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Nucleophilicity—Periodic Trends and Connection to Basicity

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Abstract: The potential energy profiles of 18 identity S_N2 reactions have been estimated by using G2-type quantum-chemical calculations. The reactions are: $X^- + CH_3{-}X \rightarrow X{-}CH_3 + X^-$ and $XH + CH_3{-}XH^+ \rightarrow {}^+HX{-}CH_3 + XH$ ($X = NH_2$, OH, F, PH_2, SH, Cl, AsH_2, SeH, Br). Despite the charge difference, the barrier heights and the geometrical requirements upon going from the reactant to the transition structure are surprisingly similar for X^- and XH. The barrier heights decrease on going from left to right in the periodic table, and increasing ionization energy (of X^- and XH) is correlated with decreasing barrier. The observed trends are explained in terms of substrates with stronger electrostatic character giving rise to lower energetic barriers due to decreased electron repulsion in the transition structure. On the basis of this study, the relationship between the kinetic concept of nucleophilicity and the thermodynamic concept of basicity has been analyzed and clarified. Since the trends in intrinsic nucleophilicity (only defined for identity reactions) and basicity are opposite, overall nucleophilicity (defined for any reaction) will be determined by the relative contribution of the two factors. Only for strongly exothermic reactions will basicity and nucleophilicity be matching.

Keywords: ab initio calculations · basicity · nucleophilic substitution · reaction mechanisms · transition states

Introduction

It is elementary knowledge that the S_N2 reaction in organic chemistry proceeds via a mechanism in which the nucleophile (Y) displaces the nucleofuge (X, leaving group) by gradually binding to the central carbon, diametrically opposed to the C–X bond, upon which the latter is weakened. The key step is passage through the Walden transition structure, in which the carbon atom is sp^2 hybridized, with partial bonds to both Y and X. The overall reaction for anionic nucleophiles can be expressed by Equation (1) and for neutral nucleophiles by Equation (2).

$$Y^- + R{-}X \rightarrow Y{-}R + X^- \quad (1)$$

$$Y + R{-}X^+ \rightarrow Y{-}R^+ + X \quad (2)$$

Figure 1 shows the enthalpy profile of a typical gas-phase S_N2 reaction (anionic case).[1,2] The situation in solution is of course more complicated, and the advantage of the simplified gas-phase situation is that it allows us to isolate the reaction partners from the surrounding solvent molecules, thereby addressing their inherent properties.[3,4]

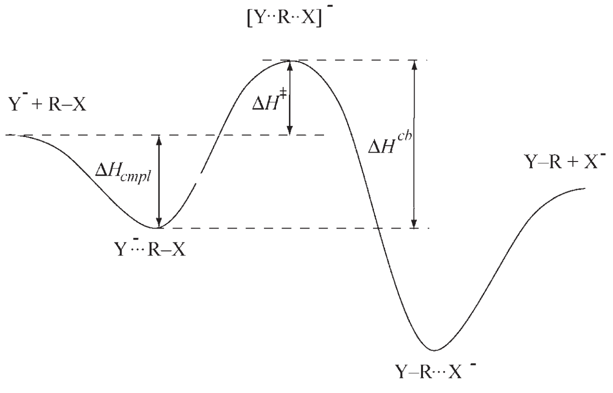

Figure 1. General enthalpy diagram for a nucleophilic substitution reaction. In addition to the reactant and product states, there are minima corresponding to weakly bound reactant-like and product-like complexes. In between these, there is a local maximum corresponding to the transition structure. The abbreviation *cb* stands for central barrier.

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Continuous efforts to unravel the molecular factors that govern reactivity have established some facts, while some questions remain unanswered.[5,6] Herein, we report how the properties of the nucleophile and nucleofuge influence the rate at which the reaction occurs, which is still not a fully understood topic. In this context, the height of the central barrier in terms of energy/enthalpy is a key issue. In addition to energy/enthalpy, the kinetics and dynamics of a gas-phase S_N2 reaction are susceptible to changes in entropy, and even to non-statistical behavior.[7,8] This is beyond the scope of this article.

According to the IUPAC definition, nucleophilicity is the ability of an attacking group, Y, to furnish nucleophilic displacement in an S_N2 reaction, while nucleofugacity is the corresponding ability of a leaving group, X. It is clear from their definitions that the chemical quantities of nucleophilicity and basicity are different. On the other hand, they are clearly related; the difficulty is stating exactly how they are related. This question has been raised by many authors,[9–18] but it still awaits a firm answer.[19] The effects of the nucleophile and nucleofuge can be conveniently separated into two parts, one associated with the reaction exothermicity, and the other with the so-called intrinsic reactivity of X and Y. The intrinsic reactivity of a given nucleophile/nucleofuge can be probed in an identity reaction, which is a reaction in which the attacking and leaving groups are identical, in anionic form [Eq. (3)].

$$X^- + R{-}X \rightarrow X{-}R + X^- \qquad (3)$$

For a given non-identity reaction, the intrinsic barrier can be expressed as the arithmetic mean of the intrinsic barriers of X and Y. The actual barrier can then be estimated relatively accurately, taking the reaction exothermicity (determined by the relative heterolytic bond dissociation energies of R−Y and R−X) explicitly into account, using Marcus theory or similar approaches.[14] This will be reflected upon at the end of this paper.

Barrier heights for S_N2 reactions, expressed as $\Delta H^{\neq}$, may range from about 100 up to several hundreds of kJ mol^{-1}. Present day experimental methodology only allows for accurate determination of barriers close to zero. Fortunately, however, quantum chemical methodology has reached a level of accuracy close to that of experiment for small molecular systems. This has opened the way for a large number of theoretical studies treating various aspects of S_N2 reactivity, including reactions not accessible to experiment. Ten years ago, Radom and co-workers reported a study on reactions of halide anions with methyl halides, for which they used the G2 method.[20] On the basis of a recent review,[6] in which these results were compared with benchmark quality calculations, it is clear that the G2 method provides very accurate estimates of the barriers. A wide range of anionic nucleophiles of the type CH_3X^- reacting with CH_3XCH_3, with X covering Groups 14–18 of the periodic table, were treated by Hoz and co-workers in 1999.[21] Using the MP2/6–311+G* method, the reactivity of a wide range of anionic and neutral nucleophiles towards methyl was studied by Ruggiero and Williams.[22] Ten years ago, Lee and co-workers published an article reporting MP2 barriers for identity reactions on allyl for the anionic nucleophiles X^- (X = NH_2, OH, F, PH_2, SH, Cl).[23] Interestingly, there exist in the literature G2 barrier heights for identity S_N2 reactions on elements other than carbon, including reactions of anionic nucleophiles with substrates in which the central carbon (CH_3) has been changed to nitrogen (NH_2 or NR_2),[24,25] oxygen (OH),[26] and phosphorus (PH_2),[27] as well as reactions of neutral nucleophiles at phosphorus,[28] sulfur,[29] and chlorine,[30] some of them including periodically systematic variation of the nucleophile.

To analyze the periodical trends for identity S_N2 reactions on carbon, providing a consistent, accurate, and sufficiently broad data set, barrier heights obtained using G2 theory are reported herein for the reactions given in Equation (4) with X = NH_2, OH, F, PH_2, SH, Cl, AsH_2, SeH, and Br, as well as the corresponding neutral nucleophiles (formally protonated X^-) [Eq. (5)] with HX = NH_3, H_2O, HF, PH_3, H_2S, HCl, AsH_3, H_2Se, and HBr.

$$X^- + CH_3X \rightarrow XCH_3 + X^- \qquad (4)$$

$$HX + CH_3XH^+ \rightarrow HXCH_3{}^+ + XH \qquad (5)$$

The goal of this study is to find the systematic periodic trends in reactivity, and to link these to the physicochemical properties of the molecules involved. The relationship between basicity and nucleophilicity will be a key issue. The correspondence between anionic (X^-) and neutral nucleophilicity (HX) will also be of interest.

Results and Discussion

Accuracy: The key results are summarized in Table 1. Before analyzing the S_N2 reaction data, it is important to establish the accuracy of the quantum-chemical method. It has been shown that on average thermochemical properties (proton affinities, ionization energies) are calculated to within $10\ \text{kJ mol}^{-1}$, provided that there is no particular difficulty in obtaining reasonable molecular and electronic structures. In the present case, it is possible to compare calculated and experimental proton affinities and methyl cation affinities. It is clear that the $10\ \text{kJ mol}^{-1}$ criterion is met (Table 1). This is reassuring, but the S_N2 reactions involve the traversing of transition structures and weakly bonded intermediate structures, both of which have more distorted electron configurations than typical covalently bonded species. Despite these challenges, a thorough analysis of the literature has demonstrated that G2 calculations of barriers for S_N2 reactions also meet the $10\ \text{kJ mol}^{-1}$ criterion in these cases. For example, for identity and non-identity S_N2 reactions of halides with methyl halides, G2 barrier heights are identical to experimentally derived numbers and benchmark ab initio data to within about $10\ \text{kJ mol}^{-1}$.[6] In the G2

Table 1. Reaction data

Nucleophile X	Method	PA[a] [kJ mol^{-1}]	MCA[b] [kJ mol^{-1}]	ΔH_{cmpl}[c] [kJ mol^{-1}]	ΔH^{cb}[c] [kJ mol^{-1}]	$\Delta H^{\neq}$[d] [kJ mol^{-1}]	ΔH^{TS}[d] [kJ mol^{-1}]	$\nu^{\neq}$ ($f^{\neq}$) **i**·cm^{-1} (mdyn Å^{-1})[e]	r^{o}[f] [Å]	$r^{\neq}$[f] [Å]
NH_3	G2	854	436	34	90	56	374	614	1.510	2.002
	exp.	854	441					(1.585)		
H_2O	G2	689	276	41	40	−1	270	499	1.518	1.953
	exp.	691	279					(0.861)		
HF	G2	486	124	43	9	−34	152	265	1.606	1.968
	exp.	484	125					(0.217)		
NH_2^-	G2	1691	1225	–	–	118	1101	613	1.465	1.993
	exp.	1691	1234					(2.035)		
OH^-	G2	1633	1153	26	85	59	1088	582	1.424	1.883
	exp.	1634	1159					(1.910)		
F^-	G2	1554	1078	55 (57)[g]	49 (49)[g]	−6 (−8[g]	1077	551	1.392	1.781
	exp.	1554	1080					(1.947)		
PH_3	G2	785	440	17	135	119	315	607	1.800	2.423
	exp.	785	440					(1.104)		
H_2S	G2	708	336	18	70	52	278	493	1.818	2.392
	exp.	705	340					(1.266)		
HCl	G2	563	200	30	43	13	181	368	1.844	2.369
	exp.	557	204					(0.630)		
PH_2^-	G2	1540	1124	–	–	103	1014	574	1.857	2.510
	exp.	1536[i]	1116					(1.944)		
SH^-	G2	1475	1034	–	–	57	970	560	1.814	2.393
	exp.	1466	1033					(2.137)		
Cl^-	G2	1404	950	44 (44)[g]	56 (56)[g]	12(12)[g]	932	511	1.777	2.307
	exp.	1395	952	51 ± 8[h]		4 ± 4[h]		(2.014)		
AsH_3	G2	763	406	13	119	96	304	555	1.898	2.462
	exp.	748						(1.109)		
H_2Se	G2	715	344	14	59	45	293	453	1.953	2.473
	exp.	708						(1.466)		
HBr	G2	586	217	15	30	15	203	360	2.003	2.478
	exp.	584	227					(0.752)		
AsH_2^-	G2	1502	1085	–	–	84	995	511	1.963	2.553
	exp.	1496						(1.632)		
SeH^-	G2	1432	999	–	–	45	948	500	1.954	2.491
	exp.	1429						(1.767)		
Br^-	G2	1358	916	40	46	6	904	452	1.947	2.444
	exp.	1354	916					(1.539)		

[a] Proton affinity. [b] Methyl cation affinity. [c] See Figure 1 for a definition of this quantity. [d] See Equation (10) for definition. [e] MP2/6–31 G(d) imaginary frequency of vibration (and corresponding negative force constant) of reaction coordinate. [f] Distance between carbon atom and main atom of nucleophile in the substrate molecule (r^{o}) and TS($r^{\neq}$), respectively. [g] Number in parentheses is G2(+) value from Glukhovstev et al. (ref. [20]). [h] Experimental value due to Larson and McMahon (ref. [31]). [i] Experimental value due to Ervin and Lineberger (ref. [32]); all other experimental values are from the NIST webbook (ref. [33]).

method, geometries are obtained with MP2(full)/6–31 G(d). This rather small basis set could give rise to less accurate bond lengths and angles than might be desirable. This problem is expected to be most pertinent in the case of the halides, especially fluorine. For this reason, Glukhovtsev et al. and others have used a modified G2 scheme, whereby geometries are optimized using a larger basis set including diffuse functions. The choice of basis set obviously has some influence on the shape of the potential energy surface and the geometries of the stationary states, but when we compare our barriers with those of Glukhovtsev, we find that the G2 barrier heights and geometries are hardly affected. On this basis, one can be confident in applying the original G2 method throughout. It provides a unified approach, it is simple, and it is sufficiently accurate for the purpose of analyzing periodic properties.

Variations in the shape of the potential energy surface; transition structure: For all identity reactions investigated, a symmetrical Walden transition structure with two identical C···X bond distances and a planar central methyl moiety was located. Both the width and the height of the central barrier show significant dependence on the nucleophile. The imaginary frequency of vibration corresponding to the reaction coordinate at the TS and the corresponding force constant are indicators of the curvature in the TS region. A flat potential energy surface gives rise to low absolute values of these quantities. Among the nucleophiles considered, hydrogen fluoride represents a borderline case in that it has the lowest (absolute number) force constant for vibration corresponding to the reaction coordinate, $f^{\neq}$, Table 1. Although this single quantity should not be taken as an absolute measure of the overall shape of the potential energy surface, it provides an indication of the binding within the transition structure. Dopfer and co-workers have studied the closely related adduct $[Ar\cdots CH_3Ar]^+$, for which a low barrier for S_N2 reaction gives rise to an inversion motion, as in ammonia. This can be inferred from the infrared photodissociation spectrum.[34] For the periodic neighbor to the right of fluorine and above argon, namely neon, the symmetrical $[Ne\cdots CH_3\cdots Ne]^+$ species does not even correspond to a flat saddle point of the potential energy surface, but is a minimum.[35,36] The same has been reported for helium.[36,37] The reactant complex, the product complex, and the transition structures have all merged into one single structure located at the bottom of a symmetrical potential energy well. This is also the case for most di-adducts, $[X\cdots EH_n\cdots X]^+$, formed between nucleophiles X and the larger third-row cations, $EH_n = PH_2$, SH, and Cl,[27–30] reflecting the ability of third-row atoms to form stable pentacoordinate molecules. Even neutral aluminum has this ability, in contrast to boron,[38] which is most probably the result of its enhanced tendency for electrostatic binding at the expense of covalency.[39] We also notice the parallel at the other extreme, namely binding in proton transfer. While the minimum-energy structure for $[(H_2O)_2H]^+$ corresponds to a situation with the proton located exactly in between the two oxygen atoms, the symmetrical $[(NH_3)_2H]^+$ is a TS and the minimum has the proton closer to one of the ammonia molecules.[40–42]

Variations in the shape of the potential energy surface; ion/molecule complex structure: All of the substrate molecules, CH_3X, considered here (except for the halides) form strong hydrogen bonds to X, giving front-side complexes of the type $CH_3X\cdots X$ (the charges have been omitted from the complexes for clarity). For all X, this complex is lower in potential energy than the back-side $X\cdots CH_3X$ complex located *en route* to the S_N2 transition structure. This constitutes an interesting situation with regard to the detailed dynamics of gas-phase S_N2 reactions, since the reactant complex may be trapped in the front-side form for an extended period of time before crossing the barrier or dissociating back to the reactants. For our purpose, the front-side complex is of less relevance, except that in a number of the cases it is the only complex that exists, and as a result of this all attempts to locate a back-side complex for $X^- = NH_2^-$, PH_2^-, SH^-, AsH_2^-, and SeH^- met with failure. Despite different starting conditions, geometry optimizations inevitably ended at the $CH_3X\cdots X$ minimum. This represents another type of collapse of the double-minimum potential, in addition to the aforementioned situation in which the Walden structure is a minimum rather than a first-order saddle point.

Central barrier or overall barrier? For several good reasons, most workers have analyzed their potential energy data in terms of height of the central barrier ΔH^{cb}. First, it resembles the key step in both the gas-phase and solution-phase S_N2 reactions, and it provides a reasonable comparison between the two media. Second, a one-step process is consistent with simple qualitative or semi-quantitative models for reaction energy profiles like Hammond's postulate and Marcus theory. Furthermore, for halides that do not form front-side complexes, it is even possible to prepare the back-side complexes in the laboratory and to study their unimolecular dissociation.[31] The discussion herein will also include this feature, but the collapse of the double-minimum potential, a requirement for defining the process given in Equation (6) limits the usefulness of comparing central barrier heights.

$$X\cdots CH_3{-}X \rightarrow X{-}CH_3 + X \tag{6}$$

It appears more logical to look at the energy difference between the symmetrical Walden structure and that of the reactants, $\Delta H^{\neq}$, since this quantity is always defined, both when the back-side complex is absent and when the double minimum has degenerated into a single minimum. In contrast to ΔH^{cb}, this is the overall barrier, which is of relevance to the direct gas-phase reaction. Another advantage lies in the opportunity to compare the binding situation in two well-defined molecular species, $[X\cdots CH_3\cdots X]$ and $CH_3{-}X$. Reactivity in this interpretation is then simply derived from a comparison between how one nucleophile molecule X (a base) binds to a methyl cation, compared to how two identical nucleophile molecules bind, subject to the constraint of an $X\cdots CH_3\cdots X$ symmetrical arrangement. In this respect, it is irrelevant whether $[X\cdots CH_3\cdots X]$ is a minimum or a saddle point. As has been pointed out in an earlier paper, a reference point for such comparisons will be the fully separated species $X + X + CH_3^+$, the former two being either both neutral or both negative.[19] At this point, we reintroduce explicit charges into the notation for clarity and strictness.

Correlation of binding in the TS and reactant with proton affinity: We define the appropriate thermochemical quantities according to Equations (7) and (8).

$$\begin{aligned} &X^{(0/-)} + CH_3^+ + X^{(0/-)} \rightarrow \\ &[X\cdots CH_3\cdots X]^{(+/-)},\ H^{TS} = -\Delta H \end{aligned} \tag{7}$$

$$\begin{aligned} &X^{(0/-)} + CH_3^+ + X^{(0/-)} \rightarrow \\ &CH_3{-}X^{(+/0)} + X^{(0/-)},\ H^{RE} = -\Delta H \end{aligned} \tag{8}$$

It can be seen that $H^{RE} = MCA$, the methyl cation affinity. With these definitions, we have for the overall barrier height, $\Delta H^{\neq} = MCA - H^{TS}$.

Plots of both *MCA* and H^{TS} against the proton affinity (*PA*) are shown in Figure 2. In the region $PA > 500\,kJ\,mol^{-1}$, which is of interest here, both *MCA* and H^{TS} display good linear correlations with *PA*.[43–47] Interestingly, the anionic (X^-) and neutral (XH) nucleophiles display similar functional behavior, despite the additional coulombic interaction in the anionic case. The anionic nucleophiles fit somewhat better to the ideal curve for *MCA* than that for H^{TS}. The opposite is true for the neutrals, which show a better fit to H^{TS} than to *MCA*. Good correlations are even found at a smaller scale. Separating anions and neutrals, and comparing *MCA* and H^{TS} values both within each group of

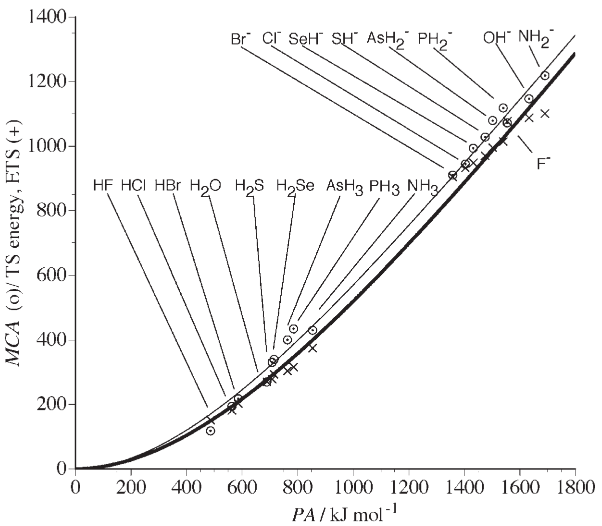

Figure 2. The plot shows the relationship between methyl cation affinity (*MCA*) and proton affinity (*PA*) for various groups for the indicated bases (circles). The thin blue line is the function $MCA = 0.885\,PA(1.000 - \exp(-PA/969))$ obtained by least-squares fit to the *MCA* data. The crosses represent the corresponding functional relationship between the TS energy, H^{TS}, and *PA*. The thick green line is the function $H^{TS} = 0.925\,PA(1.000 - \exp(-PA/1213))$ obtained by least-squares fit to the H^{TS} data. When the cross is below the circle the S_N2 identity reaction X + $CH_3X \rightarrow XCH_3$ + X has a positive $\Delta H^{\neq}$ value. The reader will see that both data sets also fit well to straight lines. However, an exponential function passing through the origin was chosen to include the hypothetical situation of a completely inert group which has zero binding to both H^+ and CH_3^+, and perhaps give a better description of the fall-off region.

the periodic table and within each period, reveals interesting and slightly different functional behavior from the overall picture. This is particularly evident for the anions. The *MCA*/*PA* relationship of Figure 2 can be understood when we accept that bonds from a given nucleophile to either a proton or a methyl cation are formed by electron donation, and that charge is dispersed in the same general way from X^- (HX) to the cation upon formation of both the CH_3–X (CH_3–XH^+) and the H–X (H–XH^+) bonds. The small proton is more effective than the carbon in its electron-acceptor capacity and the charge is better delocalized in the methyl cation. The origin of the exact slope of the linear part has been discussed in some detail by Brauman[45,46] and Uggerud.[47] The reader should note that the electron-donating ability of the principal atom of X is not only determined by the position in the periodic table. While HF is the weakest neutral base, F^- is the third strongest anionic base. The good H^{TS}/PA correlation is perhaps more surprising,[19] since the [X···CH_3···X] structure corresponds to two half-bonds rather than one full bond. From Figure 2, we see that on average the two half-bonds of [X···CH_3···X] taken together are slightly weaker than the full bond of CH_3–X. This means that the average reaction in our data set has a positive barrier ($\Delta H^{\neq} > 0$), that is, the TS is above the reactants in terms of potential energy.

Correlation of barrier height with proton affinity: The perspective of Figure 2 gives an overview of the main effect of electron donation. However, the barrier height is obtained by subtracting one large number from another, $\Delta H^{\neq} = MCA - H^{TS}$, and from a more detailed study of Figure 2 it can be inferred that there is no general and straightforward relationship between this quantity and *PA*. Instead, there are linear (anionic nucleophiles) or nonlinear (neutral nucleophiles) correlations within each row of the periodic table (see Supporting Information, Figure S1).

Correlation of barrier height with electronegativity: Electronegativity is a concept which dates back to the Pauling tradition of chemical bond theory. While bond order (vide infra) is related to bond length, electronegativity is related to bond strength. Luo and Benson have extended the original definition of electronegativity, and suggested a revised scale, V_X. Their electronegativity was shown to give linear correlation with the differences in heats of formation between hydrogen and methyl derivatives.[48] The interesting point is not that such a scale exists, but its definition. For a given element X (= NH_2, OH, F, PH_2, SH, Cl, AsH_2, SeH, Br) electronegativity is defined using the unshielded core potential of Yuan,[49] according to Equation(9), where n_X is the number of valence electrons and r_X is the covalent radius.

$$V_X = n_X/r_X \tag{9}$$

By this definition, electronegativity is no longer defined by bond strength but by bond length and valence. Inspired by this promising relationship between methyl cation and proton affinity on the one hand and size and valence on the other, we plotted the barrier $\Delta H^{\neq}$ versus V_X. It turned out (see Supporting Information, Figure S2) that this electronegativity is no better than the proton affinity as a global descriptor of nucleophilicity.

Correlation of barrier height with ionization energy: In contrast to *PA* and V_X, the ionization energy, *IE*, turned out to be the best general descriptor, and the plot is displayed in Figure 3. It is evident that the points for all anions now end up on an approximately straight line (although not perfectly linear), while the neutrals give rise to a curve that levels off at high ionization energy. No attempt has been made to fit these data to any particular function. It is clear from Figure 3 that the nucleophiles with the highest ionization energies give rise to the lowest barriers.

Basicity and related properties: Only by using *IE* instead of *PA* or V_X do the otherwise parallel three lines (one corresponding to each period) within each charge class (anion or neutral) join together into one. This discussion also shows how difficult it is to separate the effect of basicity from that of size using molecular properties. The different measures for electron-donating power (ionization energy, proton affinity, electronegativity, polarizability volume) are interrelated and related to size. In effect, they all express chemical hardness/softness in some way. Chemical hardness and electrone-

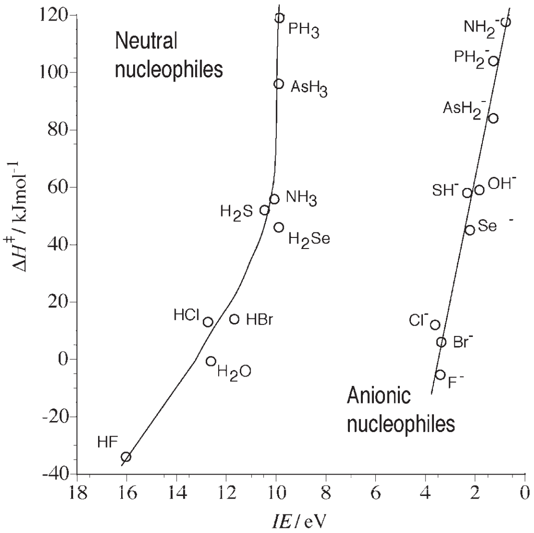

Figure 3. Relationship between barrier height ($\Delta H^{\ddagger}$) and ionization energy (IE). The IE for an anion is not a strictly defined quantity, and we simply substitute it with the negative electron affinity of the corresponding neutral molecule. The lines display the trends, but have not been mathematically fitted to the data. Please note the compressed horizontal axis, which is a result of including both neutrals and anions in the same plot.

gativity have both been given rigorous definitions within density functional theory[50,51]—which may be different from classical empirical definitions—and so in order not to get entangled in linguistic and fine theoretical discussions, we will not discuss this in any detail. We do, however, note from reading current literature that softness (in the strict definition) scales linearly with the cube root of polarizability,[52] and that the electron density at long distance decays exponentially with the square root of the IE.[53] A relationship with the unshielded core potential (the V_X electronegativity scale; [Eq. (9)]) exists according to Ray et al., who showed that for diatomic molecules there is a linear interdependence between softness (in the strict definition) and spherical capacitance (in the normal electromagnetic meaning).[54,55] In this simple model of electronic interaction, the capacitor consists of the two atomic spheres. While the core electrons and the asymptotic electron density both behave in a way that is well described by density functional theory, the behavior is more complicated at the intermediate distances typical for molecules and chemical reactions.

Neutral/anion correlation in bond length elongation: It is clear from Table 1 that the C–X bond lengths of the substrates CH_3X decrease on going from left to right in the periodic table, while the opposite tendency is seen for the protonated congeners CH_3XH^+. However, the transition structures have decreasing $CH_3\cdots X$ bond lengths on going from left to right for both anionic and neutral nucleophiles. Not unexpectedly, the C–X bond lengths of all species (reactants and transition structures) increase when going down a group. Plotting the C–X bond elongation factor $\Delta r^{\ddagger} = r^{\ddagger} - r^{o}$ (see Table 1 for definitions) for the anions versus the neutrals is illustrative and remarkable (Figure 4, left panel). The plot reveals two facts, that a straight line is obtained, and that $\Delta r^{\ddagger}$ is high for those nucleophiles giving high barriers and low for those giving low barriers. It was found that $\Delta H^{\ddagger}$ values give a rather poor overall correlation with $\Delta r^{\ddagger}$, but the barrier heights are equally well correlated to the period (see Supporting Information, Figure S3). Figure 4 (right panel) shows the correlation between the barrier for the anions (X^-) and the neutrals (XH). There is very good correlation within each period, and it can be seen that there is noticeable curvature.

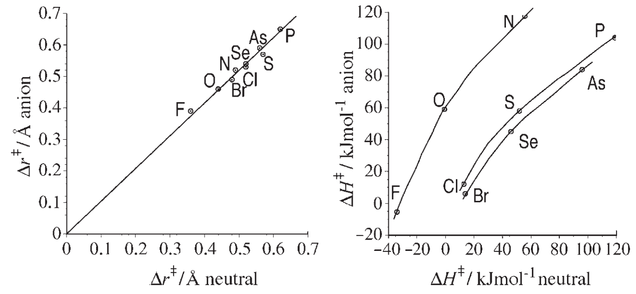

Figure 4. Plot showing the relationships between (a) the bond elongation factor ($\Delta r^{\ddagger}$) for anions (X^-) and neutrals (XH), and (b) relationships between barrier heights ($\Delta H^{\ddagger}$) for anions (X^-) and neutrals (XH).

Barrier height and electron density: From these considerations, the following summary can be made: a) the ionization energy is a more useful global descriptor for the barrier height in identity S_N2 reactions than the proton affinity or electronegativity, b) the neutral (XH) and the corresponding anionic nucleophile (X^-) show remarkably parallel behavior despite the charge difference. A qualitative picture emerges from these observations, namely that a nucleophile with a high IE (e.g., F^-) will give rise to a strong, albeit polar C–X bond in the substrate, whereby relatively little electron density is donated from the nucleophile to the methyl cation. The bond has a high electrostatic character. The route to the TS will be less demanding, since the introduction of the second F^- will not be hampered so much by electron repulsion due to the donated electron cloud. This aspect is illustrated in Figure 5. The situation is characterized by both a low $\Delta r^{\ddagger}$ and a low $\Delta H^{\ddagger}$. A better electron donor in this respect will lead to a higher barrier.

Considerations of the VB model: Shaik, Pross, and co-workers have suggested that insight into S_N2 reactivity can be gained by the use of valence bond (VB) correlation diagrams.[56–59] The barrier for the central S_N2 reaction step is the result of the avoided crossing of two curves comprising the reactant- and product-like Heitler–London valence bond states, and the barrier height is given by the model in Equation (10), where B is the avoided crossing interaction, which, in accordance with some of the earlier studies, is neglected; G_r is the promotion gap, and α a curvature factor.

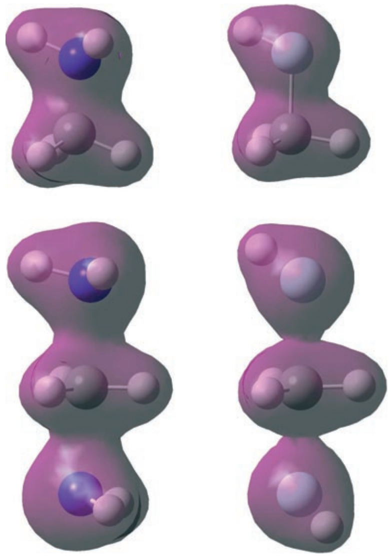

Figure 5. Electron density plots (isodensity contour set to $\rho = 0.0004$ electron/bohr^3) for CH_3NH_2 (upper left), CH_3FH^+ (upper right), and the corresponding transition structures to $[H_2N\cdots CH_3\cdots NH_2]^-$ (lower left) and $[HF\cdots CH_3\cdots FH]^+$ (lower right). A stronger electrostatic character of a bond is revealed by less electron density in between the nuclei, and more closer to the nuclei.

$$\Delta H^{cb} = \alpha G_r - B \tag{10}$$

The promotion gap is usually approximated by Equation (11), where IE_X is the vertical ionization energy of the nucleophile and EA_{RX} is the vertical electron affinity of the substrate molecule.

$$G_r = IE_X - EA_{RX} \tag{11}$$

The data presented in Figure 3 show that it would be difficult to apply this valence bond correlation approach to the present systems under consideration. For example, the promotion energy is higher for $H_2O + CH_3OH_2^+$ than for $NH_3 + CH_3NH_3^+$, while the order of the reaction barriers is the opposite. Both ΔH^{cb} and $\Delta H^{\neq}$ show this general tendency, as already discussed in connection with Figure 3.

Considerations of other models: The early work by Wolfe and co-workers established a frame of reference frequently adapted to model characteristic features of S_N2 reactions.[14,60] Their application of Marcus theory to connect non-identity and identity reactions was certainly an important contribution. However, a weak point in their theory is the use of the non-observable quantities “looseness” and “bond order”. For example, the theory requires that the conceptually vague quantity of bond order is conserved. Ruggiero and Williams gave a critical account of this and similar structure/energy relationships that have been suggested to explain identity S_N2 reactivity.[36] Neither of the traditional approaches turned out to be generally valid. Instead, Williams introduced a one-dimensional harmonic potential to correlate barrier heights.[36,61] In this model, the barrier height (starting from the back-side complex) can be expressed as $\Delta H^{cb} \sim fd^2$, where f is the force constant associated with C–X(str.) in the complex and the displacement coordinate d has been set to the distance traveled by the methyl group on going from the reactant complex to the product complex. Using this simple approach, Williams found relatively good correlation for a variety of nucleophiles, both anionic and neutral. When applied to the present data set, reasonable agreement was found for the set of the four anionic nucleophiles which form a back-side complex, but the correlation for the neutral data set was poor. Neither substituting d by the bond elongation factor $\Delta r^{\neq} = r^{\neq} - r^{o}$ (see Table 1) to be in better accordance with our analysis given above, nor substituting f by the negative force constant $f^{\neq}$ associated with the reaction coordinate (the negative eigenvalue of the TS Hessian) improves the situation.

Periodic trends: Hoz and co-workers calculated (G2) and compared anion nucleophilicity in identity S_N2 reactions of CH_3X^--type anions at carbon in terms of ΔH^{cb} values.[21] The barrier height increases on going from right to left in the periodic table depending essentially on the valence of X. Within each group, Hoz et al. observed relatively little variation among the main group elements, and they suggested the extremely simple equation $\Delta H^{cb} = p \cdot 42\,\mathrm{kJ\,mol^{-1}}$, where p is the valence of X. As already explained, this quantitative relationship cannot be estimated for our complete data set of anions since five of the nine anionic nucleophiles do not give stable back-side complexes, meaning that a ΔH^{cb} value is not defined. For the neutral nucleophiles, back-side complexes exist, but there is quite substantial variation within each group, and a simple relationship of the type Hoz et al. suggest is not observed. The situation becomes even worse by looking at $\Delta H^{\neq}$ instead of ΔH^{cb}. By applying their own intersecting-state model, Arnaut et al. were able to roughly reproduce the valence-dependent equation of Hoz et al.[62] However, the model, like the similar structure/energy relationships discussed above, depends heavily on the doubtful assumption that bond order is conserved.

Effect of the central atom on the barrier: Having shown that the IE is a good measure of nucleophilicity in identity S_N2 reactions on carbon, we will now for a moment turn our attention to other elements. S_N2 on carbon has high barriers compared to that at the neighboring elements. For the second row, barriers decrease in the sequence $CH_3 > NH_2 > OH$,[24–26,63] reflecting increasing electron-accepting ability. This seems to be the general trend for anionic nucleophiles and neutral nucleophiles. For neutral nucleophiles, it can be inferred from literature data that going down in the periodic table to $EH_n = PH_2$, SH, and Cl the barrier decreases.[27–30] Among the third-row groups, the barrier dependency on the nature of EH_n is $PH_2 < SH < Cl$ for second-row nucleophiles, but $PH_2 < SH > Cl$ for third-row nucleophiles. These results show that both size and electron-accepting properties determine the barrier height. In this connection, one should keep in mind that electrostatic binding becomes more important than covalent binding in the third and fourth rows.[39] The well-known phenomenon of decreasing S_N2 reactivity upon increased alkyl substitution at the central carbon is probably more related to the same central atom size/electron-accepting properties, and probably less to the so-called steric effect (direct repulsion from the alkyl substituents) than is generally believed.[64]

Relationship between nucleophilicity and basicity: In the final few paragraphs, the ongoing discussion of the relationship between basicity and nucleophilicity is taken up once more. One of the founders of physical organic chemistry and inventor of the "S_N2" concept, Sir Christopher Ingold, stated in his textbook that: "Reagents which act by donating their electrons to, or sharing them with, a foreign atomic nucleus will be called nucleophilic reagents, or sometimes nucleophiles."[65] Swain and Scott were the first to define nucleophilicity in a more concise way.[9] Through linear rate-energy relationships they introduced the nucleophilicity, n [Eq. (12)].

$$\log(k/k_o) = ns \tag{12}$$

In Equation (12), k_o refers to the rate of a standard reaction, and k is the rate of the reaction of the nucleophile under consideration. The parameter s is the sensitivity of the given substrate. By this appropriate definition, nucleophilicity is a kinetic property. These authors studied the displacement of bromide and other nucleofuges using different nucleophiles and substrates. Their standard reaction is given in Equation (13).

$$X^- + CH_3Br \rightarrow XCH_3 + Br^- \tag{13}$$

Swain and Scott noticed that their approach failed in correlating the concept of nucleophilicity with that of basicity. From our considerations, we are now in a position to demonstrate how the two concepts are related. For non-identity reactions, reactivity is partly steered by the combined intrinsic barriers corresponding to the incoming (Y) and outgoing groups (X), and partly by the overall exothermicity. In this context, it will be helpful to refer to the simple mathematics of Marcus theory and similar approaches.[14,60] By these approaches, the barrier height ΔH^* is given by Equation (14), ΔH^o is the enthalpy difference between the product and reactant.

$$\Delta H^* = \Delta H_0{}^*(1 + \frac{\Delta H^o}{4\Delta H_0{}^*})^2 \tag{14}$$

In its original form, Equation (15) is valid only for an elementary step, that is, $\Delta H^* = \Delta H^{cb}$, but Wolfe et al.[14] showed that to a good approximation the equation is also valid for the overall S_N2 reaction, that is, $\Delta H^* = \Delta H^{\neq}$. The intrinsic barrier, ΔH_0^*, is given by Equation (15), where $H_{0,XX}{}^*$ and $H_{0,YY}{}^*$ are the barriers for the identity reactions with X and Y, respectively.

$$\Delta H_0{}^* = \frac{1}{2}(\Delta H_{0,XX}{}^* + \Delta H_{0,YY}{}^*) \tag{15}$$

Examination of Equation (14) shows that the barrier increases when the intrinsic barrier increases, and decreases when the reaction becomes more exothermic.

The overall exothermicity is determined by the difference in heterolytic bond dissociation energy between C−Y and C−X. Since this figure can be described in terms of the methyl cation affinities of X and Y, it can be seen that strong bases will be good nucleophiles in this respect. At the same time, we have shown above that nucleophiles with low ionization energies give high barriers in identity reactions. In other words, there are two opposing forces at work. A strong base will be a poor nucleophile in terms of having a high intrinsic barrier, while it will be a good nucleophile by shifting the barrier to a lower level by stabilizing products relative to reactants. It can therefore be seen how nucleophilicity relates to basicity. Only for sufficiently exothermic reactions, when ΔH^o becomes the dominating term, is nucleophilicity steered by basicity. In other terms, combining the well-proven Marcus equation with the indicated relationship between the intrinsic barrier and IE of Figure 3, the relationship between nucleophilicity and basicity has been clarified, at least for gas-phase reactions.

Conclusion

The results of the present work demonstrate that for identity S_N2 reactions, in spite of the charge difference between X^- and HX, the energetic and geometric requirements for going from the reactant to the transition structure are surprisingly similar. It is found that the barrier heights decrease on going from left to right in the periodic table, and that within each class (X^- or XH) this correlates with decreasing ionization energy of the nucleophile. It is suggested that nucleophiles having bonds to carbon with stronger electrostatic character give rise to lower energetic barriers due to decreased electron repulsion in the transition structure. This means that poor electron donors, like the fluoride anion, are good nucleophiles in identity reactions, while good electron donors like ammonia give high barriers. Finally, the relationship between nucleophilicity and basicity has been analyzed and understood from comparing intrinsic reactivity in identity reactions by consideration of the factors that govern reaction exothermicities. Since the trends in intrinsic nucleophilicity and basicity are opposing, overall nucleophilicity will be determined by the relative contribution of the two factors. In the asymptotic limit of strongly exothermic reactions, basicity and nucleophilicity will become equivalent.

Experimental Section

Computational methods: Quantum-chemical calculations were carried out using the program system GAUSSIAN 03.[66] All relevant critical points (reactants, transition structures, intermediates, and products) on the potential energy surface were characterized by complete optimization of the molecular geometries (MP2(full)/6–31G(d)). Harmonic frequencies were obtained using HF/6–31G(d) by diagonalizing the mass-weighted Cartesian force constant matrix, calculated from the analytical second derivatives of the total energy (the Hessian). Harmonic frequencies obtained in this manner were used to calculate the zero-point vibrational energies (ZPVE) using a built-in scale factor of 0.9434.[67] Electronic energies were obtained by the G2 methodology.[68] Using the MP2(full)/6–31G(d) geometry, a series of single-point MP2, MP4, and QCISD(T) calculations are performed in order to obtain an energy estimate, which is effectively at the QCISD(T)/6–311+G(3df,2p) level. The G2 energies presented are 0 K energies including the ZPVEs. Proton affinities at room temperature (*PA*s) were estimated by adding 5/2 *RT* (with $T = 298$ K) to the 0 K enthalpy differences between the base and the corresponding acid, ignoring heat capacity differences. The methyl cation affinities (*MCA*s) were calculated analogously according to Equations (16) and (17).

$$\mathrm{A} + \mathrm{H}^{+} \rightarrow \mathrm{AH}^{+}, PA = -\Delta H^{\circ} \quad (16)$$

$$\mathrm{A} + \mathrm{CH_3}^{+} \rightarrow \mathrm{CH_3A}^{+}, MCA = -\Delta H^{\circ} \quad (17)$$

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[1] W. N. Olmstead, J. I. Brauman, *J. Am. Chem. Soc.* **1977**, *99*, 4219.
[2] J. I. Brauman, *J. Mass Spectrom.* **1995**, *30*, 1649.
[3] D. K. Bohme, L. B. Young, *J. Am. Chem. Soc.* **1970**, *92*, 7354.
[4] D. K. Bohme, G. I. Mackay, *J. Am. Chem. Soc.* **1981**, *103*, 978.
[5] S. S. Shaik, H. B. Schlegel, S. Wolfe, *Theoretical Aspects of Physical Organic Chemistry: The S_N2 Reaction*, John Wiley, New York, **1992**.
[6] J. K. Laerdahl, E. Uggerud, *Int. J. Mass Spectrom.* **2002**, *214*, 277.
[7] W. L. Hase, *Science* **1994**, *266*, 998.
[8] M. L. Chabinyc, S. L. Craig, C. K. Regan, J. I. Brauman, *Science* **1998**, *279*, 1882.
[9] C. G. Swain, C. B. Scott, *J. Am. Chem. Soc.* **1953**, *75*, 141.
[10] J. O. Edwards, *J. Am. Chem. Soc.* **1954**, *76*, 1540.
[11] J. O. Edwards, *J. Am. Chem. Soc.* **1956**, *78*, 1819.
[12] M. J. Pellerite, J. I. Brauman, *J. Am. Chem. Soc.* **1980**, *102*, 5993.
[13] M. J. Pellerite, J. I. Brauman, *J. Am. Chem. Soc.* **1983**, *105*, 2672.
[14] S. Wolfe, D. J. Mitchell, H. B. Schlegel, *J. Am. Chem. Soc.* **1981**, *103*, 7694.
[15] E. M. Arnett, K. E. Molter, *Acc. Chem. Res.* **1985**, *18*, 339.
[16] J. M. Harris, S. P. McManus, *Adv. Chem. Ser.* **1987**, *215*, 1.
[17] F. G. Bordwell, T. A. Cripe, D. L. Hughes, *Adv. Chem. Ser.* **1987**, *215*, 137.
[18] R. Lucius, R. Loos, H. Mayr, *Angew. Chem.* **2002**, *114*, 97–102; *Angew. Chem. Int. Ed.* **2002**, *41*, 91–95.
[19] E. Uggerud, *J. Chem. Soc. Perkin Trans. 2* **1999**, 1459.
[20] M. N. Glukhovtsev, A. Pross, L. Radom, *J. Am. Chem. Soc.* **1995**, *117*, 2024.
[21] S. Hoz, H. Basch, J. L. Wolk, T. Hoz, E. Rozental, *J. Am. Chem. Soc.* **1999**, *121*, 7724.
[22] G. D. Ruggiero, I. H. Williams, *J. Chem. Soc. Perkin Trans. 2* **2001**, 448.
[23] I. Lee, C. K. Kim, B.-S. Lee, *J. Phys. Org. Chem.* **1995**, *8*, 473.
[24] R. Yi, H. Basch, S. Hoz, *J. Org. Chem.* **2002**, *67*, 5891.
[25] Y. Ren, J. L. Wolk, S. Hoz, *Int. J. Mass Spectrom.* **2002**, *221*, 59.
[26] Y. Ren, J. L. Wolk, S. Hoz, *Int. J. Mass Spectrom.* **2002**, *220*, 1.
[27] T. I. Solling, A. Pross, L. Radoma, *Int. J. Mass Spectrom.* **2001**, *210/211*, 1.
[28] T. I. Solling, S. B. Wild, L. Radom, *Inorg. Chem.* **1999**, *38*, 6049.
[29] T. I. Solling, L. Radom, *Chem. Eur. J.* **2001**, *7*, 1516.
[30] T. I. Solling, L. Radom, *Eur. J. Mass Spectrom.* **2000**, *6*, 153.
[31] J. W. Larson, T. B. McMahon, *J. Am. Chem. Soc.* **1984**, *106*, 517.
[32] K. E. Ervin, C. W. Lineberger, *J. Chem. Phys.* **2005**, *122*, 194303
[33] S. G. Lias, H. M. Rosenstock, K. Deard, B. W. Steiner, J. T. Herron, J. H. Holmes, R. D. Levin, J. F. Liebman, S. A. Kafafi, J. E. Bartmess, E. F. Hunter, in *NIST Chemistry Webbook (http://webbook.nist.goc/chemistry)*, 1997.
[34] R. V. Olkhov, S. A. Nizkorodov, O. Dopfer, *J. Chem. Phys.* **1998**, *108*, 10046.
[35] O. Dopfer, R. V. Olkhov, J. P. Maier, *J. Chem. Phys.* **2000**, *112*, 2176.
[36] G. D. Ruggiero, I. H. Williams, *J. Chem. Soc, Perkin Trans. 2* **2002**, 591.
[37] R. V. Olkhov, S. A. Nizkorodov, O. Dopfer, *J. Chem. Phys.* **1999**, *110*, 9527.
[38] F. A. Cotton, G. Wilkinson, C. B. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1999**.
[39] M. Czerw, A. S. Goldman, K. Krogh-Jespersen, *Inorg. Chem.* **2000**, *39*, 363.
[40] R. Attig, J. M. Williams, *Angew. Chem.* **1976**, *88*, 507; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 491.
[41] J. Roziere, J. M. Williams, *Inorg. Chem.* **1976**, *15*, 1174.
[42] H. J. Berthold, W. X. Preibsch, E. Vonholdt, *Angew. Chem.* **1988**, *100*, 1581; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1524.
[43] T. B. McMahon, P. Kebarle, *Can. J. Chem.* **1985**, *63*, 3160.
[44] T. B. McMahon, T. Heinis, G. Nicol, J. K. Hovey, P. Kebarle, *J. Am. Chem. Soc.* **1988**, *110*, 7591.
[45] J. Brauman, C. C. Han, *J. Am. Chem. Soc.* **1988**, *110*, 5611.
[46] J. I. Brauman, C. C. Han, *J. Am. Chem. Soc.* **1989**, *111*, 3485.
[47] E. Uggerud, *Eur. Mass Spectrom.* **2000**, *6*, 131.
[48] Y. R. Luo, S. W. Benson, *J. Am. Chem. Soc.* **1989**, *111*, 2480.
[49] H. C. Yuan, *Acta Chim. Sin. (Engl. Ed.)* **1964**, *30*, 341.
[50] J. P. Perdew, R. G. Parr, M. Levy, J. L. Balduz Jr., *Phys. Rev. Lett.* **1982**, *49*, 1691.
[51] R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**.
[52] P. K. Chattaraj, U. Sarkar, *J. Phys. Chem. A* **2003**, *107*, 4877.
[53] M. Levy, R. G. Parr, *J. Chem. Phys.* **1976**, *64*, 2707.
[54] N. K. Ray, L. Samuels, R. G. Parr, *J. Chem. Phys.* **1979**, *70*, 3680.
[55] J. R. Sabin, S. B. Trickey, S. P. Apell, J. Oddershede, *Int. J. Quant. Chem.* **2000**, *77*, 358.
[56] D. J. Mitchell, H. B. Schlegel, S. Shaik, S. Wolfe, *Can. J. Chem.* **1985**, *63*, 1642.
[57] A. Pross, S. Shaik, *J. Am. Chem. Soc.* **1981**, *103*, 3702.
[58] A. Pross, *Adv. Phys. Org. Chem.* **1985**, *21*, 99.
[59] S. Shaik, A. Shurki, *Angew. Chem.* **1999**, *111*, 616; *Angew. Chem. Int. Ed.* **1999**, *38*, 586.
[60] S. Wolfe, D. J. Mitchell, H. B. Schlegel, *J. Am. Chem. Soc.* **1981**, *103*, 7692.
[61] V. Moliner, I. H. Williams, *J. Am. Chem. Soc.* **2000**, *122*, 10895.
[62] L. G. Arnaut, A. A. C. C. Pais, S. J. Formosinho, *J. Mol. Struct.* **2001**, *563–564*, 1.
[63] Å. M. Øiestad, A. C. Petersen, V. Bakken, J. Vedde, E. Uggerud, *Angew. Chem.* **2001**, *113*, 1345; *Angew. Chem. Int. Ed.* **2001**, *40*, 1305.
[64] C. K. Regan, S. L. Craig, J. I. Brauman, *Science (Washington, DC)* **2002**, *295*, 2245.
[65] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, NY, **1953**.
[66] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. Montgomery, J. A. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V.

Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, GAUSSIAN 03, Gaussian, Inc., Wallingford CT, **2004**.

[67] A. P. Scott, L. Radom, *J. Phys. Chem.* **1996**, *100*, 16502.

[68] L. A. Curtiss, K. Raghavachari, G. W. Trucks, J. A. Pople, *J. Chem. Phys.* **1991**, *94*, 7221.

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