611	(-0.41400)
14	-0.19115	-0.31220	-0.32084	(-0.34970)			
$CN\text{-}COO^-$	-0.24205	(-0.25967)					
$CN\text{-}CH_2O^-$	-0.15972	(-0.17608)					

Scheme 1 Selected MOs together with their orbital energies [HF/6–311+G(d,p)//B3LYP/6–31G(d) results; in a.u.] for some acids and bases discussed in the text illustrating the importance of orbitals lying lower than HOMO, which play the most significant role in the protonation reaction (PRIMOs, given within round brackets).

$$(H_2N)HC{=}NH + H_2C{=}CH_2 = (H_2N)HC{=}CH_2 + H_2C{=}NH + \varepsilon_1 - E_{conj}^{(1)} \quad (9)$$

$$(H_2N)_2C{=}NH + H_2C{=}CH_2 = (H_2N)_2C{=}CH_2 + H_2C{=}NH + \varepsilon_2 - E_{conj}^{(2)} \quad (10)$$

If the conjugation interactions between the NH_2 group(s) and the C=C double bonds ε_1 and ε_2 were negligible, then a change in energy of reactions 9 and 10 would give $E_{conj}^{(1)}$ and $E_{conj}^{(2)}$, which would directly provide conjugation in formamidine and guanidine, respectively. This is not the case, however, since the rotation barrier in aminoethene is not zero. If the nitrogen lone pair of electrons assumes an orientation, which would prevent π-conjugation, then the total electronic energy rises by 5.2 kcal mol^{-1}, according to the MP2(fc)/6–311+G(d,p)//HF/6–31G(d) calculations [32], which represents a reasonable estimate of the energy ε_1. Then the conjugation effect in diaminoethene can be deduced by homodesmotic reaction

$$(H_2N)_2C{=}CH_2 + H_2C{=}CH_2 = 2\ (H_2N)HC{=}CH_2 + 2\ \varepsilon_1 - \varepsilon_2 \quad (11)$$

The adopted model yields ε_2 = 13.6 kcal mol^{-1}. By using eqs. 9 and 10, one obtains $E_{conj}^{(1)}$ = 16.1 and $E_{conj}^{(2)}$ = 27.8 in kcal mol^{-1}. It appears that the conjugation effect in the initial bases formamidine and guanidine is considerable due to the significant π-back bonding effects of electron lone pairs. However, the corresponding cationic resonance effect triggered by protonation is much stronger. *Voilá*:

$$(H_2N)HC{=}N^+H_2 + H_2C{=}CH_2 = (H_2N)HC{=}CH_2 + H_2C{=}N^+H_2 + \varepsilon_1 - E^+_{res}{}^{(1)} \quad (12)$$

$$(H_2N)_2C{=}N^+H_2 + H_2C{=}CH_2 = (H_2N)_2C{=}CH_2 + H_2C{=}N^+H_2 + \varepsilon_2 - E^+_{res}{}^{(2)} \quad (13)$$

It turns out that $E^+_{res}{}^{(1)}$ and $E^+_{res}{}^{(2)}$ are 34.7 and 51.5 kcal mol^{-1}, respectively, thus indicating that an increase in the stabilization of conjugate acids of formamidine and guanidine is $E^+_{res}{}^{(1)} - E_{conj}^{(1)}$ = 18.6 and $E^+_{res}{}^{(2)} - E_{conj}^{(2)}$ = 24.1, correspondingly. An alternative way in estimating the cationic resonance in protonated guanidine [32] shows that it lies within the range of 24–27 kcal mol^{-1}. A large cationic resonance contribution to basicity of guanidine is compatible with a high relaxation energy term $E(ei)^{(n)}{}_{rex}$. It should be pointed out that these two entities are broadly similar, but they are by no means identical. For one thing, $E(ei)^{(n)}{}_{rex}$ describes relaxation of the radical cation $B^{\bullet+}$, whereas the cationic resonance gives stabilization of conjugate acid BH^+ after completion of the protonation process.

It is of interest to find a difference in APAs between imino and amino nitrogen in guanidine. A triad APA(**2a**) – APA(**2b**) = [–36.1; 36.1; 32.2] = 32.2 kcal mol^{-1} shows that the imino position is more basic by 32.3 kcal mol^{-1}, which is exactly a difference between the $(BAE)^{\bullet+}$ terms. The latter is in harmony with the hybridization concept, which indicates that sp^2 hybrids form stronger bonds than sp^3 ones [10,16]. It is noteworthy that a difference in basicity between two basic sites in ambident compounds is always given by a difference in the bond association energies, because the first two terms should exactly cancel out (see eq. 5). It should be noted in passing that a negative contribution arising from Koopmans' term is due to the fact that amino nitrogen lone pair is described by HOMO, which is higher in energy than HOMO-1 (i.e., PRIMO orbital) accommodating the σ-lone pair of imino nitrogen (Scheme 1).

Extension of the π-network in **3a** leads to an appreciable increase in the relaxation energy (91.0 kcal mol^{-1}) and the proton affinity (246.2 kcal mol^{-1}) [33], which is in harmony with the enlarged number of cationic resonance structures. It is noteworthy that **3a** qualifies as a superbase according to a widely accepted threshold of 245.3 kcal mol^{-1} given by the proton affinity of DMAN [34]. The present B3LYP results for **2c** and **3b** confirm this conclusion. The respective APAs are 252.2 and 265.9 kcal mol^{-1}. The relaxation term in the latter compound is larger by 17.2 kcal mol^{-1}, thus proving the point.

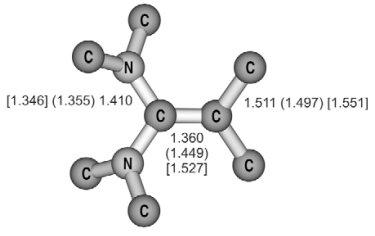
Let us examine simple phosphazenes **4–6** by considering B3LYP results [35]. The parent compound **4** is more basic than NH_3, because APA(**4**) – APA(NH_3) = [14.3; –16.3; 29.5] = 27.5 kcal mol^{-1}. The first two terms practically cancel out, and the decisive edge is given by higher bond association en-

ergy. It follows that a predominant influence is given by a final-state effect. An opposite situation is found in phosphazene **4** substituted by three NMe_2 groups and one methyl group giving **5**. The proton affinity is increased by 60 kcal mol^{-1}, and triadic analysis yields APA(**5**) – APA(NH_3) = [55.3; 26.9; –22.5] = 59.7 kcal mol^{-1}. It appears that the relaxation term and the bond association energy contribute together 4.4 kcal mol^{-1} to the amplified APA, with the former term prevailing over the diminishing effect of the $(BAE)^{\bullet+}$ energy. A lion's share in enhancement of basicity of **5** belongs to Koopmans' ionization energy, implying that HOMO of **5** is by 55.3 kcal mol^{-1} higher than that in NH_3. Therefore, superbasicity of **5** is a result of the initial-state effect supported by the intermediate relaxation effect. Replacement of the dimethylamino groups in **5** by bis(dimethylamino)guanidine moieties in **6** is of interest, since the latter compound attains a highly basic APA of 287.2 kcal mol^{-1} [35]. Triadic analysis reveals that an increase of 26.6 kcal mol^{-1} is again a combined result of the initial and intermediate stages in the protonation process. Specifically: APA(**6**) – APA(**5**) = [18.6; 11.7; –3.7] = 26.2 kcal mol^{-1}.

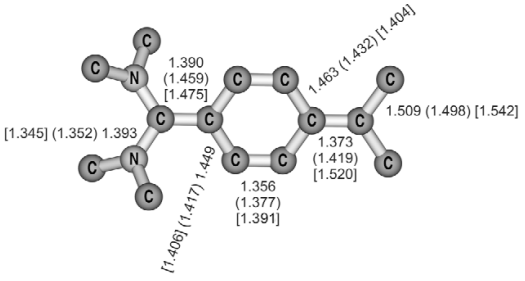
Recently, it was found that phosphorus could be a very basic atom in some specific bonding situations [36]. Hence, let us briefly discuss APAs of compounds **7–9**, which are 187.2, 242.6, and 278.8 kcal mol^{-1}, respectively [36]. First, a difference in APA relative to NH_3 reveals that APA(**7**) – APA(NH_3) = [27.3; –19.4; –21.4] = –13.5 kcal mol^{-1}, indicating that PH_3 is less basic because of considerably smaller relaxation and bond association energies. The origin of the strong amplification of basicity of phosphine (PH_3) derivatives upon NMe_2 and $N{=}C(NMe_2)_2$ triple substitution is easily established by the corresponding triads, which yield APA(**8**) – APA(**7**) = [45.7; 29.3; –19.6] = 55.4 kcal mol^{-1} and APA(**9**) – APA(**7**) = [78.1; 32.3; –18.8] = 91.6 kcal mol^{-1}. It follows that respectable basicity of **8** and **9** is a result of synergism between the initial-state effect and intermediate relaxation energy.

It is perhaps surprising that the carbon atom can be very basic, if placed in the appropriate chemical environment. In order to illustrate this claim, we examine here two compounds, **10** and **11**. Protonation at the carbon atom possessing two methyl groups yields APAs of 250.5 and 273.5 kcal mol^{-1}, respectively. Triadic analysis shows that the difference in proton affinity APA(**11**) – APA(**10**) = [41.2; –18.0; –0.2] = 23.0 kcal mol^{-1}, which is a consequence of the increased orbital energy of the HOMO in **11**, thus reflecting a predominant initial-state effect. Intuitively, one would expect an overwhelming relaxation effect instead, in view of the aromatization of the central ring induced by protonation in $\mathbf{11H^+}$. A closer look at the structural parameters (Scheme 2) reveals that the six-membered ring in $\mathbf{11H^+}$ does undergo aromatization indeed, but it is overshadowed by stronger cationic resonance effect in $\mathbf{10H^+}$, which leads to a substantially higher relaxation in the smaller system (by 18 kcal mol^{-1}). This finding becomes apparent by inspecting the changes in relevant geometrical data for systems **10** and **11** induced upon electron ejection in radical cation and afterwards by subsequent addition of hydrogen atom to produce protonated form (Scheme 2). The reason behind the higher relaxation energy in $\mathbf{10^{\bullet+}}$ is that the protonated carbon is directly bound to the $C(NMe_2)_2$ fragment. In contrast, this fragment is placed at the other end of the $\mathbf{11H^+}$ system. Concomitantly, a smaller portion of the excess positive charge is left for the cationic resonance.

Triphenylmethyl (trityl) moiety is widely used in organic synthesis as a protecting group. It is, therefore, of interest to examine its effect on basicity of, e.g., NH_2 group as in **12**. The MP2 calculations [37] show that APA(**12**) – APA(NH_3) = [11.4; 35.5; –20.4] = 26.5 kcal mol^{-1}, meaning that a prevailing influence is exerted by the relaxation effect. A noteworthy detail is given by finding that PRIMO is a relatively low-lying HOMO-6 orbital (Scheme 1).



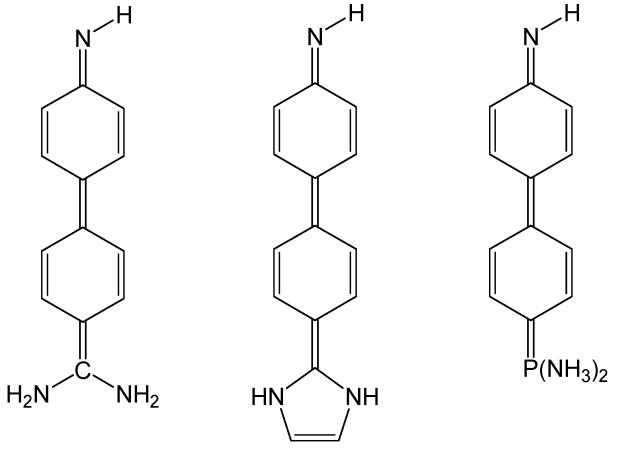
10



11

Scheme 2 Relevant structural parameters for bases **10** and **11** in their neutral forms, radical cations (given within round brackets) and protonated structures (placed within square brackets) as obtained by B3LYP/6–31G(d) level of theory. Hydrogen atoms are omitted for clarity.

The aromatic stabilization effect becomes decisive if the aromatization occurs in a domino fashion [38–40]. Representative systems are provided by **13–15** (Fig. 2). They possess the imino spearhead, which is the basic site, and a tail given by either $=C(NH_2)_2$, $=P(NH_2)_3$ fragments or by a 1,3-diamino-2-methylenecyclopentene ring [38]. It appears that all rings in **13–15** undergo aromatization upon protonation and that benzene moieties are rotated by ~33° relative to each other in order to minimize perturbation of their aromatic sextets. The dihedral angle of the plane involving five-membered ring in $\mathbf{14H^+}$ is ~22°. Triadic analysis reveals that APA(**13**) – APA(**1**) = [28.4; 71.3; –24.6] = 75.1; APA(**14**) – APA(**1**) = [37.6; 67.6; –25.3] = 79.9 and APA(**15**) – APA(**1**) = [43.8; 68.0; –25.9] = 85.9 kcal mol^{-1}, indicating that the relaxation energy has a decisive influence on the high basicity in harmony with the aromatic domino effect. We note in passing that the bond association energy diminishes APAs by ~25 kcal mol^{-1}. In contrast, the orbital energies of PRIMOs in **13–15** are higher than in **1** by 28.4, 37.6, and 43.8 kcal mol^{-1}, respectively, thus increasing basicity. It is interesting to note in this respect that the principal MOs in systems **13–15** are HOMO–4 (Scheme 1), and yet they are less stable than HOMO in **1**. This is a rather nice illustration of the fact that peripheral or frontier MOs are not the most important ones in some chemical reactions.



13 **14** **15**

Fig. 2 Extended superbases possessing imine spearhead as a protonation center and differing in the tail of the system.

Finally, one should point out that DFT calculations of APAs in acetonitrile by using the isodensity polarized continuum proved useful in reproducing and predicting pK_a values in the same solvent [41]. Their interpretation is beyond the scope of this article.

DEPROTONATION ENERGIES AND ACIDITIES OF NEUTRAL ORGANIC ACIDS AND SUPERACIDS

Brønsted acidity is defined by the enthalpy change ΔH_{acid} for the gas-phase reaction 14

$$AH \rightarrow A^- + H^+ - \Delta H_{acid}(AH) \tag{14}$$

where ΔH_{acid} is given by $\Delta H_{acid} = \Delta E_{acid} + \Delta(pV)$. Instead of actual deprotonation of the acids AH we shall consider a reverse reaction of protonation of the conjugate base anion A^-. Adopting the trichotomy paradigm, one readily obtains [42]

$$\Delta H_{acid}(AH) = APA(A_\alpha^-) = -IE(A^-)_{n,\alpha}{}^{Koop} + E(ei)^{(n)}{}_{rex} + (BAE)_\alpha{}^\bullet + 313.6 \text{ kcal mol}^{-1} \tag{15}$$

Terms appearing in eq. 15 have their usual meaning. It is important to keep in mind that Koopmans' ionization energy mirrors the effect of the final state (conjugate base A^-) for the deprotonation reaction, whereas the bond association energy describes the influence of the initial state (neutral acid AH). Let us consider acidity of some substituted methanes [43] by using G2(MP2) method. Results are presented in Table 2. The computed ΔH_{acid} enthalpies are within the experimental errors [21]. It is useful to keep in mind that stronger acids have smaller numerical ΔH_{acid} values, which imply easier release of the acidic proton. The parent compound CH_4 will serve as a gauge molecule in discussing variation in the proton affinities of the corresponding conjugate bases. The influence of halogen atoms F, Cl, and Br is described by the following triads: Δ[APA(F)] = [–17.6; 13.3; –3.1] = –7.4; Δ[APA(Cl)] = [–33.7; 18.2; –4.9] = –20.4; and Δ[APA(Br)] = [–41.0; 20.4; –3.7] = –24.3 kcal mol^{-1}. It appears that the bond association energy (alias the homolytic C–H bond scission energy) decreases, thus increasing the acidity of methyl halides by 3–5 kcal mol^{-1}. A decisive influence, however, is exercised by Koopmans' ionization energies, which dominate over the increasing relaxation effect. As a net result, the APAs(A^-) are decreased by –4.3, –15.5, and –20.6 kcal mol^{-1}, respectively, thus enhancing acidity. One concludes that the latter is a consequence of a better accommodation of the negative excess charge in the final state. Substantial amplification of acidity is found in NC, CN, and NO_2 substituted methanes as evidenced by ΔH_{acid} values of 383.8, 374.9, and 357.8 kcal mol^{-1}, correspondingly. Triple substitution by the cyano group gives $\Delta H_{acid}[CH(CN)_3]$ = 302.4 kcal mol^{-1}, which is already below the superacidity threshold defined by the gas-phase acidity of sulfuric acid [$\Delta H_{acid}(H_2SO_4)$ = 306.3 kcal mol^{-1}]. What is behind all these high acidities? It is a result of a combined effect of three terms appearing in triadic formula. The corresponding triads read: Δ[APA(NC)] = [–16.5; –9.3; –8.5] = –34.3; Δ[APA(CN)] = [–24.6; –10.8; –7.8] = –43.2; Δ[APA(NO_2)] = [–47.8; –8.7; –3.8] = –60.3; and finally Δ[APA($CN)_3$] = [–82.1; –11.1; –22.5] = –115.7 in kcal mol^{-1}, which proves the point. Koopmans' contribution is particularly large in the $CH(CN)_3$ case (–82.1 kcal mol^{-1}). The anion $C(CN)_3^-$ has a planar D_{3h} structure, and its HOMO is very stable. In other words, the excess negative charge is very comfortably distributed over the central carbon atom and three peripheral CN groups. This is not surprising, because there are two very important features of the CN substituent, which make it an ideal acidifying factor in polysubstituted systems. It exhibits large electron-withdrawing ability and has very modest spatial requirements. They make the cyano group a perfect building block in designing organic superacids as we shall see in what follows.

Table 2 Gas-phase acidity of substituted methanes and triadic analysis of absolute proton affinities of their conjugate bases obtained by the G2(MP2) method (in kcal mol^{-1}).[a]

Molecule	ΔH_{acid}(exp)	$(IE)_n^{Koop}$	$E(ei)^{(n)}_{rex}$	$(BAE)^{\bullet}$	APA(A^-)
CH_4	[418.0 ± 3.5]	$(25.2)_1$	23.9	105.8	418.1
CH_3F	[409.0 ± 4.0]	$(42.8)_1$	37.2	102.7	410.7
CH_3Cl	[396.0 ± 3.1]	$(58.9)_1$	42.1	100.9	397.7
CH_3Br	[392.7 ± 3.1]	$(66.2)_1$	44.3	102.1	393.8
CH_3NC	[380.6 ± 2.1]	$(41.7)_1$	14.6	97.3	383.8
CH_3CN	[374.8 ± 2.0]	$(49.8)_1$	13.1	98.0	374.9
CH_3NO_2	[358.0 ± 5.0]	$(73.0)_1$	15.2	102.0	357.8
$CH(CN)_3$		$(107.3)_1$	12.8	83.3	302.4

[a]Koopmans' ionization energies correspond to HF/6–311+G(3df,2p)//MP2(full)/6–31G(d) calculations. The homolytic bond association energies were calculated by the unrestricted G2(MP2) approach. The experimental data (given within square brackets) are taken from reference 21.

We found that cyclic and polycyclic organic compounds provide excellent backbones for neutral superacids. An example *par excellence* is provided by pentacyanocyclopentadiene (PCCP) **16a**, which is one of the simplest organic superacids. We found that conventional PCCP **16a** possessing HC(sp^3)–CN fragment (Fig. 3) is not the most stable tautomer. Instead, the prototropic tautomer **16b** is more stable by 7 kcal mol^{-1}, as obtained by the B3LYP/6–311+G(d,p)//B3LYP/6–31G(d) method [43]. It is in place to point out here that the B3LYP method describes atomic and molecular electron affinities rather well as discussed *in extenso* by Schaefer et al. [44]. Since deprotonation of **16a** and **16b** yields the same conjugate base, which in turn is a planar highly symmetric (D_{5h}) $(CN)_5C_5^-$ anion, the former (less stable) tautomer is more acidic. Specifically, their ΔH_{acid} values are 256.5 and 263.5 kcal mol^{-1}, respectively. Our result was corroborated by a recent experimental work of Richardson and Reed [45], who managed to protonate PCCP anion and provide data, which are in accordance with our prediction of a greater stability of tautomer **16b** possessing keteneimine moiety. The latter was also confirmed by a subsequent ab initio study by Schaefer and coworkers [46]. A triadic analysis of acidity of **16b** relative to parent cyclopentadiene (**CP**) gave APA(**16b**) – APA(**CP**) = [–99.4; 13.1; –3.7] = –90.0 kcal mol^{-1}, providing a convincing evidence that high acidity of **16b** is a consequence of enormous stability of the HOMO in the $(CN)_5C_5^-$ anion [43]. Once again, the final-stage effect proves to be of pivotal importance. We would like to mention in passing that in heavily cyano-substituted polycyclic hydrocarbons possessing a single C–H acidic center, there is usually at least one prototropic tautomer involving =C=NH keteneimine moiety exhibiting the largest stability, to mention only nonacyanofluorene [47], azatriquinanes [48], Rees polycyanated compounds [49], and some other polycyano polycyclic hydrocarbons [50]. It is important to indicate that the anionic resonance is strong in all polycyanated conjugate bases and that it is very efficient in dispersing the negative charge overall in the system. This means that the excess electron density is completely delocalized, thus making organic superacids excellent candidates for formation of weakly coordinated ion pairs.

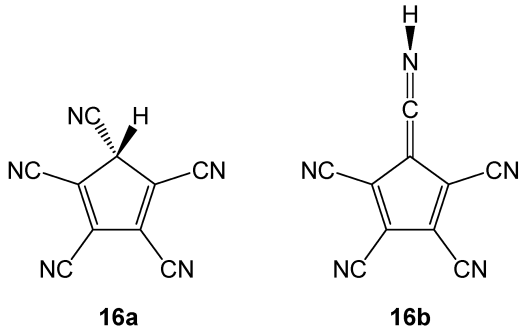


Fig. 3 Prototropic tautomerism of pentacyano-substituted cyclopentadiene. Tautomer **16b** possessing acidic proton as a part of keteneimine fragment is more stable.

A fundamental question of larger acidity of carboxylic acids compared to alcohols raised extensive debates over the last few decades. An explanation found in most textbooks reveals that a stabilizing anionic π-resonance interaction present in R–COO$^-$ makes carboxylic proton more acidic. Such anionic π-resonance effect is absent in alcohols yielding lower acidity—a clear final-state effect. On the other hand, some authors claim that acidity of these two classes of compounds is determined by the ground-state potential exerted on the proton in neutral acid AH [51]. Our results are in harmony with the former explanation. For that purpose, we shall consider acidity of some simple carboxylic acids and phenols given in Table 3. It is immediately evident that in all matching pairs, a carboxylic acid is always more acidic than alcohol. These differences are not so pronounced in aromatic molecules but are quite large in aliphatic pairs. Trichotomy analysis shows that, for example, APA(HCOO$^-$) – APA(CH_3O^-) = [–51.6; 13.2; –1.6] = –40.0 and APA(C_6H_5–COO$^-$) – APA(C_6H_5–O$^-$) = [–15.5; –6.7; 13.4] = –8.8 kcal mol^{-1}, providing evidence for the decisive influence of the final state, namely deprotonated anion, mirrored through Koopmans' ionization contribution. The rest of the data presented in Table 3 is found to be along the same line. Moreover, particularly in the aromatic systems, the (BAE)$^\bullet$ term describing properties of the initial state (neutral AH acid) predicts completely opposite behavior of the acidity, or in other words, alcohols to be more acidic than carboxylic acids. However, the latter is not the case since the Koopmans' term prevails and has the dominant role in enhancing the acidity of carboxylic acids. The same trend of changes in all three contributions governing acidity is observed in a much larger spectra of substituted aliphatic compounds [42] as well as in *para*-substituted benzoic acids [52] and phenols [53]. The interpretative value of triadic paradigm is best illustrated by discussion of a close relation between calculated acidities of *para*-substituted phenols and benzoic acids and Hammett's σ_p^- constants [52,53]. In particular, it is found that the superacidifying group S(O)(=NSO_2CF_3)CF_3 substituted at the *para* position in phenol immensely stabilizes the PRIMO (HOMO-2) orbital, which very well accommodates the excess electron [52]. Polysubstituted aromatic systems deserve particular attention. It was shown by theoretical considerations and computations that acidity of multiply substituted benzenes follows a very simple additivity rule [54]. It appears that each substituent affects acidity in a way, as if the others were nonexistent. It was proved by extensive experimental work that this independent substituent approximation works pretty well [55–58]. Consequently, one can get a good idea about acidity in polysubstituted aromatics, if the additivity rule is employed and the effects of single substituents are interpreted by triadic formula.

In conclusion, we would like to emphasize that C–H acidities of planar hydrocarbons (apart from the C(sp^3)–H center) heavily substituted by CN groups can reach record values in acidity [48–50], in some cases lowering the corresponding ΔH_{acid} value to around ~237 kcal mol^{-1} [49]. Unfortunately, they are not synthesized as yet. It should also be mentioned that they exhibit unprecedented acidities in dimethylsulfoxide (DMSO) as well [48–50,59].

Table 3 Gas-phase acidities of selected carboxylic acids and alcohols delineated according to the trichotomy analysis (in kcal mol^{-1}) as obtained with ROMP2(fc)/6–311+G(d,p)//B3LYP/6–31G(d) model.[a]

Molecule	$IE(A^-)_n^{Koop}$	$IE(A^-)_1^{ad}$	$E(ei)^{(n)}_{rex}$	$(BAE)^\bullet$	$APA(A^-)$	$APA(A^-)_{exp}$
H–COOH	$(118.0)_1$	71.9	46.1	102.2	343.9	340.1 ± 4.6
H–CH_2OH	$(66.4)_1$	33.5	32.9	103.8	383.9	382.0 ± 1.0
CN–COOH	$(162.9)_2$	97.4	65.5	102.2	318.4	
CN–CH_2OH	$(110.5)_2$	61.2	49.3	106.4	358.8	
C_6H_5–COOH	$(139.4)_4$	74.1	65.3	100.0	339.5	340.2 ± 2.2
C_6H_5–OH	$(123.9)_3$	51.9	72.0	86.6	348.3	347.5 ± 1.9
4-F–C_6H_4–COOH	$(143.6)_4$	77.5	66.1	100.4	336.5	337.0 ± 2.1
4-F–C_6H_4–OH	$(128.0)_3$	52.5	75.5	84.4	345.5	346.8 ± 2.1
4-CN–C_6H_4–COOH	$(153.5)_4$	84.9	68.6	100.9	329.6	327.8 ± 2.1
4-CN–C_6H_4–OH	$(149.0)_3$	64.9	84.1	83.0	331.7	332.2 ± 2.1

[a]Koopmans' ionization energies correspond to HF/6–311+G(d,p)//B3LYP/6–31G(d) calculations. The experimental data (given within square brackets) are taken from reference 21.

HYDRIDE AFFINITIES

Hydride ion (H^-) is not as versatile a reactant as the proton. Nevertheless, it plays an important role in some (bio)chemical reactions [60,61]. It is the simplest Lewis base, and its interactions with Lewis acids (LAs) provide an important clue about acid–base reactions at Lewis scale. The gas-phase hydride affinity (HA) of the LA under scrutiny is obtained as the negative value of the enthalpy for the following reaction:

$$LA + H^- \rightarrow (LA_\alpha H)^- - HA(LA_\alpha) \tag{16}$$

where α signifies the site of the hydride ion attack. Employing the trichotomy paradigm, one obtains a system of equations:

$$H^- - e^- \rightarrow H^\bullet - IE(H^-) \tag{17}$$

$$LA + e^- \rightarrow LA_\alpha^{\bullet-} + EA(LA)_1^{ad} \tag{18}$$

$$LA_\alpha^{\bullet-} + H^\bullet \rightarrow (LA_\alpha H)^- + (BAE)_\alpha^- \tag{19}$$

Equation 17 describes ionization of the hydride ion H^- and formation of the hydrogen atom, which requires investment in energy $IE(H^-)$. The latter is experimentally determined to be 17.4 kcal mol^{-1}. Further, eq. 18 describes electron attachment to the LA, which yields an LA radical anion with an energy gain given by the first adiabatic electron affinity of the LA $EA(LA)_1^{ad}$. The last equation (19) provides the energy of the homolytic bond association $(BAE)_\alpha^-$ between two radicals, which creates the $LA_\alpha H^-$ anion. By combining eqs. 16–19, one obtains

$$HA(LA_\alpha) = EA(LA)_1^{ad} - IE(H^-) + (BAE)_\alpha^- \tag{20}$$

In full analogy with the proton attachment reaction, we shall employ Koopmans' approximation and consider resolution of the adiabatic electron affinity into two contributions:

$$EA(LA)_1^{ad} = EA(LA)_n^{Koop} + E(ea)^{(n)}_{rex} \tag{21}$$

where $E(ea)^{(n)}_{rex}$ denotes the reorganization energy triggered by the electron attachment. Hence, the final formula reads

$$HA(LA_\alpha) = EA(LA)_{n,\alpha}^{Koop} + E(ea)^{(n)}_{rex} + (BAE)_\alpha^- - 17.4 \text{ kcal mol}^{-1} \tag{22}$$

which corresponds to partitioning of the H^- attack into three consecutive steps. Koopmans' term describes genuine properties of the initial LA. Let us consider attachment of the hydride ion to one of the most important class of LAs, halogen derivatives of borane molecule $BH_{3-m}X_m$ (X = F, Cl, Br; m = 0–3). Results of the G2(MP2) calculations [62] are given in Table 4. It appears that the PRIMOs are lowest unoccupied molecular orbitals (LUMOs) in all cases (n = 1) corresponding to the "empty" 2p orbital on the central boron atom, which acts as an acceptor of the H^-. Generally speaking, the HA will be larger than the homolytic B–H association bond energy, if the boron halide can accommodate an additional electron in exothermal fashion with a released energy higher than 17.4 kcal mol^{-1}. This is not the case with one notable exception given by BBr_3. Its first adiabatic electron affinity is positive, being 19.0 kcal mol^{-1}. Another important comment is related to Koopmans' approximation, which neglects the relaxation and electron correlation effects. These errors tend to cancel to a great deal for ionization of neutral molecules [5,22]. However, they add up in the calculation of electron affinities, thus producing negative values [63]. In spite of that, we believe that EA_n^{Koop} values provide meaningful information for closely related molecules. Let us briefly discuss the trend of changes of HAs selecting BH_3 as a standard [$HA(BH_3)$ = 73.1 kcal mol^{-1}]. It turns out that substitution of halide atoms increases the bond association energies in all cases (Table 4). Two subsets of compounds are of particular interest: boron fluorides and boron bromides. The former have HAs lower than BH_3, which is somewhat surprising. The latter subset $BH_{3-m}Br_m$ (m = 1, 2, 3) has HA values significantly higher than BH_3. Triadic analysis sheds light on this difference in behavior. The triads related to fluorides are $HA(BH_2F)$ – $HA(BH_3)$ = [–18.2; 4.4; 3.5] = –10.3; $HA(BHF_2)$ – $HA(BH_3)$ = [–38.9; 18.2; 7.8] = –12.9; and $HA(BF_3)$ – $HA(BH_3)$ = [–64.9; 50.1; 12.5] = –2.3 (in kcal mol^{-1}). It follows that sequential substitution by fluorine atoms induces attenuation in Lewis acidity. The reason is that the price to be paid in placing the excess electron in LUMO increases with the number of fluorine atoms and the Koopmans' term becomes more negative. This can be easily explained by a very strong electronegativity of fluorine atoms, which stabilize occupied and destabilize unoccupied MOs. Consequently, the HA values are decreasing, because Koopmans' term exerts a dominating influence. In contrast, the adiabatic electron affinities of $BH_{3-m}Br_m$ (m = 1, 2, 3) are positive, assuming values 3.6, 11.5, and 19.0 kcal mol^{-1}, respectively, implying that the corresponding radical anions are, in principle, stable species. Differential triads for these molecules read: $HA(BH_2Br)$ – $HA(BH_3)$ = [4.1; 2.6; 6.5] = 13.2; $HA(BHBr_2)$ – $HA(BH_3)$ = [6.9; 7.6; 8.1] = 22.7; and $HA(BBr_3)$ – $HA(BH_3)$ = [10.0; 12.1; 7.8] = 29.9 (in kcal mol^{-1}). It appears that Koopmans' term enhances HAs. Moreover, a synergy of all three terms contributes to high HA values of bromoboranes. Interestingly, chlorine derivatives exhibit HAs that lie between patterns observed by fluorine and bromine derivatives. More specifically, $HA(BH_2Cl)$ – $HA(BH_3)$ = [–0.6; 2.0; 5.6] = 7.0; $HA(BHCl_2)$ – $HA(BH_3)$ = [–1.7; 7.6; 8.0] = 13.9; and $HA(BCl_3)$ – $HA(BH_3)$ = [–2.2; 14.8; 8.8] = 21.4 (in kcal mol^{-1}). It seems that chlorine derivatives are stronger Lewis acids than BH_3, although not as strong as bromine counterparts. Unlike in bromoboranes, where the pronounced HAs are a combined effect of all three terms, in chloroboranes Koopmans' contribution slightly reduces Lewis acidity of these molecules and only the remaining two terms enhance their HAs, making them less potent Lewis acids than bromine derivatives.

The methodology described above is readily applicable to organic molecules. Without going into detail, we shall present the main results of the B3LYP calculations to HAs of some mono- and tetrasubstituted ethenes $H_2C{=}CHR$ (R = CN, NO_2) and $R_2C{=}CR_2$ (R = CN, NO_2) [64]. It is found that derivatives involving CN and NO_2 groups possess positive adiabatic electron affinities, implying that the corresponding anions can be formed in an exothermal way. Specifically, the $EA(LA)_n^{Koop}$ values in mono- and tetranitroethene are 27.7 kcal mol^{-1} and 94.2 kcal mol^{-1}, respectively. The corresponding triads obtained by taking parent ethene as a gauge molecule are [71.5; –7.0; 1.0] = 65.5 and [144.6; –13.7; 10.8] = 141.7 kcal mol^{-1}, in the same order, which underline the overwhelming influence of the Koopmans' electron affinity or in other words predominance of the initial-state effect. The same holds for mono- and tetracyanoethene although the numbers are different. The corresponding triads are [48.8;

–9.6; 4.6] = 43.8 and [142.5; –24.7; –14.9] = 102.9 kcal mol^{-1}. Both tetracyano- and tetranitroethene exhibit extremely high HAs of 117.9 and 156.7 kcal mol^{-1}, respectively.

Another interesting finding is that the β-carbon atoms in monosubstituted ethene derivatives are the most susceptible to H^- attack as a rule. It turned out that HAs are fairly well correlated with the adiabatic electron affinity [64], which in turn is able to reproduce a general trend of changes. However, if quantitative information is desired, then full energetic account embodied in triadic formula 22 is necessary.

In summary, the trichotomy paradigm proved very useful in rationalization of HAs of a large variety of organic compounds [64–66], enabling the design of systems exhibiting predetermined properties such as, e.g., hydride sponges.

Table 4 HAs obtained by the G2(MP2) method and their resolution into triadic components (in kcal mol^{-1}).[a]

Molecule	$(EA)_n^{Koop}$	$E(ea)^{(n)}_{rex}$	$(EA)_1^{ad}$	$(BAE)^-$	HA
BH_3	$-(43.2)_1$	40.1	–3.1	93.6	73.1
BH_2F	$-(61.4)_1$	44.5	–16.9	97.1	62.8
BHF_2	$-(82.1)_1$	58.3	–23.8	101.4	60.2
BF_3	$-(108.1)_1$	90.2	–17.9	106.1	70.8
BH_2Cl	$-(43.8)_1$	42.1	–1.7	99.2	80.1
$BHCl_2$	$-(44.9)_1$	47.7	2.8	101.6	87.0
BCl_3	$-(45.4)_1$	54.9	9.5	102.4	94.5
BH_2Br	$-(39.1)_1$	42.7	3.6	100.1	86.3
$BHBr_2$	$-(36.3)_1$	47.8	11.5	101.7	95.8
BBr_3	$-(33.2)_1$	52.2	19.0	101.4	103.0

[a]Koopmans' electron affinities are calculated by the HF/6–311G(d,p)//MP2(full)/6–31G(d) model.

CONCLUDING REMARKS

The main aspects and importance of modeling in chemistry are discussed *in extenso*. It was strongly emphasized that acceptable models should avoid the *Scylla* of too many details and the *Charybdis* of oversimplification. Further, it is pointed out that progress in natural science requires a harmonious development in experimental, theoretical, computational, and interpretive research. The latter component is pivotal in rationalizing the plethora of experimental and computational results by unearthing common roots between seemingly unrelated data. The art of modeling is demanding since many pitfalls have to be circumvented. We shall mention two out of many misconceptions found in the literature. The first belongs to mathematician Norbert Wiener, who argued that the best model of a cat is another cat or, even better, the cat itself. The fact of the matter is that a model has to satisfy criterion of simplicity and that it is never a perfect description of a true object. On the other end of the scale, one can find empirical models lacking a proper theoretical justification. We shall illustrate this point by quoting Gilli and Gilli [67]: "From a philosophical point of view chemistry differs widely from physics because of the large use it makes of *chemical models* or *chemical theories* not derived from more basic physico-mathematical theories, but directly inferred from the whole of experimental data." This statement might have been fitting 100 years ago, but it is obviously obsolete now. Physically sound models are needed in contemporary chemistry.

We believe that the presented evidence convincingly shows that the trichotomy paradigm provides a useful tool in attempts to better understand acidity, basicity, and hydride affinities in general and their salient characteristics in organic compounds. It should be stressed that unveiling the underlying principles governing these properties enabled computational design of non-ionic organic superacids, super-

bases, proton and hydride sponges, as well as some interesting ion pairs, therefore aiding the experimental research.

REFERENCES

1. P. A. M. Dirac. *Proc. R. Soc.* **123**, 714 (1929).
2. K. B. Lipkowitz, D. B. Boyd (Eds.). *Reviews in Computational Chemistry*, Vols. 1–22, Wiley-VCH, New York (1990–2005).
3. P. Politzer, Z. B. Maksić. *Theoretical and Computational Chemistry*, Vols. 1–16, Elsevier, Amsterdam (1994–2005).
4. D. R. Yarkony (Ed.). *Modern Electronic Structure Theory*, Vols. 1–2, World Scientific, Singapore (1995).
5. C. J. Cramer. *Essentials of Computational Chemistry*, John Wiley, Chichester (2002).
6. T. Helgaker, P. Jørgensen, J. Olsen. *Molecular Electronic–Structure Theory*, John Wiley, New York (2000).
7. D. Young. *Computational Chemistry*, John Wiley, New York (2001).
8. L. Pauling. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, 3rd ed., Cornell University Press (1960).
9. G. S. Hammond, J. Osteryoung, T. H. Crawford, H. B. Gray. *Models in Chemical Science – an Introduction to General Chemistry*, W. A. Benjamin, Menlo Park (1971).
10. R. McWeeny. *Coulson's Valence*, 3rd ed., Oxford University Press, Oxford (1979).
11. Z. B. Maksić (Ed.). *Modelling of Structure and Properties of Molecules, Ellis Horwood*, Chichester (1987).
12. Z. B. Maksić (Ed.). *Theoretical Models of Chemical Bonding*, Vols. 1–4, Springer Verlag, Berlin (1990–1991).
13. A. Rauk. *Orbital Interaction Theory of Organic Chemistry*, Wiley Interscience, New York (2001).
14. William of Okham, a priest in England in the 14th century, put forward the following criterion: "Essentia non sunt multiplicanda praeter necessitatem", literary meaning that entities are not to be multiplied unless necessary. A better translation would be: "A satisfactory proposition should contain no unnecessary complication."
15. Z. B. Maksić. *Modelling – a Search for Simplicity, in Theoretical Models of Chemical Bonding, Vol. 1, Atomic Hypothesis and the Concept of Molecular Structure*, Z. B. Maksić (Ed.), p. 13, Springer-Verlag, Berlin (1990).
16. Z. B. Maksić. *Pure Appl. Chem.* **55**, 307 (1983).
17. Z. B. Maksić. In *Symmetry – Unifying Human Understanding*, I. Hargittai (Ed.), p. 697, Pergamon Press, New York (1986).
18. Z. B. Maksić, W. J. Orville-Thomas. *Prologue to Pauling's Legacy – Modern Modelling of the Chemical Bond*, Z. B. Maksić, W. J. Orville-Thomas (Eds.), Elsevier, Amsterdam, (1999).
19. Z. B. Maksić, R. Vianello. *J. Phys. Chem. A* **106**, 419 (2002).
20. T. Koopmans. *Physica* **1**, 104 (1933).
21. P. J. Linstrom, W. G. Mallard (Eds.). NIST Chemistry WebBook, NIST Standard Reference Database Number 69, June 2005, National Institute of Standards and Technology, Gaithersburg MD, 20899 (<http://webbook.nist.gov>).
22. Z. B. Maksić, R. Vianello. *J. Phys. Chem. A* **106**, 6515 (2002).
23. S. P. McGlynn, K. Wittel, L. Klasinc. In *Theoretical Models of Chemical Bonding, Vol. 3, Molecular Spectroscopy, Electronic Structure and Intramolecular Interactions*, Z. B. Maksić (Ed.), p. 63, Springer Verlag, Berlin (1991).
24. E. Honneger, E. Heilbronner. In *Theoretical Models of Chemical Bonding, Vol. 3, Molecular Spectroscopy, Electronic Structure and Intramolecular Interactions*, Z. B. Maksić (Ed.), p. 99, Springer Verlag, Berlin (1991).

25. M. Eckert-Maksić. In *Theoretical Models of Chemical Bonding, Vol. 3, Molecular Spectroscopy, Electronic Structure and Intramolecular Interactions*, Z. B. Maksić (Ed.), p. 153, Springer Verlag, Berlin (1991).
26. (a) A. H. Zewail. *Angew. Chem., Int. Ed.* **40**, 4371 (2001); (b) A. H. Zewail. *Nature* **412**, 279 (2001).
27. (a) J. Hatani, J. Leverque, D. Zeitler, H. Niikura, H. Pépin, J. C. Kieffer, P. B. Corkum, D. M. Villeneuve. *Nature* **432**, 867 (2004); (b) J. Hatani, J. Leverque, D. Zeitler, H. Niikura, H. Pépin, J. C. Kieffer, P. B. Corkum, D. M. Villeneuve. *Phys. Rev. Lett.* **94**, 123902 (2005).
28. H. Stapelfeldt. *Nature* **432**, 809 (2004).
29. W. H. E. Schwarz. *Angew. Chem., Int. Ed*. **45**, 2 (2006).
30. C. A. Deakyne. *Int. J. Mass Spectrom*. **227**, 601 (2003).
31. (a) P. George, M. Trachtmann, C. W. Bock, A. M. Brett. *Tetrahedron* **32**, 313 (1976); (b) P. George, M. Trachtmann, C. W. Bock, A. M. Brett. *J. Chem. Soc., Perkin Trans. 2* 1222 (1976).
32. Z. B. Maksić, B. Kovačević. *J. Org. Chem.* **65**, 3303 (2000).
33. R. Vianello, B. Kovačević, Z. B. Maksić. *New J. Chem.* **26**, 1324 (2002).
34. E. D. Raczynska, M. Decouzon, J.-F. Gal, P.-C. Maria, K. Wozniak, R. Kurg, S. N. Cairns. *Trends Org. Chem.* **7**, 95 (1998).
35. B. Kovačević, Z. B. Maksić. *Tetrahedron Lett.* **47**, 2553 (2006).
36. B. Kovačević, Z. B. Maksić. *Chem. Commun.* 1524 (2006).
37. R. Vianello, H. Maskill, Z. B. Maksić. *Eur. J. Org. Chem.* 2581 (2006).
38. I. Despotović, Z. B. Maksić, R. Vianello. *New J. Chem.* **31**, 52 (2007).
39. Z. B. Maksić, B. Kovačević. *J. Phys. Chem. A* **102**, 7324 (1998).
40. Z. B. Maksić, Z. Glasovac, I. Despotović. *J. Phys. Org. Chem.* **15**, 499 (2002).
41. B. Kovačević, Z. B. Maksić. *Org. Lett.* **3**, 1523 (2001).
42. Z. B. Maksić, R. Vianello. *ChemPhysChem* **3**, 696 (2002).
43. R. Vianello, J. F. Liebman, Z. B. Maksić. *Chem. Eur. J.* **10**, 5751 (2004).
44. J. C. Rienstra-Kiracofe, G. S. Tschumper, H. F. Schaefer III. *Chem. Rev.* **102**, 231 (2002).
45. C. Richardson, C. A. Reed. *Chem. Commun.* 706 (2004).
46. R. L. Lord, S. E. Wheeler, H. F. Schaefer III. *J. Phys. Chem. A* **109**, 10084 (2005).
47. Z. B. Maksić, R. Vianello. *Tetrahedron Lett*. **45**, 8663 (2004).
48. R. Vianello, Z. B. Maksić. *Tetrahedron Lett.* **46**, 3711 (2005).
49. R. Vianello, Z. B. Maksić. *Chem. Commun.* 3412 (2005).
50. (a) R. Vianello, Z. B. Maksić. *Tetrahedron* **61**, 9381 (2005); (b) R. Vianello, Z. B. Maksić. *Eur. J. Org. Chem*. 3571 (2005).
51. O. Exner, P. Čársky. *J. Am. Chem. Soc.* **123**, 9564 (2001) and refs. cited therein.
52. R. Vianello, Z. B. Maksić. *J. Phys. Org. Chem.* **18**, 699 (2005).
53. R. Vianello, Z. B. Maksić. *Tetrahedron* **62**, 3402 (2006).
54. Z. B. Maksić, D. Kovaček, M. Eckert-Maksić, I. Zrinski. *J. Org. Chem*. **61**, 6717 (1996).
55. H. H. Büker, N. M. M. Nibbering, D. Espinoza, F. Mougin, M. Schloser. *Tetrahedron Lett.* **38**, 8519 (1997).
56. M. Schloser. *Angew. Chem., Int. Ed.* **110**, 1497 (1998).
57. M. Schloser, F. Mougin, J. Porwisiak, W. Dmowski, H. H. Büker, N. M. M. Nibbering. *Chem. Eur. J.* **4**, 1281 (1998).
58. D. Kuck. *Angew. Chem., Int. Ed.* **39**, 125 (2000).
59. R. Vianello, Z. B. Maksić. *Eur. J. Org. Chem*. 5003 (2004).
60. M. B. Smith, J. March. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 5th ed., John Wiley, New York (2001).
61. L.-S. Lee, K.-H. Chow, M. M. Kreevoy. *J. Am. Chem. Soc.* **124**, 7755 (2002) and refs. cited therein.
62. R. Vianello, Z. B. Maksić. *Inorg. Chem*. **44**, 1095 (2005).

63. A. Szabo, N. S. Ostlund. *Modern Quantum Chemistry*, MacMillan, New York (1982).
64. R. Vianello, N. Peran, Z. B. Maksić. *Eur. J. Org. Chem*. 526 (2007).
65. R. Vianello, N. Peran, Z. B. Maksić. *J. Phys. Chem. A* **110**, 12870 (2006).
66. N. Peran, R. Vianello, Z. B. Maksić. Manuscript in preparation.
67. G. Gilli, P. Gilli. *J. Mol. Struct*. **552**, 1 2000.