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Hydride Affinities of Substituted Alkenes: Their Prediction by Density Functional Calculations and Rationalisation by Triadic Formula

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The hydride affinities (HAs) of ethene and its derivatives produced by substituents that vary greatly in their donor/acceptor properties are studied by the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) method. The computed values are in very good agreement with the available experimental data. A useful by-product of the calculations of thermodynamic data are the estimated adiabatic electron affinities. It turns out that derivatives involving monosubstituted CN and NO_2 groups, disubstituted CN, NO_2 and CF_3 groups and ethenes polysubstituted by these strongly electron-accepting functionalities possess positive electron affinities, which implies that the corresponding ions are formed by energy release and are thus quite stable species. The most favourable sites of the hydride ion attack are identified and the trend of changes of hydride affinities is analysed and interpreted by a triadic formula, which discriminates between the initial, intermediate and final state properties. It is found that hydride affinities are rather well correlated with the adiabatic electron affinities, which means that the initial state (neutral molecule) and intermediate step (relaxation of the nuclei and electrons upon electron capture) effects are predominant factors. The quantitative information on the H^- affinities can be obtained, however, only by including all terms appearing in the triadic formula. It is shown that Pearson's HSAB concept does not work for hydride affinities. The idea of using hydride affinities as a measure of the electrophilic propensity of molecules is put forward.

Introduction

It is common knowledge that the proton is pivotal in defining Brønsted acids and bases. The proton is the simplest Lewis acid and at the same time is a very hard electrophile. An immense number of scientific papers have been dedicated to the problems of proton affinity or the deprotonation energy of organic, inorganic and biological molecules. In contrast, considerably less attention has been dedicated to its counterpart — the smallest Lewis base and the simplest nucleophile — the hydride ion H^-. Although hydride ion is not as versatile as a proton, it nevertheless plays an important role in many chemical reactions.[1] For example, reduction of carbonyl compounds to alkoxides by the use of hydride donors such as $LiAlH_4$, $NaBH_4$, AlH_3, H_2/catalyst or B_2H_6 is a key step in many chemical transformations.[1] Furthermore, intramolecular 1,2- and transannular hydride shifts are widely used in carbocation rearrangements chemistry.[2,3] It is also important to mention that intermolecular hydride transfers have long been exploited industrially,[4–7] and experimental measurements of the hydride affinities of quinones,[8] organic radicals[9] and organic cations[10,11] in some solvents have been performed by Parker and co-workers.[8–11] Recently, a new and facile method for determining the hydride affinities of olefins in MeCN was introduced based on the use of *N*-methylacrodinium cation as a strong hydride acceptor.[12] The biochemical relevance of the hydride transfer is evidenced by the acceptor coenzymes NAD^+ and $NADP^+$, which include reactions catalysed by a number of dehydrogenases,[13–15] and the interconversion of galactose and glucose,[16] to mention just a few. In spite of these efforts, it is rather unfortunate that the number of experimentally measured hydride affinities (HAs) is rather limited,[17] particularly because these values could also serve as a useful probe of electrophilicity for a series of molecules. The number of theoretical treatments is not abundant either. They include some semi-empirical calculations of the gas-phase hydride affinities of toluene derivatives and some aromatics,[18] heterocyclic five-membered rings[19] and ab initio estimates of HA values involving group I and group II metals,[20] the structure and relative stability of halogenated carbocations mirrored by the computed HAs,[21] heterosubstituted carbonyls (XYC=O, α,β-unsaturated aldehydes and cycloalkanones)[22] and some selected carbonyl compounds, carbenium ion acceptors, fulvene, borane and SiH_3^+ with particular empha-

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sis on the H^- transfer and location of the transition states.[23] It should also be noted that hydride transfer between $XYC{=}CHCH_3$ donors and $XYC{=}CHCH_2^+$ acceptors has been studied by Würthwein, Mayr and coworkers.[24] The work on the interpretative side of the problem was not quite conclusive, however, as it focused on the electron charge redistribution upon hydride addition[25,26] or use of the isodesmic reactions in treating hydride affinities,[22] both of which suffer from some interpretative imperfections. The atomic charge distribution is just one parameter that affects the hydride affinities in an implicit and, consequently, non-transparent way, apart their arbitrary formal definition. In particular, the widely used QTAIM[27] (quantum theory of atoms in molecule) charges for this purpose[25,26] are known to greatly exaggerate the charge migration in molecules (see below).[28–32] The isodesmic reactions are able to provide correct estimates of the initial- and final-state contributions to the HAs,[22] but the process of hydride ion addition is much more subtle than that, as will be discussed at some length in this paper. A better and more detailed description is offered by the triadic approach, which has been successfully applied to proton affinities of neutral molecules[33] (Brønsted basicity) and anions[34] (Brønsted acidity). The triadic (trichotomy) formula has some distinct advantages over more traditional ways of rationalizing the trend of changes in acidity and basicity over series of related compounds, as thoroughly discussed by Deakyne in a recent review,[35] and this approach has also proved useful in explaining the substituent effects and their influence on acidity and basicity.[36] It is gratifying that the triadic paradigm can be easily extended to hydride affinities, as shown recently in the case of borane (BH_3) derivatives.[37] Building on these results we consider here the HAs of the mono-substituted ethenes $H_2C{=}CHR$ (R = CH_3, C_2H_5, C_3H_7, C_6H_5, $CH{=}CH_2$, CN, NO_2, F, NH_2, OH and CF_3) in order to assess their influence on the hydride affinity of the parent molecule. Some interesting disubstituted molecules are studied too. In addition, cyclopropene and $CH_2{=}NH$ are also examined as an example of a double bond embedded in a small three-membered ring and the simplest compound possessing an imine bond, respectively. Finally, derivatives of ethene containing multiple CN and NO_2 groups (**1t**–**1w**) are also considered since very high hydride affinities can be expected in these compounds. The purpose of this work is manifold: (a) to find positions most susceptible to H^- attack and provide reliable theoretical HAs of compounds that have not been investigated experimentally previously; (b) to pinpoint alternative, energetically less favourable sites of H^- attachment; and (c) to shed more light on the underlying principles governing HAs, as revealed by the triadic formula. Point (b) is a distinct advantage of the theoretical approach over the experimental methodology since all nucleophilic centres are treated on an equal footing. Theory can also provide a simple answer as to why some sites are more prone to react with H^- than others. All these aspects are of equal importance. It is essential to have available as much data on the HAs as possible, as they are interesting per se, and it is also quintessential to contribute towards their understanding. The latter is a prerequisite for rationalizing the experimental and computational data, thus aiding in the development of new concepts that might be useful when it comes to designing new compounds with predetermined hydride affinities, such as hydride sponges. In addition to the energetic considerations, we shall briefly discuss structural features of hydrides, the changes in hybridisation and redistribution of the charges induced by the H^- nucleophilic attack.

Theoretical Framework and Computational Details

The gas-phase hydride affinities (HAs) are defined by the negative enthalpy change of reaction (1).

$$M + H^- \rightarrow (M_\alpha H)^- - (HA)_\alpha \qquad (1)$$

where M is a molecule in its oxidized state and $(M_\alpha H)^-$ is its reduced form. The site of the H^- attack is denoted by α. It is convenient for interpretative purposes to resolve this process into three consecutive steps, namely (a) the ionisation of the H^- atom, (b) the electron attachment to the studied molecule M and (c) the formation of a new homolytic bond between the two newly formed radicals $M^{\cdot-}$ and $H^{\cdot}$. These are described by the adiabatic ionisation energy of the hydride ion $IE_1^{ad}(H^-)$, the first adiabatic electron affinity of the molecule in question $EA_1^{ad}(M)$ and the bond association energy $(BAE)_\alpha^{\cdot-}$ between two radicals $M^{\cdot-}$ and $H^{\cdot}$, respectively. The thermodynamic balance of Equation (1) yields (2).

$$(HA)_\alpha = EA_1(M)^{ad} + (BAE)_\alpha^{\cdot-} - 17.4\ \mathrm{kcal\,mol^{-1}} \qquad (2)$$

where 17.4 $\mathrm{kcal\,mol^{-1}}$ is the experimentally determined ionisation energy of H^-.[38] It should be mentioned that both the adiabatic electron affinity and $(BAE)_\alpha^{\cdot-}$ terms include the zero-point vibration energy (ZPVE) contribution, which provide the "cold energy" part of the hydride affinity at $T = 0$ K. The warming up of vibrational corrections to room temperature ($T = 298.15$ K) is subsequently included in both terms, whereas $(5/2)RT$ is attached to the bond association energy for obvious reasons. This completes the expression $(HA)_\alpha$ for the "warm" hydride affinities shown in Equation (2).

It is useful to delineate the inherent properties of the initial state of a molecule M under study from other interlocked effects acting in the resulting anion $(M_\alpha H)^-$ in order to provide a better understanding of reaction (1). However, it would be incorrect to identify $EA_1(M)^{ad}$ with genuine initial properties of a molecule M because the adiabatic electron attachment involves relaxation of both electron density and spatial structural parameters defined by the equilibrium positions of the atomic nuclei. In order to single out the initial properties one has to invoke Koopmans' theorem,[39] which states that the electron affinity $EA_n(M)^{Koop}$ is approximately given by the negative energy, $-\varepsilon_n$, of the corresponding unoccupied orbital calculated within the Hartree–Fock (HF) model. In other words, the electron attachment is considered to be a sudden event and neither nuclei nor electrons are allowed to relax. Despite the highly approximate nature of Koopmans' clamped nuclei and frozen electron picture, the calculated $EA_n(M)^{Koop}$ values are very useful when applied to families of intimately related molecules.[40] It is noteworthy that $EA_n(M)^{Koop}$ does not necessarily correspond to the first electron affinity ($n = 1$) because the empty MO associated with accommodation of the excess negative charge in the electron capture event might be higher in energy than the LUMO ($n = 1$). This important detail deserves a comment. First, it is easy to identify the MO in question since it is the one which plays a pivotal role in the forthcoming formation of a new $(M_\alpha H)^-$ bond. For that reason we shall term it the principal molecular orbital (PRIMO). Secondly, if an additional electron is placed in a virtual (LUMO + m) orbital, where m is a positive natural number ($m = n - 1$), the corresponding electron configuration might be unbound. However, the present approach retains its interpretative value in a formal sense even in this case if the trend of changes in a series of (closely) related compounds is considered, as pointed out above. It is noteworthy that canonical Hartree–Fock molecular orbitals, or their equivalent linear combinations of the bond orbitals, are extremely useful for interpreting molecular photoelectron spectra (PES), thus describing fairly faithfully the particular molecular fragments or their intramolecular interactions, as has been convincingly documented in a plethora of scientific papers.[41] Hence, the approximate one-electron model contains a grain of truth, just like some other simple physical concepts describing chemical bonding.[42] Having said that, we would like to mention that the success of the occupied outer MOs in rationalizing PE spectra is a result of an approximate cancellation of the relaxation and electron-correlation effects. This is not the case with the unoccupied (LUMO + m) orbitals once occupied by an excess electron, which implies that the single electron MO description of the H^- affinities should not be overinterpreted. In spite of that, the MO picture is useful in discussing hydride affinities among families of closely related molecules. Finally, it should be stressed that the electron attachment is not an instantaneous phenomenon. It occurs in real time and involves relaxation of the electrons and nuclei in the $M^{\cdot-}$ anion, which is determined by the reorganisation energy defined by

$$E(\mathrm{ea})^{(n)}_{\mathrm{rex}} = EA_1(M)^{ad} - EA_n(M)^{Koop} \quad (3)$$

where "ea" within parentheses denotes the electron attachment. Positive $EA_1(M)^{ad}$ values imply that the electron is in a bound state. It should be noticed that relaxation involves an interplay between the initial and final state effects and is an intermediate step on its own. Hence, the resulting triadic formula for addition of H^- ion to the molecule M, which yields the accompanying hydride affinity, takes the form shown in Equation (4).

$$(HA)_\alpha = EA_n(M)^{Koop} + E(\mathrm{ea})^{(n)}_{\mathrm{rex}} + (BAE)_\alpha^{\cdot-} - 17.4\ \mathrm{kcal\,mol^{-1}} \quad (4)$$

As a good compromise between the feasibility of the method and accuracy on one side and feasibility combined with economy (in terms of computer time) on the other, we employed the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) method, hereafter denoted as B3LYP. Geometry optimisations, verification of the minima on the Born–Oppenheimer potential energy hypersurface and calculation of the thermodynamic parameters corresponding to room temperature (298.15 K) were performed at the efficient B3LYP/6-31G(d) level. Koopmans' electron affinities were obtained with the HF/6-311G(2df,p)//B3LYP/6-31G(d) model. Radical anions were treated by the unrestricted formalism at the UB3LYP/6-311+G(2df,p)//UB3LYP/6-31G(d) level. All computations were performed with Gaussian 98.[43]

Results and Discussion

Geometries

We shall first check the performance of the B3LYP/6-31G(d) method in reproducing the structural parameters of the parent ethene. For that purpose we shall compare bond lengths obtained by several theoretical models and their computational procedures, such as HF/6-31G(d), B3LYP/6-31G(d), B3LYP/6-31+G(d,p) and MP2(fc)/6-31G(d), and compare the predicted structural parameters with the experimental C=C and C–H bond lengths of 1.337(2) and 1.086 Å, respectively.[44] The results presented in Figure 1 show that the HF model yields bond lengths that are too short, and these, in turn, are elongated by inclusion of the electron correlation, for obvious reasons. It appears that the bond lengths estimated by the B3LYP/6-31+G(d,p) and MP2(fc)/6-31G(d) methods are in very good accordance with the measured data. A comparison of the structural parameters predicted by the B3LYP/6-31G(d) procedure with those produced by two more accurate methods mentioned above for **1a**, **1a**$^{\cdot-}$ and **1aH**$^-$ reveals that the overall agreement is satisfactory. Given that result, and the well-known fact that the total molecular energy is not highly sensitive to the ground-state geometries provided the electron correlation effect is taken into account by using a large and flexible basis set, we are inclined to conclude that the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) computational scheme is adequate for our purposes.

The structural parameters of substituted ethenes and their changes upon the electron and subsequent hydrogen atom attachments leading to radical anions and hydrides, respectively, are displayed in Figure 2. It should be pointed out that only the structures of the most stable hydrides are presented. The first striking feature of the monosubstituted ethenes is that the most susceptible site for the H^- attack is, as a rule, the β-carbon atom (C^2). There are, however, some notable exceptions. In first place is the methyl derivative, where H^- attachment occurs at the α-carbon. The same holds for ethenes monosubstituted by NH_2 and OH groups (**1j** and **1k**, respectively). In the trisubstituted systems **1t**

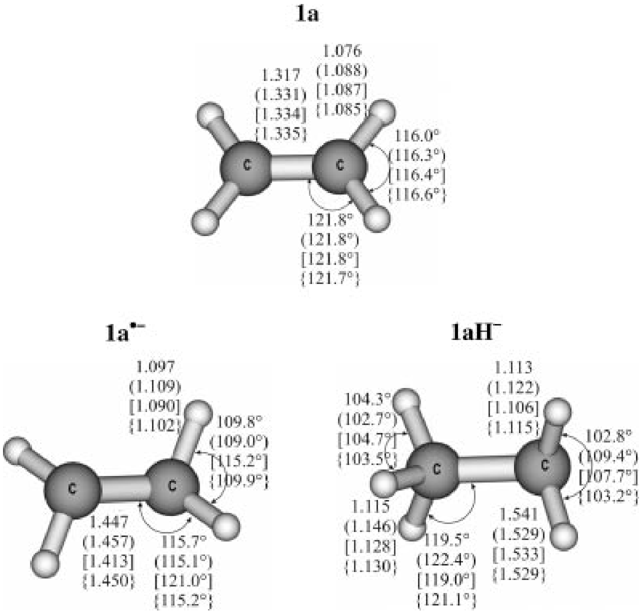


Figure 1. Bond lengths [Å] and bond angles [°] in ethane, its anion and hydride derivative as calculated at HF/6-31G(d), B3LYP/6-31G(d) (in round brackets), B3LYP/6-31+G(d,p) (in square brackets) and MP2/6-31G(d) (in curly brackets).

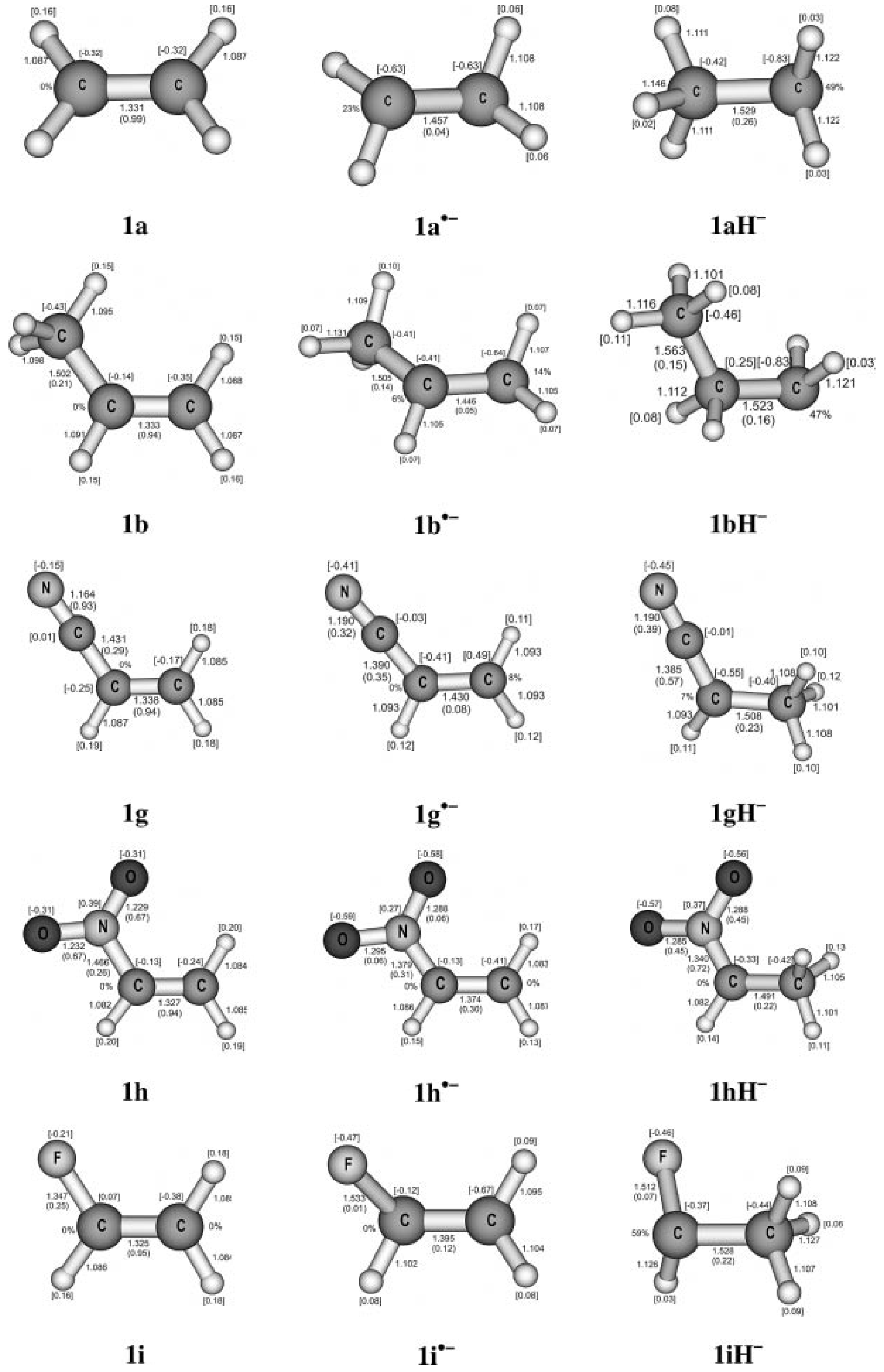
and **1u** the monosubstituted centre is more prone to nucleophilic attack by H^- ion. An interesting case is given by methylpropene (**1m**), which is transformed into the *tert*-butyl anion **1mH$^-$** by H^- attachment at the β-carbon. Finally, methanimine (**2**) undergoes attack at the carbon atom. It should be stressed that the hydride ion attack at the α-carbon leads to dissociation of the NO_2 group in mono- (**1h**) and 1,1-disubstituted derivatives (**1r**). In the case of the fluoro derivative (**1i**), the F^- anion forms a complex with the rest of the molecule with a $C\cdots F^-$ distance of 1.79 Å.

Important structural information is provided by the pyramidalisation of the three-coordinate atoms. The degree of pyramidalisation can be readily estimated by formula (5).[45]

$$DP\ (\%) = [360° - \sum_{i=1}^{3} \alpha_i^{\circ}]/0.9° \qquad (5)$$

where DP is the degree of pyramidalisation and the summation is extended over the bond angles α_i of the pyramidal atom in question. The maximal pyramidalisation, by definition occurs if all three bond angles are 90°. It is worth noting that the DP values of the CH_2 fragments in **1a$^{\cdot-}$** and **1aH$^-$** are 23% and 49%, respectively (Figure 2). A smaller pyramidalisation in the former radical anion can be explained by the fact that the excess electron is placed in the π-antibonding MO, which provides the principal molecular orbital (see below). Consequently the π-double bond is destroyed by formation of two hybrid AOs populated by approximately 1.5 electrons, which could be termed semi-lone pairs. They mutually repel each other, leading to the out-of-plane shift of the CH_2 groups in an *anti* fashion. This picture is corroborated by the Löwdin atomic charges[46] of the carbons and the π-bond order, which are –0.63 and 0.04 (in |e|), respectively. Concomitantly, the C–C bond is considerably longer (by 0.126 Å) than in neutral **1a**. We shall digress slightly at this point as the choice of atomic charges is an important ingredient of the interpretative procedure. Although all atomic charges are arbitrary, it is clear that some definitions are more reliable than others. The question therefore arises as to which criteria are the best for testing the atomic charges in molecules. In our opinion a very good criterion is given by the calculations of the ESCA shifts,[47] which, in turn, can be estimated with good accuracy by the electrostatic potentials at the nuclei estimated in the atomic monopole approximation.[48] A reasonable way of calculating atomic charges is offered by the stockholder recipe.[49] On the other hand, the QTAIM charges based on Bader's virial partitioning of the molecular 3D space into atomic domains divided by the electron density zero-flux surfaces[27,28] are far from perfect. For instance, within the latter scheme the oxygen gross atomic electron populations are typically between 9 and 9.5 electrons, which suggests an electron density drift of 1.0–1.5 |e| even in small molecules like CO, H_2CO and CH_3OH and therefore differs from all other methods.[28–32] This implies ionic bonding in these molecules, which is incompatible with chemical experience and wisdom. Maslen and Spackman[30,31] have shown that the density shift occurs even in promolecules, where it should, by definition, be zero. Thus, the asymptotic behaviour is wrong. An additional difficulty with both stockholder and QTAIM atomic charges is the fact that they are not centred at the nuclei, which means that higher multipoles than monopoles have to be included in the electrostatic calculations.[50] The problem of atomic charges is therefore not yet settled. Having this in mind, we have chosen Löwdin charges in the present work for the simple reason that symmetric orthogonalisation of the initial non-orthogonal basis set functions circumvents the problem of partitioning of the mixed densities. Additionally, Löwdin charges do not suffer the drawback of Mulliken gross orbital densities, which can assume values larger than two electrons or negative magnitudes. Thus, Löwdin charges are conceptually very appealing. We do not pretend, however, that this is the best possible definition of the atomic charges.

In **1aH$^-$** a lone pair is "completely" formed at the CH_2 group. Since it requires a very high s character, the C^2 carbon is additionally pyramidalized due to the pronounced p character of the hybrids describing the C–H and C–C bonds. Rehybridisation leads to a further increase in the bond lengths by 0.072 Å. A weak interaction between the lone pair and two C–H bonds of the other (C^1) carbon atom, placed in the staggered position, is reflected in the bond order of 0.26. We note, in passing, that the excess negative charge is distributed over both carbons, not only in **1a$^{\cdot-}$** (as required by symmetry) but also, to a large extent, in hydride **1aH$^-$**. A similar pattern is observed in alkyl-substituted ethenes (cf. **1b** in Figure 2), with one important difference — the terminal carbons are negatively charged while the central one is positive. Obviously, this is a consequence of Coulomb interactions.



1a $\mathbf{1a^{\bullet-}}$ $\mathbf{1aH^-}$

1b $\mathbf{1b^{\bullet-}}$ $\mathbf{1bH^-}$

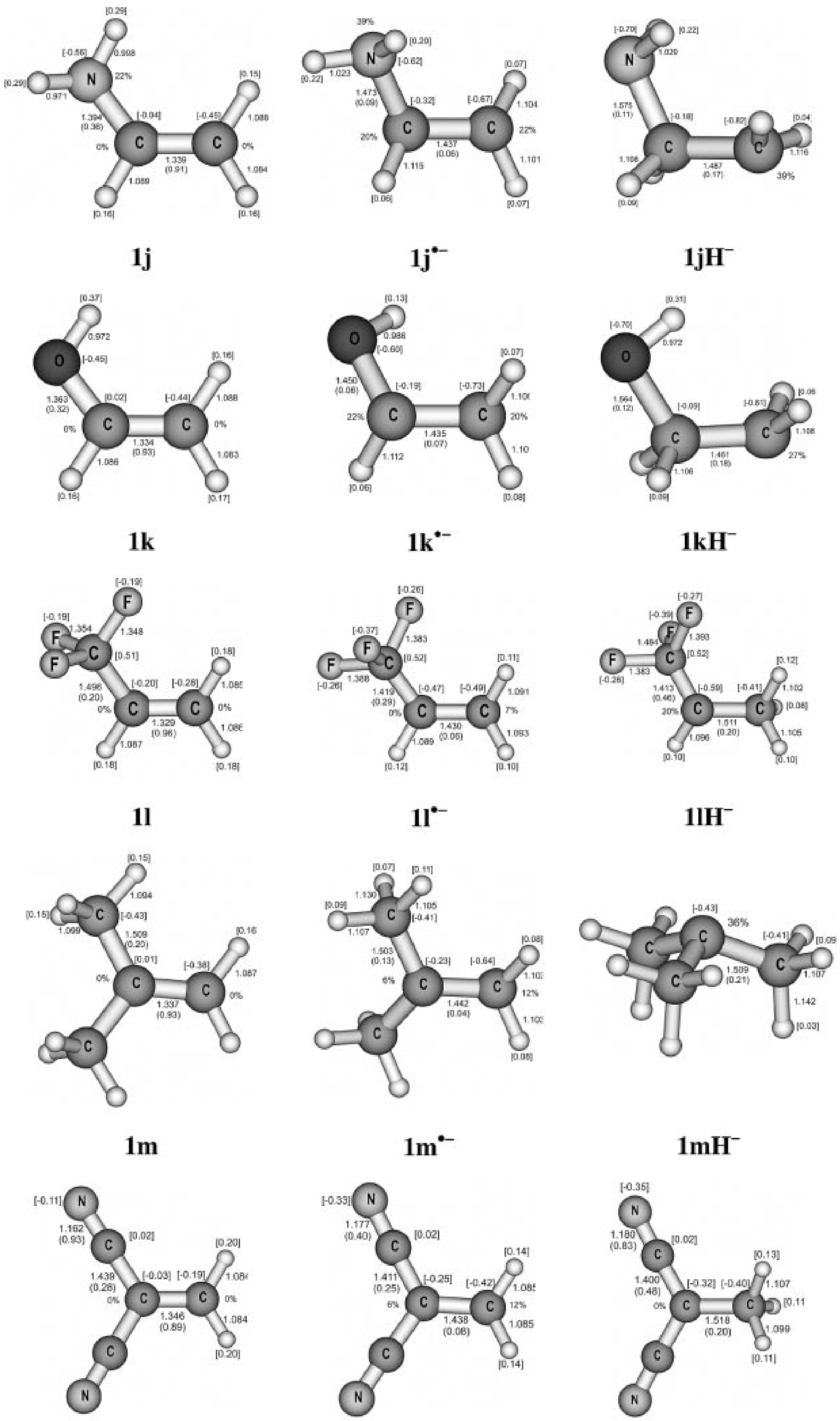
1g $\mathbf{1g^{\bullet-}}$ $\mathbf{1gH^-}$

1h $\mathbf{1h^{\bullet-}}$ $\mathbf{1hH^-}$

1i $\mathbf{1i^{\bullet-}}$ $\mathbf{1iH^-}$

Figure 2. Selected bond lengths [Å] and degrees of pyramidalisation [%] obtained by the B3LYP/6-31G(d) method, the π-bond orders (in round brackets) and Löwdin atomic charges (in square brackets; in |e|) [obtained by the HF/6-31G(d)//B3LYP/6-31G(d) method] for some characteristic substituted ethenes, their anions and hydrides.

Derivatives **1g** and **1h**, which contain highly electronegative CN and NO_2 substituents, respectively, deserve particular attention. The degree of non-planarity of the C^2 atom in $\mathbf{1g^{\cdot-}}$ and the C^1 atom in $\mathbf{1gH^-}$ is small (8% and 7%, respectively), and the carbon atom of the CN group is electroneutral in all three systems **1g**, $\mathbf{1g^{\cdot-}}$ and $\mathbf{1gH^-}$. There is a modest π-resonance effect between the C≡N and C=C bonds in the parent compound **1g**, and this is enhanced in



1j **1j$^{\bullet-}$** **1jH$^-$**

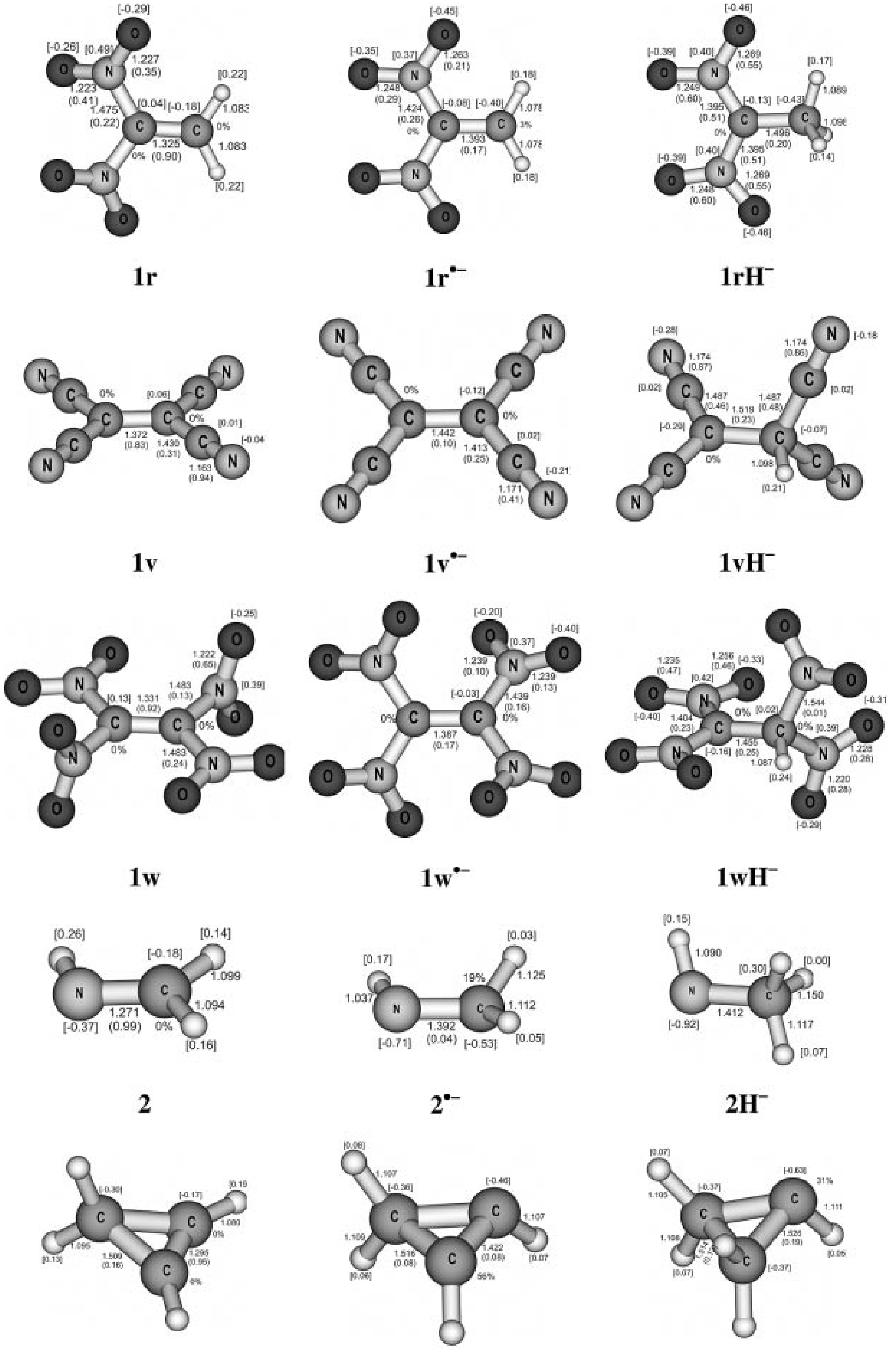
1k **1k$^{\bullet-}$** **1kH$^-$**

1l **1l$^{\bullet-}$** **1lH$^-$**

1m **1m$^{\bullet-}$** **1mH$^-$**

1q **1q$^{\bullet-}$** **1qH$^-$**

Figure 2. (*continued*)



1r **1r**$^{\bullet-}$ **1rH**$^-$

1v **1v**$^{\bullet-}$ **1vH**$^-$

1w **1w**$^{\bullet-}$ **1wH**$^-$

2 **2**$^{\bullet-}$ **2H**$^-$

3 **3**$^{\bullet-}$ **3H**$^-$

Figure 2. (*continued*)

1g$^{\cdot-}$ and **1gH**$^-$, as evidenced by the C^1–C π-bond orders of 0.35 and 0.57, respectively. At the same time, the π-bond order of the C=N double bond perpendicular to the molecular plane of the heavy atoms drops in these two species to 0.32 and 0.39, respectively (Figure 2). A high negative charge placed at nitrogen corroborates the presence of a substantial anionic resonance over the $^-$N=C=C fragment in **1g**$^{\cdot-}$ and **1gH**$^-$. Similarly, the molecular framework in **1h**, **1h**$^{\cdot-}$ and **1hH**$^-$ is planar. A strong anionic resonance is observed in the hydride **1hH**$^-$, where nitrogen and oxygen atoms carry large positive (0.37) and negative (–0.57) charges, respectively. The π-bond order along the N–C^1 bond is high (0.72), whereas the π-bond order between the N and O atoms is 0.45, as expected intuitively, because of the customary anionic resonance effect $^-O–N^+=O \leftrightarrow O=N^+–O^-$ in the NO_2 fragment. The pronounced pyramidalisation of the C^1 atom (59%) in **1iH⁻** is in agreement with the very strong electronegativity of fluorine, which prefers a high p content of the corresponding hybrid AO at the bound C^1 carbon. Consequently, the other two bonds emanating from C^1 also possess large p characters, thus increasing the s content of the lone pair. It is therefore not surprising that the C–C bond length of 1.528 Å is close to that in ethane. It is remarkable, however, that the negative charge is almost evenly distributed over all three heavy atoms.

Hydride ion attachment in **1j** and **1k** is more favourable at C^1. In both cases the terminal carbons and heteroatoms gain the lion's share of the excess negative charge. On the other hand, the CF_3 substituent prefers formation of a lone pair at the C^1 atom since this enables a strong negative hyperconjugation of the lone pair with the C–F bonds, as evidenced by their increased bond length and the high π-bond order (0.46) between the respective carbon atoms.

The *tert*-butyl anion **1mH⁻** has a DP of 36%. The structure has C_{3v} symmetry and a practically uniform distribution of the negative charge over the carbons.

In 1,1-dicyanoethylene (**1q**), and its anion **1q**$^{\cdot-}$ and hydride **1qH⁻**, all heavy atoms are coplanar. The carbon atom belonging to the CN group is electroneutral, and there is a strong anionic resonance $^-N=C=C$ between the CN group and the substituted carbon atom, as evidenced by the corresponding π-bond order of 0.48.

The carbons and nitrogens in the 1,1-dinitro derivatives **1r**, **1r**$^{\cdot-}$ and **1rH⁻** are planar, but the NO_2 groups are rotated out of plane around the C–N bonds in order to avoid strong mutual repulsion. The nitrogens are substantially positively charged, and there is a pronounced anionic resonance between the NO_2 groups and the central carbon.

Tetracyanoethylene (**1v**) and its anion **1v**$^{\cdot-}$ are planar systems, but two CN groups at the carbon bonded to the H atom in **1vH⁻** are placed in a plane perpendicular to the molecular one. In all three molecules, the anionic resonance takes place in the NC–C^n–C^m fragments, albeit to varying extents, where *n* and *m* are natural numbers [n, m = 1,2 ($n \neq m$)].

Tetranitroethylene (**1w**) has a very interesting conformation, where two diagonally placed NO_2 groups in *trans* positions are in the molecular plane, while the remaining two are in the planes perpendicular to the main molecular plane (Figure 2). There is no significant resonance effect between the NO_2 groups and the central C=C double bond.

The hydride ion attack at cyclopropene **3** occurs at one C atom of the double bond, which leads to the formation of a lone pair at the other CH centre carrying the largest negative charge. The rest of the data presented in Figure 1 speak for themselves.

An interesting result of all these calculations is that H^- attacks the carbon atom possessing lower electron density, as expected intuitively, although there are some surprises. The hydride ion attachment occurs at C atoms with significantly higher electron densities in monosubstituted systems **1h** and **1i** and disubstituted derivatives **1m**, **1q** and **1r** (Figure 2). In these cases the H^- attack is not exactly nucleophilic, but some caution has to be exercised because this finding holds for the Löwdin atomic charges employed here. Thus, some other definitions of the atomic charges have to be examined before a final conclusion can be drawn.

Finally, it is important to mention that some spin contamination is always present in the unrestricted calculations of the electronic structure of open-shell systems. It is commonly accepted that this is acceptable if the expectation value of the S^2 operator is around 0.75.[50] This condition was fulfilled in all the calculations performed on the radical anions examined in this work.

Energetic Properties

Ethene

A case study was performed on the parent molecule — ethene — in order to test the performance of the B3LYP scheme since this simple system serves as a reference for mono- and polysubstituted derivatives. For that purpose we carried out some additional calculations employing G2, G3 and G3(MP2) protocols. The results are compared with the experimental value for HA (12.9 kcal mol^{-1}) in Table 1. The first observation to be made is that geometry optimisation with the larger 6-31+G(d,p) basis set did not improve the calculated B3LYP hydride affinity; on the contrary, the deviation from the measured value was even larger. It turns out that the G2 and G3(MP2) results are in very good agreement with experiment, whereas the G3 and B3LYP values are too large by 1.2 and 2.1 kcal mol^{-1}, respectively, which is not bad either. One can therefore conclude that accordance with experiment is good for all theoretical schemes, especially if it is taken into account that the experimental error bars are usually ±2 kcal mol^{-1}.

A breakdown of the hydride affinity into triadic components is of importance because it can shed light on the accuracy of the B3LYP trichotomy analysis by pinpointing sources of possible errors. The Koopmans' term is practically the same in all computational procedures, as expected, because it is obtained by the same HF model. It appears, however, that the first adiabatic electron affinity $EA_1(M)^{ad}$ calculated by the B3LYP scheme is too high (too low in absolute values) by 6.2 kcal mol^{-1} compared to the G2 result. In contrast, the bond association energy is too small by 4.4 kcal mol^{-1}. Hence, a good estimate of the hydride affinity by the B3LYP approach is the result of a cancellation of errors to a large extent. Since Koopmans' contribution is fairly accurate, it follows that the relaxation effect is less accurate according to Equation (3). In fact, the $E(ea)^{(n)}_{rex}$ term calculated by the B3LYP method is too large by 6.6 kcal mol^{-1} (Table 1). The bottom line is that

Table 1. Comparison of the theoretical and experimental hydride affinity of ethene [kcal mol^{-1}] and its resolution into triadic components as obtained by various theoretical models.

Model	$(EA)_n^{\mathrm{Koop}}$	$(EA)_1^{\mathrm{ad}}$	$E(\mathrm{ea})^{(n)}_{\mathrm{rex}}$	$(BAE)^{\cdot -}$	HA(thr)
B3LYP/6-311+G(2df,p)// B3LYP/6-31G(d)	$(-102.4)_1$	–36.8	65.6	69.2	15.0
B3LYP/6-311+G(2df,p)// B3LYP/6-31G+(d,p)	$(-102.0)_1$	–34.0	68.0	67.3	15.9
G2	$(-101.9)_1$	–43.0	58.9	73.6	13.2
G3(MP2)	$(-101.9)_1$	–42.7	59.2	73.4	13.3
G3	$(-101.9)_1$	–41.6	60.3	73.1	14.1
MP2(fc)/6-311+G(2df,p)// B3LYP/6-31G(d)	$(-102.4)_1$	–41.8	60.6	72.3	13.1
Experiment[38]					12.9

the $EA_1(M)^{ad}$ and $(BAE)_\alpha^{\cdot -}$ terms computed by the B3LYP method are not as accurate as one might wish, in particular due to inherent troubles in calculating the electron affinity, as is well known. However, the hydride affinities are nevertheless quite acceptable because of partial cancellation of errors. Keeping this in mind, we shall employ triadic analysis when discussing the hydride affinities of substituted ethenes. It is plausible to assume that the trend of changes will be correctly reproduced because inaccuracies in estimated HA values will be neutralised to a large extent.

Substituted Ethenes

The first comment to be made is that the agreement with available experimental data is surprisingly good. This lends credence to the assumption that other theoretical HA values are good as well and that they can be safely used instead of the missing measured data. The effect of substituents can be conveniently interpreted by selecting ethene as a gauge molecule and taking a difference, ΔHA, of the studied system relative to the parent compound:

$$[\Delta\mathrm{HA}(\mathbf{M})]_\alpha = [\Delta(\mathrm{EA}_n^{\mathrm{Koop}});\ \Delta E(\mathrm{ea})^{(n)}_{\mathrm{rex}};\ \Delta(\mathrm{BAE})_\alpha^{\cdot -}] \tag{6}$$

where

$$\Delta(\mathrm{EA}_n^{\mathrm{Koop}}) = \mathrm{EA}_n(\mathbf{M})^{\mathrm{Koop}} - \mathrm{EA}_1(\mathbf{1a})^{\mathrm{Koop}} \tag{6a}$$

$$\Delta[E(\mathrm{ea})^{(n)}_{\mathrm{rex}}] = E(\mathrm{ea})^{(n)}_{\mathrm{rex}}(\mathbf{M}) - E(\mathrm{ea})^{(1)}_{\mathrm{rex}}(\mathbf{1a}) \tag{6b}$$

$$\Delta(\mathrm{BAE})_\alpha^{\cdot -} = (\mathrm{BAE})_\alpha^{\cdot -}(\mathbf{M}) - (\mathrm{BAE})_\alpha^{\cdot -}(\mathbf{1a}) \tag{6c}$$

where **M** stands for the molecule under study. The square brackets in Equation (6) imply the summation of three terms within.

Let us consider the monosubstituted ethenes first. The alkyls are not very interesting, because they affect the HA values very little. In addition, the difference between the C^1 and C^2 reaction sites is also small. Phenyl and ethenyl are more intriguing substituents since a large anionic resonance effect via the π-electrons is expected. However, triadic analysis shows that $\Delta\mathrm{HA}(\mathbf{1e^2})$ = [42.0; –7.0; –1.4] = 33.6 kcal mol^{-1}, which means that the main reason for the increased HA lies in the stabilisation of the PRIMO, which in this case is the lowest unoccupied MO. Surprisingly, the relaxation effect is smaller than in **1a** by 7 kcal mol^{-1}. Where did the anionic resonance disappear? One is tempted to conclude that the latter can be retrieved from the difference between the first adiabatic electron affinities, which is 35.1 kcal mol^{-1}. This would be highly misleading, however, because $EA_1(M)^{ad} = EA_n(M)^{Koop} + E(ea)^{(n)}_{rex}$ [see Equation (3)]. It appears that the difference in $EA_1(M)^{ad}$ is a consequence of the very low PRIMO orbital energy in **1e**. Thus, the PRIMO orbital is much more stabilized already in the neutral initial compound styrene (**1e**) than in **1a**, which has nothing to do with the anion $\mathbf{1e^{\cdot -}}$. It follows as a corollary that there is no anionic resonance in the latter anion despite the presence of a phenyl ring. It should be noted within this context that the (anionic) resonance and relaxation effects are related, but it should always be kept in mind that they generally differ by their very definitions. The difference in the hydride affinities between the positions C^1 and C^2 in **1e** is determined by the difference in the bond association energies, which holds, in general, if various sites within the same molecule are considered. In the case of the C^1 site in $\mathbf{1eH^-}$ the $(BAE)^{\cdot -}$ term is smaller by 26.5 kcal mol^{-1}.

Similarly, in 1,3-butadiene (**1f**) we have a triad [29.6; –2.7; –2.7] = 24.2 kcal mol^{-1} which reflects the same pattern and leads to the same conclusions, the only difference being in the actual numbers for the particular terms. The C^1 site is less favourable by 21.4 kcal mol^{-1}.

The CN and NO_2 groups represent substituents of particular importance, since the corresponding anions $\mathbf{1g^{\cdot -}}$ and $\mathbf{1h^{\cdot -}}$ are very stable species in view of their positive electron affinities of 2.4 and 27.7 kcal mol^{-1}, respectively, which imply that the electron capture is an exothermic process. Triadic analysis $\Delta\mathrm{HA}(\mathbf{1g^2})$ = [48.8; –9.6; 4.6] = 43.8 kcal mol^{-1} and $\Delta\mathrm{HA}(\mathbf{1h^2})$ = [71.5; –7.0; 1.0] = 65.5 kcal mol^{-1} reveals the same mechanism enhancing the hydride affinity, which occurs due to large stabilisation of the LUMOs (Figure 3). The relaxation effect counteracts this, but to a much smaller extent, and the influence of Koopmans' term is overwhelming. The C^1 position in $\mathbf{1g^1}$ is energetically less advantageous by 23.9 kcal mol^{-1}.

For F and CF_3 groups the HA values are as follows: $\Delta\mathrm{HA}(\mathbf{1i^2})$ = [–2.7; 9.8; 1.2] = 8.3 kcal mol^{-1} and $\Delta\mathrm{HA}(\mathbf{1l^2})$ = [23.4; 5.4; 7.5] = 36.3 kcal mol^{-1}. Both substituents do not

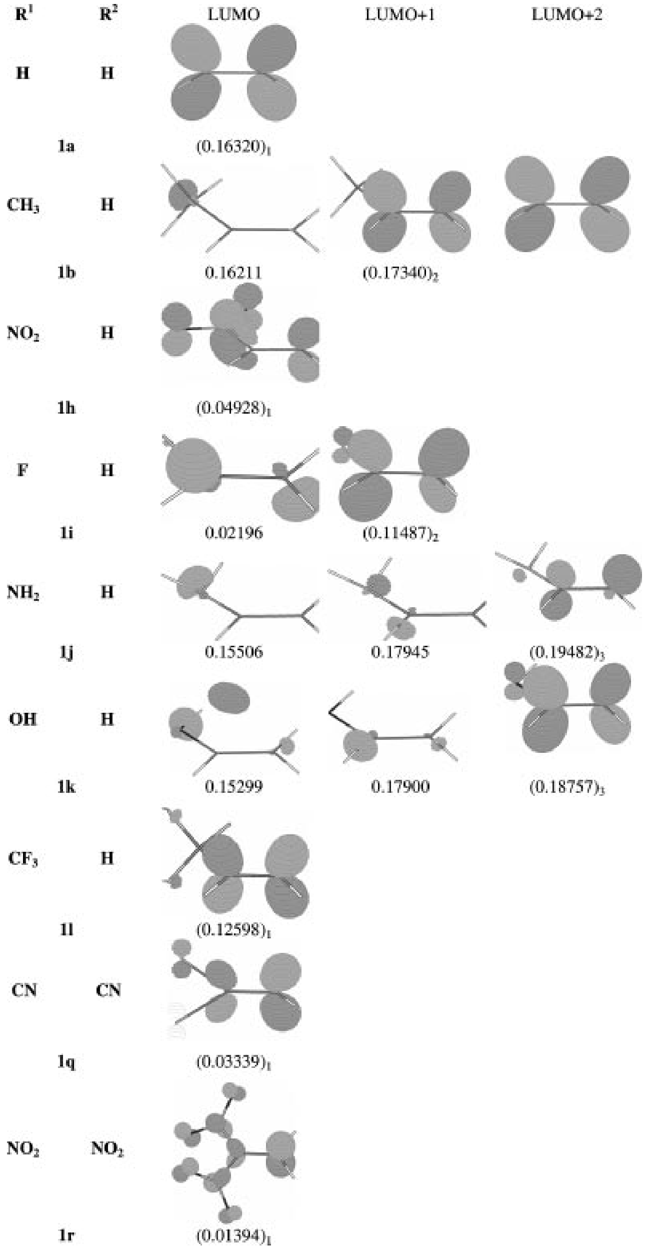


Figure 3. Principal molecular orbitals calculated by the HF/6-311G(2df,p)//B3LYP/6-31G(d) model together with their orbital energies [a.u.] in parentheses.

behave in a typical manner. Koopmans' term is slightly less favourable for F substitution, but the relaxation contribution amplifies the hydride affinity. The CF$_3$ group considerably increases the HA value (36.3 kcal mol^{-1}) as a consequence of the synergy of all terms.

The NH$_2$ (**1j**) and OH (**1k**) derivatives undergo nucleophilic H$^-$ attack at position C^1, which is unusual. It is noteworthy that the PRIMOs in both molecules lie relatively high in orbital energy and are LUMO+2 orbitals (Figure 3). Hence, Koopmans' term diminishes the hydride affinity. The corresponding triads are ΔHA(**1j^2**) = [–19.8; 17.0; 5.0] = 2.2 kcal mol^{-1} and ΔHA(**1k^1**) = [–15.3; 17.5; 10.7] = 12.9 kcal mol^{-1}. In both cases the negative contribution of the Koopmans' term is overcompensated by a joint effect of the relaxation and bond association energies, which stabilize hydrides **1j^{1}H$^-$** and **1k^{1}H$^-$**.

1,1-Disubstituted ethenes containing NO$_2$ and CF$_3$ groups (**1r** and **1s**, respectively) possess remarkable features since their electron affinities are appreciably positive and the corresponding anions **1r**$^{\cdot-}$ and **1s**$^{\cdot-}$ (Table 2) should be stable species. The electron affinity of **1r**, in particular, is rather large (51.2 kcal mol^{-1}). Triadic analysis yields ΔHA(**1r^2**) = [93.6; –5.6; 13.4] = 101.5 kcal mol^{-1} and ΔHA(**1s^2**) = [43.3; 6.6; 13.2] = 63.1 kcal mol^{-1}. It appears that both molecules exhibit high hydride affinities. Koopmans' term dominates in amplifying the HAs. The disubstituted CF$_3$ derivative enjoys a synergy of all three terms, just like in the case of the CF$_3$-monosubstituted ethene **1l**.

Polysubstituted ethenes **1t**–**1w** are of particular interest. It should be noted that the polynitro compounds **1u** and **1w** are probably of academic interest only due to their high energy content,[51] which means that their synthesis is not very likely. Nevertheless, it is worth noting that the electron affinity of **1u** and **1w** is remarkably high (79.8 and 94.2 kcal mol^{-1}, respectively), whereas their corresponding hydride affinities of 125.4 and 141.7 kcal mol^{-1} deserve particular attention because they are record values. It is striking that even their HF LUMOs are bonding orbitals (Table 2). The respective triads are: ΔHA(**1v^2**) = [130.7; –14.1; 8.7] = 125.3 kcal mol^{-1} and ΔHA(**1w^2**) = [144.6; –13.7; 10.7] = 141.6 kcal mol^{-1} thus convincingly proving the point that stabilisation of the principal molecular orbitals (i.e. LUMOs in these cases) exerts a predominating effect. More useful compounds from the practical point of view seem to be the tri- and tetrasubstituted cyanoethylenes **1t** and **1v**. They possess electron affinities of 60.2 and 81.0 kcal mol^{-1}, respectively, which are also respectably high. The triadic components are as follows: ΔHA(**1t^1**) = [116.7; –19.8; –2.6] = 94.3 kcal mol^{-1} and ΔHA(**1v**) = [142.5; –24.7; –14.9] = 102.9 kcal mol^{-1}. The Koopmans' term once again exerts an overwhelming effect, which is considerably diminished by relatively large relaxation and bond association contributions. In spite of that, **1t** and **1v** exhibit high hydride affinities. It should be noted that the LUMOs in **1t** and **1v** are strongly stabilized to such an extent that they become bonding MOs once populated by an electron.

Finally, a few words about systems **2** and **3** are needed here. The hydride affinity of **2** has been measured and it is gratifying that the calculated value is in very good accordance with this experimental result. The more favourable position for the H$^-$ attachment is the carbon atom. Attack of hydride at the nitrogen results in a hydride affinity of only 10.2 kcal mol^{-1}, which is lower by 16.2 kcal mol^{-1}. The underlying reason is, of course, the smaller bond energy term describing attachment of the H atom to nitrogen in the anion **2**$^{\cdot-}$ (Table 2). Nucleophilic attack of the hydride ion at cyclopropene **3** is described by the triad ΔHA(**3**) = [–0.7; 13.7; 15.2] = 28.2 kcal mol^{-1}, which implies that

Table 2. Relative stabilities of hydrides obtained by H^- attack on ethene and its $R^1R^2C^1=C^2H_2$ derivatives, and resolution of the calculated hydride affinities into triadic components [kcal mol^{-1}].[a] Methanimine and cyclopropene are also considered in order to include some systems possessing atypical double bonds.

R^1	R^2	Molecule	$(EA)_n^{Koop}$	$(EA)_1^{ad}$	$E(ea)^{(n)}_{rex}$	$(BAE)^{\cdot-}$	HA	ΔHA
H	H	**1a**	$(-102.4)_1$	–36.8	65.6	69.2	15.0 (12.9 ± 2.1)	0.0
H	CH_3	**1b**^{1}	$(-108.8)_2$	–36.0	72.8	69.3	15.9 (14.6 ± 2.1)	0.9
		1b^2	$(-108.8)_2$	–36.0	72.8	68.1	14.8	0.2
H	C_2H_5	**1c**^{2}	$(-96.4)_1$	–32.8	63.6	67.9	17.7	2.2
		1c^1	$(-96.4)_1$	–32.8	63.6	66.2	16.0	1.0
H	C_3H_7	**1d**^{2}	$(-107.8)_2$	–31.4	76.4	66.5	17.7	2.7
		1d^1	$(-107.8)_2$	–31.4	76.4	64.9	16.1	1.1
H	C_6H_5	**1e**^{2}	$(-60.4)_1$	–1.7	58.6	67.8	48.6 (49.0 ± 2.2)	33.6
		1e^1	$(-60.4)_1$	–1.7	58.6	41.3	22.1	7.1
H	$CH=CH_2$	**1f**^{2}	$(-72.8)_1$	–10.0	62.9	66.5	39.2	24.2
		1f^1	$(-72.8)_1$	–10.0	62.9	45.1	17.7	2.7
H	CN	**1g**^{2}	$(-53.6)_1$	2.4	56.0	73.8	58.8 (57.1 ± 2.2)	43.8
		1g^1	$(-53.6)_1$	2.4	56.0	49.9	34.9	19.9
H	NO_2	**1h**^{2}	$(-30.9)_1$	27.7	58.6	70.2	80.5 (80.1)	65.5
H	F	**1i**^{2}	$(-105.1)_2$	–29.7	75.4	70.4	23.3	8.3
H	NH_2	**1j**^{2}	$(-122.2)_3$	–39.6	82.6	74.2	17.2	2.2
		1j^1	$(-122.2)_3$	–39.6	82.6	67.7	10.6	4.4
H	OH	**1k**^{2}	$(-117.7)_3$	–34.6	83.1	79.9	28.0	13.0
		1k^1	$(-117.7)_3$	–34.6	83.1	65.9	13.9	1.1
H	CF_3	**1l**^{2}	$(-79.0)_1$	–8.0	71.0	76.7	51.2	36.2
		1l^1	$(-79.0)_1$	–8.0	71.0	59.8	34.4	19.4
CH_3	CH_3	**1m**^{2}	$(-106.2)_2$	–32.8	73.4	68.6	18.4 (15.5 ± 2.1)	3.4
		1m^2	$(-106.2)_2$	–32.8	73.4	65.7	15.5	0.5
CH_3	C_2H_5	**1n**^{1}	$(-105.1)_2$	–29.3	75.7	67.3	20.6	5.6
		1n^2	$(-105.1)_2$	–29.3	75.7	63.2	16.5	1.5
CH_3	C_6H_5	**1o**^{1}	$(-66.3)_1$	–2.4	63.8	66.9	47.1 (48.9)	32.1
		1o^1	$(-66.3)_1$	–2.4	63.8	42.3	22.4	7.4
CH_3	CN	**1p**^{2}	$(-60.7)_1$	–0.1	60.6	73.2	55.7 (56.7)	40.7
		1p^1	$(-60.7)_1$	–0.1	60.6	50.8	33.3	18.3
CN	CN	**1q**^{2}	$(-21.0)_1$	32.5	53.4	81.4	96.4	81.4
		1q^1	$(-21.0)_1$	32.5	53.4	34.2	49.3	34.3
NO_2	NO_2	**1r**^{2}	$(-8.8)_1$	51.2	60.0	82.6	116.5	101.5
CF_3	CF_3	**1s**^{2}	$(-59.1)_1$	13.1	72.2	82.4	78.1	63.1
		1s^1	$(-59.1)_1$	13.1	72.2	50.6	46.4	31.4
tricyanoethylene		**1t**^{2}	$(14.3)_1$	60.2	45.8	66.6	109.4	94.4
		1t^1	$(14.3)_1$	60.2	45.8	44.5	87.2	72.2
trinitroethylene		**1u**^{2}	$(28.3)_1$	79.8	51.5	77.9	140.4	125.4
		1u^1	$(28.3)_1$	79.8	51.5	67.2	129.7	114.7
tetracyanoethylene		**1v**	$(40.1)_1$	81.0	40.9	54.3	117.9	102.9
tetranitroethylene		**1w**	$(42.2)_1$	94.2	51.9	80.0	156.7	151.7
methanimine		**2**^{2}	$(-95.7)_1$	–26.1	69.6	70.1	26.4 (25.3)	11.4
		2^1	$(-95.7)_1$	–26.1	69.6	53.9	10.2	5.3
cyclopropene		**3**	$(-103.1)_1$	–23.7	79.3	84.4	43.3 (41.7)	28.3

[a] Available experimental data given within parentheses are taken from ref.[38]. The sites for the H^- attack are denoted by superscripts 1 and 2, which correspond to carbon atom C^1 and C^2, respectively. The subscripts 1,2 and 3 refer to LUMO, LUMO+1 and LUMO+2 molecular orbitals, respectively. In tricyanoethylene and trinitroethylene H^- addition takes place at the singly substituted C^2 atom.

highly strained C=C double bond has an appreciably larger hydride affinity than the archetypal ethene. This is a consequence of a combined contribution of the relaxation and $(BAE)^{\cdot-}$ terms.

General Considerations

It is of some interest to examine whether there is a single dominant feature which determines the behaviour of substituted ethenes and gives a trend of changes of their hydride affinities. An obvious candidate is Koopmans' electron affinity, because it varies in a large range of 164.4 kcal mol^{-1}. On the other hand, the (BAE)$^{\cdot-}$ term has a very small range of values spread between 34.2 (**1q^1**) and 84.4 (**3**) kcal mol^{-1}, with a large clustering around 60 kcal mol^{-1}, hence it is not likely that the (BAE)$^{\cdot-}$ contribution to the total hydride affinity plays a decisive role. A plot of calculated HA values against Koopmans' term is shown in Figure 4. There is an obvious trend that increased Koopmans' electron affinity, EA_n^{Koop}, leads to higher hydride affinities. However, the correlativity of the two sets of data is not good, as evidenced by the R^2 factor of 0.94 and relatively large average absolute error of 9.1 kcal mol^{-1}. Nevertheless, it is fair to say that Koopmans' term is a dominant factor, although it can provide only qualitative information. A much better correlation is obtained if Koopmans' and the relaxation terms are combined in a way to give the first adiabatic electron affinity, EA_1^{ad}. The straight line depicted in Figure 5 has the form HA = 1.02 EA_1^{ad} + 54.9 kcal mol^{-1}, with a correlation coefficient of 0.97 and an average absolute deviation (AAD) of 5.6 kcal mol^{-1}. It follows that the trend of changes in HAs is fairly well described by the ability of a compound to accommodate the excess electron density in its anion radical. This conclusion is compatible with chemical intuition. Having said that, it should be pointed out that the correlation of HA against EA_1^{ad} still leaves much to be desired because the AAD is too high. Deviations from the straight line in Figure 5 are caused by variation in the bond association energies (BAE)$^{\cdot-}$, which should be explicitly taken into account if a more accurate quantitative estimate of the hydride affinity is required. It is worth noting in this respect that the (BAE)$^{\cdot-}$ term itself does not exhibit any correlation whatsoever with the HA values. A lesson to be taken home is that all three terms occurring in the triadic analysis should be explicitly taken into account if a quantitative description of hydride affinities is needed.

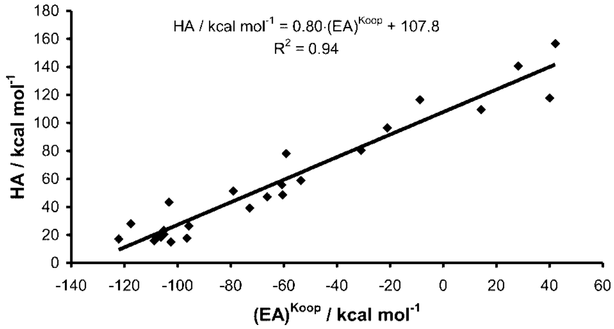


Figure 4. A plot of the theoretical hydride affinities against Koopmans' electron affinities.

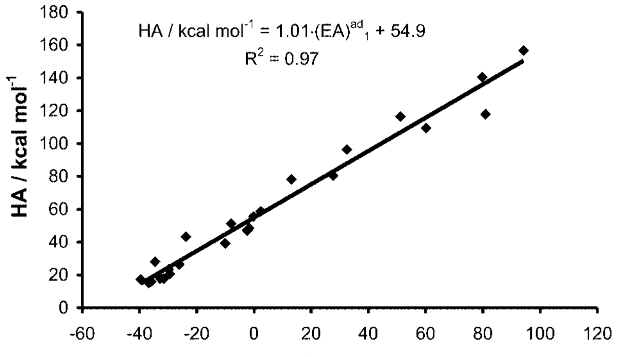


Figure 5. The linear relationship between the theoretical hydride affinities and adiabatic electron affinities.

It would be useful to get insight into the hydride affinities by a simple principle like the hard-soft-acid-base (HSAB) criterion put forward by Pearson some forty years ago.[52,53] According to this concept a hard Lewis acid will interact strongly with hard bases. Similarly, soft acids will form stable compounds (complexes) with soft bases. Both H$^-$ and ethene derivatives qualify as soft Lewis bases and acids, respectively,[1,54] therefore a linear correlation between the hydride affinities and the absolute value of a difference between the hardness of the H$^-$ anion [η(H$^-$)] and that of substituted ethenes denoted by M [η(M)] might be expected. According to Pearson, the absolute hardness of an atom or a molecule is given by (7).[54]

$$\eta = \frac{I - A}{2} \cong -\frac{\varepsilon(\mathrm{HOMO}) - \varepsilon(\mathrm{LUMO})}{2} \qquad (7)$$

where I and A stand for the first adiabatic ionisation potential and electron affinity, respectively, and are commonly replaced by the negative orbital energies of the HOMO and LUMO, respectively. By using formula (7) in its single electron approximation one can readily obtain the absolute hardness values, η(M), which are presented in Table S1 of the Supporting Information. The value of η(H$^-$) is 117.5 kcal mol^{-1}. An attempt at correlating hydride affinities with $|\eta(\mathrm{H}^-) - \eta(\mathrm{M})|$ is illustrated in Figure 6, which resembles the shrapnel distribution of a gun discharge. Since both H$^-$ and alkenes are soft, we tried to find a correlation between HA and $|\sigma(\mathrm{H}^-) - \sigma(\mathrm{M})|$, where σ stands for the softness parameter $\sigma = (1/\eta)$.[54] The distribution of points is similar to that in Figure 6. One can therefore safely conclude that the HSAB criterion does not apply to the hydride affinities.

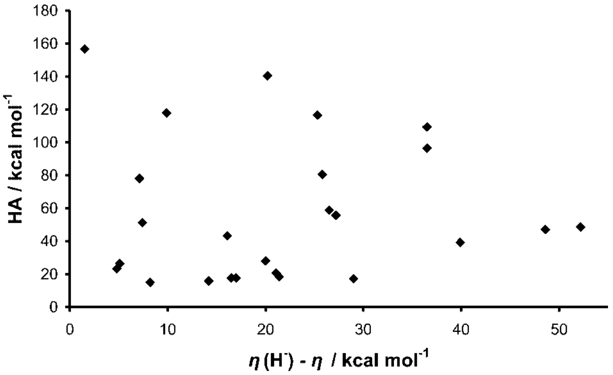


Figure 6. The lack of any correlation between the difference in absolute hardness of H$^-$ and the examined substituted ethenes on one side and the calculated hydride affinities on the other.

As a final comment we would like to stress that the H^- affinities might be useful in defining a scale of the electrophilic propensities (ELPRO) of the studied substituted ethenes. The highest electrophilic propensities are exhibited by tetranitroethylene (**1w**), trinitroethylene (**1u**), tetracyanoethylene (**1v**) and 1,1-dinitroethylene (**1r**), whereas the lowest ELPRO value is found in parent ethene.

Concluding Remarks

We have shown that the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) method is fairly reliable in reproducing and predicting the hydride affinities of substituted ethenes. The accuracy is better than expected due to cancellation of errors in terms occurring in the triadic formula. The adiabatic electron affinities, which are less accurate but still good enough for interpretative purposes, are useful by-products of the present analysis. The derivatives involving single CN and NO_2 substituents and more than one CN, NO_2 and CF_3 substituents possess positive adiabatic electron affinities, thus implying that the corresponding anions can be formed in an exothermal way. These systems fit the picture behind the triadic formula (4) particularly well provided that the electron affinity is larger than 17.4 kcal mol^{-1}, being the ionization energy of H^-. It appears that the hydride affinities are fairly well correlated with the adiabatic electron affinities. This means that the trend of changes of hydride affinities is well described by the initial state (neutral molecule) effect and intermediate (relaxation of the electron and nuclei upon attachment of an additional electron) effect. The full energetic account embodied in triadic formula (4) is necessary if quantitative results are desired.

The β-carbons are most susceptible to H^- attack, as a rule, although exceptions (α-carbon H^- attachment) are found for single CH_3, NH_2 and OH substituents. H^- attack at the α-carbon leads to dissociation of the substituent in the case of NO_2 (**1h**) and 1,1-dinitroethylene (**1r**). In the case of **1i**, the H^- attack at the substituted C^1 atom results in a complex of ethene with F^- at a distance of 1.79 Å from the latter and the host α-C atom.

The present results indicate that Pearson's HSAB principle fails to give an acceptable description of hydride affinities in substituted ethenes.

Finally, the H^- affinities can serve a useful purpose of defining the electrophilic propensity (ELPRO) of the studied ethenes. The highest electrophilic propensities are exhibited by tetranitroethylene (**1w**), trinitroethylene (**1u**), tetracyanoethylene (**1v**) and 1,1-dinitroethylene (**1r**), whereas the lowest ELPRO value is found in parent ethene.

Acknowledgments

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[1] M. B. Smith, J. March, *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 5th ed., John Wiley & Sons, New York, **2001**.

[2] A. C. Cope, M. M. Martin, M. A. McKervey, *Q. Rev. Chem. Soc.* **1966**, *20*, 119–152.

[3] F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry*, 4th ed., Springer Science and Business Media Inc., New York, **2000**, Part A, pp. 316–323.

[4] G. A. Olah, A. Molnár, *Hydrocarbon Chemistry*, Wiley-Interscience, New York, **1995**.

[5] E. M. Arnett, R. A. Flowers, A. E. Meekhof, L. Miller, *J. Am. Chem. Soc.* **1993**, *115*, 12603–12604.

[6] E. M. Arnett, R. A. Flowers, R. T. Ludwig, A. E. Meekhof, S. A. Walek, *J. Phys. Org. Chem.* **1997**, *10*, 499–513.

[7] G. A. Olah, G. K. S. Prakash, J. Sommer, *Superacids*, Wiley-Interscience, New York, **1995**.

[8] J.-P. Cheng, K. L. Handoo, J. Xue, V. D. Parker, *J. Org. Chem.* **1993**, *58*, 5050–5054.

[9] K. L. Handoo, J.-P. Cheng, V. D. Parker, *J. Am. Chem. Soc.* **1993**, *115*, 5067–5072.

[10] V. D. Parker, *Acta Chem. Scand.* **1992**, *46*, 1133–1147.

[11] J.-P. Cheng, K. L. Handoo, V. D. Parker, *J. Am. Chem. Soc.* **1993**, *115*, 2655–2660.

[12] X.-Q. Zhu, M. Zhang, Q.-Y. Liu, X.-X. Wang, J.-Y. Zhang, J.-P. Cheng, *Angew. Chem. Int. Ed.* **2006**, *45*, 3954–3957.

[13] D. Ostovic, I.-S. Lee, R. M. G. Roberts, M. M. Kreevoy, *J. Org. Chem.* **1985**, *50*, 4206–4211.

[14] M. M. Kreevoy, A. T. Kotchevar, *J. Am. Chem. Soc.* **1990**, *112*, 3579–5583.

[15] I.-S. Lee, K.-H. Chow, M. M. Kreevoy, *J. Am. Chem. Soc.* **2002**, *124*, 7755–7761 and references cited therein.

[16] P. A. Frey, *FASEB J.* **1996**, *10*, 461–470.

[17] E. P. Hunter, S. G. Lias, in *NIST Chemistry WebBook, NIST Standard Reference Database Number* 69 (Ed. W. G. Mallard), National Institute of Standards and Technology, Gaithersburg, MD, **2003** (http://webbook.nist.gov).

[18] G. P. Bean, *J. Org. Chem.* **1993**, *58*, 7336–7340.

[19] R. Karaman, J.-T. Huang, J. L. Fry, *J. Org. Chem.* **1991**, *56*, 188–195.

[20] P. G. Wenthold, *Int. J. Mass Spectrom.* **2000**, *195/196*, 319–325.

[21] C. H. Reynolds, *J. Am. Chem. Soc.* **1992**, *114*, 8676–8682.

[22] R. E. Rosenberg, *J. Am. Chem. Soc.* **1995**, *117*, 10358–10364.

[23] S. Gronert, J. R. Keeffe, *J. Am. Chem. Soc.* **2005**, *127*, 2324–2333.

[24] E.-U. Würthwein, G. Lang, L. H. Schappele, H. Mayr, *J. Am. Chem. Soc.* **2002**, *124*, 4084–4092.

[25] M. Mandado, C. Van Alsenoy, R. A. Mosquera, *Chem. Phys. Lett.* **2005**, *405*, 10–17 and references cited therein.

[26] M. Mandado, C. Van Alsenoy, R. A. Mosquera, *J. Phys. Chem. A* **2004**, *108*, 7050–7055.

[27] R. F. W. Bader, *Atoms in Molecules, A Quantum Theory*, Oxford University Press, Oxford, **1990**.

[28] R. F. W. Bader, P. M. Bedall, J. Preslak, *J. Chem. Phys.* **1973**, *58*, 557–566.

[29] N. C. J. Stutchbury, D. L. Cooper, *J. Chem. Phys.* **1983**, *79*, 4967–4972.

[30] M. A. Spackman, E. N. Maslen, *J. Phys. Chem.* **1986**, *90*, 2020–2027.

[31] E. N. Maslen, M. A. Spackman, *Aust. J. Phys.* **1985**, *38*, 273–287.

[32] For a thorough analysis of the definitions of atomic charges and their critical appraisal see: K. Jug, Z. B. Maksić, in *Theoretical Models of Chemical Bonding, Part 3. Molecular Spectroscopy, Electronic Structure and Intramolecular Interactions* (Ed.: Z. B. Maksić), Springer Verlag, Berlin, Heidelberg, **1991**, p. 235.

[33] Z. B. Maksić, R. Vianello, *J. Phys. Chem. A* **2002**, *106*, 419–430.

[34] Z. B. Maksić, R. Vianello, *ChemPhysChem* **2002**, *3*, 696–700.

[35] C. A. Deakyne, *Int. J. Mass Spectrom.* **2003**, *227*, 601–616.

[36] a) R. Vianello, Z. B. Maksić, *J. Phys. Org. Chem.* **2005**, *18*, 699–704; b) R. Vianello, Z. B. Maksić, *Tetrahedron* **2006**, *62*,

3402–3411; c) R. Vianello, H. Maskill, Z. B. Maksić, *Eur. J. Org. Chem.* **2006**, 2581–2589.

[37] R. Vianello, Z. B. Maksić, *Inorg. Chem.* **2005**, *44*, 1095–1102.

[38] S. G. Lias, *Ionisation Energy Evaluation*, in *NIST Chemistry WebBook*, *NIST Standard Reference Database Number 69* (Eds.: P. J. Linstrom, W. G. Mallard), June **2005**, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).

[39] T. Koopmans, *Physica* **1933**, *1*, 104–113.

[40] S. P. McGlynn, K. Wittel, L. Klasinc, in *Theoretical Models of Chemical Bonding, Part 3. Molecular Spectroscopy, Electronic Structure and Intramolecular Interactions* (Ed.: Z. B. Maksić), Springer Verlag, Berlin-Heidelberg, **1991**, p. 99.

[41] See for example: a) E.Honneger, E.Heilbronner, in *Theoretical Models of Chemical Bonding*, part 3 (Ed.: Z. B. Maksić), Springer Verlag, Berlin, Heidelberg, **1991**, p. 99; M. Eckert-Maksić, in *Theoretical Models of Chemical Bonding*, part 3 (Ed.: Z. B. Maksić), Springer Verlag, Berlin, Heidelberg, **1991**, p. 153 and references cited therein.

[42] See for example: a) C. Trindle, *Croat. Chem. Acta* **1984**, *57*, 1231b) Z. B. Maksić, *Prologue: Modeling – A Search for Simplicity*, in *Theoretical Models of Chemical Bonding*, part 1 (Ed.: Z. B. Maksić), Springer Verlag, Berlin, Heidelberg, **1990**.

[43] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Jr., Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q.Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and A. J. Pople, GAUSSIAN 98 (Revision A.10), Gaussian, Inc., Pittsburgh PA, **1998**.

[44] J. H. Callomon, E. Hirata, K. Kuchitsu, W. J. Lafferty, A. G. Maki, C. S. Pote, in *Landoldt-Bernstein*, vol. 7 (Eds.: K. H. Hellwege, A. M. Hellwege), Springer Verlag, Berlin, **1976**.

[45] Z. B. Maksić, B. Kovačević, *J. Chem. Soc., Perkin Trans. 2* **1999**, 2623–2629.

[46] P. O. Löwdin, *J. Chem. Phys.* **1950**, *18*, 365–375.

[47] Z. B. Maksić, in *Theoretical Models of Chemical Bonding, Part 3. Molecular Spectroscopy, Electronic Structure and Intramolecular Interactions*, (Ed.: Z. B. Maksić), Springer Verlag, Berlin-Heidelberg, **1991**, p. 289 and references cited therein.

[48] Z. B. Maksić, K. Rupnik, *Z. Naturforsch., Teil A* **1983**, *38*, 308.

[49] F. L. Hirshfeld, *Theor. Chim. Acta* **1977**, *44*, 129–138.

[50] C. J. Cramer, *Essentials of Computational Chemistry*, 2nd ed., John Wiley & Sons, Chichester, **2004**.

[51] The interested reader should consult: *Energetic Materials*, parts 1 and 2 (Eds.: P. Politzer, J. S. Murray), Elsevier, Amsterdam, **2003**.

[52] R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.

[53] *Hard and Soft Acids and Bases* (Ed.: R. G. Pearson), Dowden, Hutchingson Ross Publishing Company, Stroutsburg, **1973**.

[54] R. G. Pearson, in *Theoretical models of Chemical Bonding*, vol. 2 (Ed.: Z. B. Maksić), Springer Verlag, Berlin, Heidelberg, **1990**, p. 45 and references cited therein.

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