Inductive Effects on Proton Affinity of Benzene Derivatives: Analysis Using Fictitious Hydrogen Atoms

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Received: August 1, 2008; Revised Manuscript Received: January 9, 2009

Pure inductive effects on the gas-phase basicity of seven benzene derivatives (3- and 4-substitution) are monitored in a continuous way using fictitious hydrogen atoms bearing an adjustable nuclear charge Z^*. This approach (H* method) affords three main advantages over existing treatments: such entities are by definition purely inductive (without any underlying assumptions), use of empirical parameters is circumvented, and yet the method has been designed to remain particularly easy to use. We directly establish the linear dependence of proton affinities on inductive effects and, more quantitatively, measure accurate sensitivities ρ_I^* analogous to Taft's coefficients. Functional centers exhibit contrasted values, up to a factor of 3, which finds an interpretation within the framework of the HSAB theory. The sensitivities ρ_I^* for 3- and 4-substitution are quantified. The associated para/meta ρ_I^* ratio ranges from 1.02 to 1.16 according to the functional center. These values, always slightly superior to unity, denote a contribution of π electrons in the transmission of the inductive effect. This effect, first identified by Exner, is shown to account for ca. 30% of the basicity of benzoic acid, which is taken as an example.

1. Introduction

Substituent effects have proved to be one of the most challenging problems in physical and organic chemistry, as witnessed by the immensely large number of publications (see ref 1 for a recent review) since the discovery of the Hammett equation 70 years ago.[2] Changing a hydrogen into another atom or group of atoms induces a series of modifications of all properties of the substrate, whose magnitudes are very weak (typically 1% or 2%). Yet, stringent control of these perturbations is mandatory for the development of efficient synthesis strategies and interpretation of spectroscopic data.

Deep insight comes from the recognition that several contributions need to be distinguished to rationalize, for instance, differences between 3- and 4-substitution[3,4] of benzenic compounds. Electronic (inductive and resonance) and sometimes additional nonelectronic contributions (steric, hydrogen bonds, ...) condense themselves in a subtle interplay to give rise to an overall substituent effect. Achieving a clear assignment of each of these nonobservable components is highly challenging, and chances for definitive conclusions become extremely rare. Indeed, explorations of substitution usually consider a finite subset of substituents, which inevitably introduces a significant scatter. The latter is further amplified by using empirical substituent constants, with a specific series of values for each contribution that has to be taken into account.

Paradoxically enough, a much more robust approach toward a sound understanding of substituent effects could consist of bypassing real entities and investigating each contribution separately. In a second time, a mapping with real substituents could be proposed, where each substituent pertubation would simply be written as a (linear) combination of well-understood components.

Theoretical chemistry is particularly well suited for such purposes: many useful chemical concepts such as atomic charges, molecular orbitals, topological analysis, etc., are now routinely accessible. The definition of these nonobservable quantities is not straightforward. Yet, if wisely used, they may provide new insights into the fundamental nature of substituent effects. Many workers have contributed to this line of research. One could hardly be exhaustive, but we cite some of the most popular approaches: use of geometrical constraints, mostly rotation[5] but also distance elongation[6] to (partly) switch off resonance components, separation of $\sigma-\pi$ electrons,[7] etc. Most recently, the use of constrained Schrödinger equations[8] and the valence-bond model[9] have been proposed to refine the separation of resonance effects. Results are encouraging, although these methods might still suffer from the shortcoming of considering real substituents (and the associated scatter).

We designed an approach where we sought to mimic pure inductive effects.[10] We proposed the use of fictitious hydrogen atoms, whose nuclear charge Z^* is adjustable; hence, the name of the H* method. Such an entity acts as a *pure* inductive acceptor for a value of Z^* greater than 1. As Z^* is increased, its force will be continuously increased. In previous communications,[11,12] we validated and applied this method to properties that were shown to exhibit exotic (counter-intuitive) inductive effects.

For two main reasons, we are naturally led to investigate protonation reactions of benzene derivatives, differing by their functional center (FC) (Figure 1).

First, the Hammett equation was originally proposed for ionization rate constants of benzoic acids. On the other hand, protonation/deprotonation is of tremendous importance in many biological events and certainly requires an in-depth understanding.

Surprisingly enough, even on these reference reactions, substituent effects do not always follow the Hammett equation

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10.1021/jp806871r CCC: $40.75
Published on Web 02/25/2009

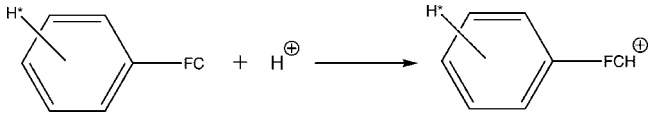


Figure 1. General protonation reaction of benzene derivatives considered in this study. FC denotes a generic basic functional center. An H* atom (see definition in text) is placed on position 3 or 4 to mimic a purely inductive effect, and the analysis of the response to this perturbation is analyzed.

nor more general dual-substituent parameters (DSP) treatments. Such failures are often delicate to trace back with certitude: for instance, Exner and Böhm only recently established the nonvalidity of empirical treatments for basicity of 3- and 4-substituted benzonitriles.[13]

While one usually investigates *total* substituent effects on a particular series of compounds, we present an accurate picture of inductive-only effects on proton affinities for a family of aromatic compounds, which should allow us to explore the role of the functional center.

2. Methodology and Calculation Details

Calculations of absolute proton affinities in very close agreement with known experimental values (sub kcal·mol^{-1}) usually require the use of the most sophisticated ab initio methods with zero-point energy (ZPE) corrections.[13,14] Yet, density functional theory (DFT) has proved to yield excellent results for prediction of substituent effects as the latter are intrinsically *relative* quantities.[14] Thus, we employed the widely used DFT hybrid functional B3LYP[15,16] with a standard Pople basis set 6-311++G**. In a very recent comparative study of quantum methods for reproducing proton affinities of γ-butyrolactone and 2-pyrrolidinone,[17] this level of theory was found to outperform more expensive wave function-based methods for calculations of absolute proton affinities, thus comforting us in this choice.

Geometries were fully optimized at this level of theory. Frequency calculations needed for ZPE corrections were not performed in this study. Basicity is commonly measured by the proton affinity, noted E_{pa} hereafter, which we simply define as the difference between total electronic energies of acid and basic forms. All electronic energies were obtained with the Gaussian03 series of programs.[18]

The technical scheme for using H* atoms makes use of hand-defined pseudopotentials to mimic the variation of the nuclear charge Z^* of hydrogen atoms. It has been extensively described in an earlier communication.[10] In the expression

$$V(r) = -\frac{Z-n}{r} + \sum_j c_j r^{n'-2} e^{-\alpha r^2} \qquad (1)$$

by imposing $n = 0$, $\alpha = 0$, and $n' = 1$, one can adjust the c_j coefficient to impose the value of Z^*. This has the main advantage to avoid any parasitic electrostatic effects, which would inevitably occur for a molecule bearing a varying and nonentire nuclear charge. We indeed verified the neutrality of this operation by preliminary test calculations, as published elsewhere.[10]

3. Results and discussion

3.1. Choice of a Panel of Benzene Derivatives and Validation of the Computational Approach. Seven benzene derivatives have been chosen to form a representative panel. Their structures, listed in Table 1, differ only by their respective functional center, FC: two neutral (NH_2, $CH{=}CH_2$) and five negatively charged (COO^-, SO_3^-, O^-, S^-, CH_2^-). It should be noted that the site of gas-phase protonation of aniline is not firmly established (N vs C4 base) and is highly dependent on the level of theory. Actually, at the B3LYP/6-311++G** level of theory, one finds that the C4 position is the favored site of proton attachment (by 2.9 kcal/mol). We chose nevertheless to investigate the N protonation in this study to enlarge the representativeness of our panel.

A *systematic* overestimation of the calculated proton affinities compared to experimental values (ref 19) is observed, with a maximal error for quinuclidine (**7**) of 12.3 kcal·mol^{-1} (averaged unsigned error 7.7 kcal·mol^{-1}). This offset could be obtained by taking into account thermodynamic contributions. Yet, this would lead in turn to similar conclusions, as we are only interested in *relative* quantities.

3.2. Evolution of Proton Affinity with Respect to an Additional Inductive Effect: General Trends in the Panel Studied. In this section, we monitor inductive continuous effects on the proton affinity of a series of benzene derivatives. For each compound, we considered effects of an H* substitution on positions 3 (meta) and 4 (para). A rule of thumb to assign realistic values to Z^* was derived from the construction of a simple mapping with atomic electronegativities. Z^* charges reproducing potassium and fluorine electronegativities were found to be, respectively, 0.576 and 1.541 at the B3LYP/6-31G** level of theory. Thus, we monitor proton affinities in the presence of additional pure inductive effects over the widest range of Z^* realistic charges, i.e., from 0.5 to 1.5 au.

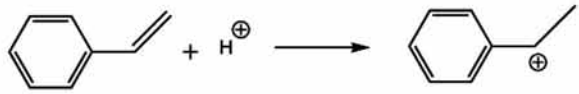
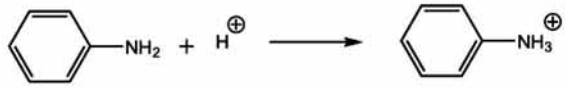
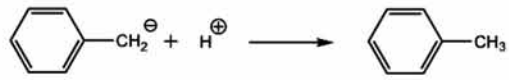
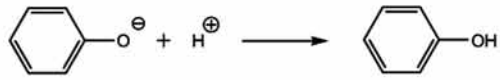
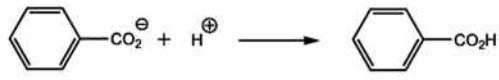
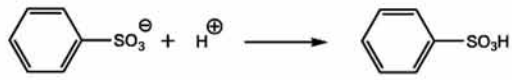
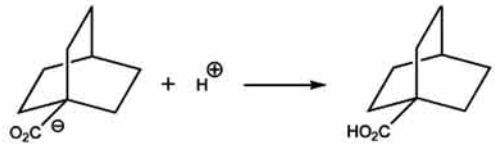
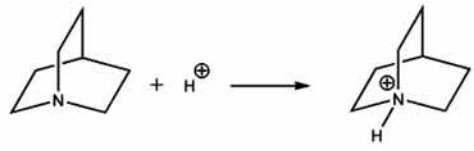
We first comment on the qualitative evolution of $E_{pa} = f(Z^*)$. All compounds exhibit similar trends, regardless of the functional center, FC, or position of substitution n: we thus only reported one curve, for 4-H*-benzocarboxylate (**4**), in Figure 2 (solid line).

In perfect agreement with previous results,[14,20−23] the proton affinity is systematically weakened in the presence of an additional inductive acceptor (increasing Z^* charges). This decrease corresponds to a larger (stabilizing) effect on the (negative) charged moiety in the presence of an acceptor. This interpretation now constitutes a consensus, clearly established by many studies involving homodesmotic reactions[23b] and recently comforted by the recent triadic formula proposed by Vianello et al.[24] The higher sensitivity of charged compounds governs the evolution of E_{pa}, whereas effects on the corresponding neutral moiety are weaker and less regular.[22,23] Separate calculations on the bicyclo-[2.2.2]-octane 1-carboxylic and its corresponding anion (**6bis** in this study) have shown that the substituent effects in the anion are eight times greater.[23b] We obtained a very similar value for the aromatic benzoic acid and benzoate anion (**6**).

Substituent effects are found to be rather important (∼10%) with regard to the typical order of magnitude of substituent effects (1−2%), even though we are dealing with *pure* inductive effects that are not counterbalanced by any other contributions (e.g., retrodonation). This marked sensitivity is also a well-established fact and comforts the privileged use of ionization reactions for defining substituent constants.

The evolution of proton affinity E_{pa} is perfectly linear over the range of Z^* (R^2 are all superior to 0.99): as a corollary, inductive effects are most likely additive. Some properties have been reported to present such a behavior,[25] while in contrast, others were found to exhibit nonlinear effects (for instance, the activation energy of Diels−Alder reaction[12]). Thus, one has to

TABLE 1: Sensitivities to a Pure Inductive Effect, ρ_I* (kcal·mol^{-1}·au^{-1}), for a Family of Protonation Reactions[a]

Label	Protonation reaction	$E_{pa}^{calc.}$	ρ_I^3*	ρ_I^4*	ρ_I^4*/ρ_I^3*
(1)		212.7	-52.5	-53.5	1.02
(2)		217.7	-38.0	-41.5	1.09
(3)		389.6	-43.4	-49.6	1.16
(4)		354.3	-35.2	-41.7	1.16
(5)		342.7	-32.3	-35.0	1.08
(6)		346.1	-21.8	-24.8	1.13
(7)		322.6	-15.6	-17.4	1.11
(6bis)		350.1	—	-17.2	—
(8bis)		235.0	—	-32.8	—

[a] They bear an H* atom whose inductive force is continuously adjustable; 3 and 4 refer to the position of substitution with respect to the functional center, FC. ρ_I* coefficients correspond to the slope of the linear regression $E_{pa}^* = f(Z^*)$; all regression coefficients R^2 are superior to 0.99, see Figure 2. The level of theory is B3LYP/6-311++G**.

properly establish the linearity, especially as charged species could have attenuation or saturation effects.

Other functional centers (compounds **3** and **5**−**7**) exhibit the same behavior. The interpretation is immediately transferable to *neutral* bases (**1** and **2**): an acceptor strongly destabilizes the positively charged acid form, also leading to a decrease of E_{pa}. More quantitatively, sensitivities toward an inductive effect vary (i) significantly with the functional center FC, as analyzed in

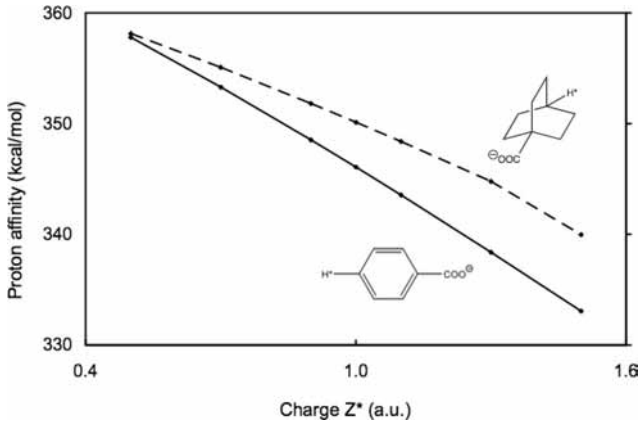


Figure 2. Relative evolution of proton affinity E_{pa} for H*-substituted benzoic carboxylate (**6**) (solid line) and the associated molecular bridge, bicyclo-[2.2.2]-octanes (**6bis**) (dashed line) as a function of the nuclear charge Z^*. The level of theory is B3LYP/6-311++G**. The lesser sensitivity of the saturated compound is quantified and analyzed in section 3.4.

section 3.3, and (ii) slightly, but interestingly, with respect to the position of substitution (3 vs 4) as discussed in section 3.4.

3.3. Compared Sensitivities of Various Bases on Inductive Effects. To explore quantitatively the role of FC, we are naturally led to define the sensitivity toward an inductive effect as

$$\rho_I^{n*} = \left(\frac{\partial E_{pa}{}^*}{\partial Z^*}\right)_{Z^*=1.0} \quad (2)$$

where the asterisk denotes the use of H* atoms and n denotes the position of substitution, here 3 or 4.

As E_{pa} varies linearly with the Z^* charge, ρ_I^* simply corresponds to the slope of the linear regression. Its value is always negative, and the more negative ρ_I^*, the higher the sensitivity. This quantity is analogous to empirical coefficients (Taft's ρ_I[3] or Swain-Lupton's f[4]). Yet, a mapping with the substituent coefficient scales cannot be proposed due to a π contamination that strongly affects empirical values for lone-pair substituents; a more detailed discussion can be found in ref 10.

In this subsection, analysis of the FC dependence is based on sensitivities for 4-substitution (para); corresponding values of ρ_I^{4*} for each acido−basic couple are listed in Table 1. The conclusions are straightforwardly transferable to H* substitution on the meta (3) position.

First, neutral bases (i.e., styrene (**1**) and aniline (**2**)) are most sensitive to inductive effects in our panel. Their respective ρ_I^{4*} values, of −53.5 and −41.5 kcal·.mol^{-1}·au^{-1}, are among the highest in our panel and should be scaled to the nonsubstituted proton affinities for an unbiased comparison.

This marked sensitivity arises from the lesser stabilization of a negatively charged compound by an inductive acceptor compared to the corresponding destabilization of a positively charged moiety.

Even restricting our attention to negatively charged bases (**3**−**7**), which constitute the largest category of our panel, sensitivities vary roughly by a factor of 3. Values of ρ_I^{4*} range from −49.6 to −17.4 kcal·mol^{-1}·au^{-1} for toluenate (**3**) and benzosulfonate (**7**). This contrasted behavior may be blurred by the schematic representation of Figure 1, where a common notation FC denotes the functional center. To gain some insight on its origin, let us first consider the three compounds **3**−**5** (respectively FC = CH_2^-, O^-, S^-). The decrease of ρ_I^* (roughly 25%) can be rationalized in terms of the HSAB (hard/soft acid/base) principle. The latter, proposed in the early 1960s by Pearson,[26] stipulates that hard bases associate more favorably with hard acid. The notion of hardness is related to the charge, polarizability, and electronegativity of FC.[27] It found a solid foundation within the framework of DFT two decades later[28] and is one of the most widely used concepts in physical and organic chemistry.

In this study, it is found to control the response to an electrostatic effect. Since H^+ is a hard acid, it gives stronger bonds with harder bases: acceptor substituents are expected to diminish their hardness by reducing the negative charge on the basic site. This effect is further enhanced as the negative charge of the basic form is π delocalized on the functional centers (compounds **6** and **7**). 3-Substition (meta) values are close to −15 kcal·mol^{-1}·au^{-1}, which is roughly halved compared to other not FC-delocalized bases (**3**−**5**).

In this section, we have shown that the sensitivity toward inductive effects is also strongly influenced by the nature of the functional center FC (charge, hardness, and π delocalization). We are familiar with such a relation for resonance contributions, which can usually be anticipated by writing down Lewis formula (and can lead to the so-called exaltation effect[29]).

It would be beyond the scope of this study to investigate inductive effects on aliphatic compounds, for which polarization effects play a crucial role.[30,31] Nevertheless, two cyclic saturated-chain compounds, bicyclo-[2.2.2]-octane carboxylate (**6bis**) and quinuclidine (**8bis**), have been included in our set. They are found to be less sensitive to an inductive perturbation compared to the corresponding aromatic systems. This strongly suggests a non-negligible contribution of π electrons in the transmission of inductive effects, which is analyzed in the next subsection.

3.4. Comparison between Meta vs Para Substitution: An Estimate of the Role of π Electrons in the Transmission of Inductive Effects. For an aromatic compound, the variation of sensitivity ρ_I^* for para (4) with respect to meta (3) positions arises from two competitive factors: (i) an attenuation of inductive effects transmission by both through-space and through-bonds mechanisms[32] and (ii) a stronger contribution of the conjugated π system for 4-substitution, as the π electrons transmit a certain part of inductive effects. The latter is known in the literature as the π-inductive effect, as first identified by Exner in spectroscopic data.[33]

The ratio ρ_I^4/ρ_I^3 (sometimes denoted as λ in the literature) is a common measure for estimating the relative weights of these two contributions. A value close to unity denotes similar overall inductive effects on para (4) and meta (3) positions, denoting a compensation of the two aforementioned effects. This is precisely one of the two key assumptions initially introduced by Taft and co-workers for building up their $\sigma-\pi$ separation.[3] The hypothesis $\rho_I^4/\rho_I^3 \approx 1$ is satisfactory for proton affinities (and, more generally, for reaction properties), but a more quantitative assignment is a delicate task. Successive values of 1.00, 1.14,[34] and 1.06[35] have been proposed for benzoic acid (**4**), and it is not clear which one should be taken.

Our theoretical approach enables a direct and accurate estimation of the ratio ρ_I^{4*}/ρ_I^{3*}. Values are listed in the last column of Table 1. As expected, inductive sensitivities are found to be similar for 3- and 4-substitutions, with a ratio close to unity. Its value is systematically greater than 1 (ranging from 1.02 (**1**) to 1.16 (**3** and **4**)), which confirms the existence of a π-inductive effect. Its strength is reinforced as the functional

center has a lone pair with a donating character for the benzene ring. The intermediate value (1.08) for protonation of thiophenolate (**5**) probably reflects a weaker conjugation for energetic considerations. One can note that the experimental values of proton affinity for compounds **3** and **4** are also in agreement with weak conjugation with the aromatic ring.

Estimating the weight of the π-inductive effect relative to the "classic" inductive/field effect is a legitimate question. Clearly, this value is dependent on the system considered: for both the sake of comparison and historical reasons, we chose to consider the most popular compound, benzoic carboxylate (**6**). The ratio ρ_I^{4*}/ρ_I^{3*} (1.13) cannot be used directly to infer such an estimate (which would be 13%) because the π-inductive effect is counterbalanced by the simultaneous attenuation of an inductive effect (through-space and through-bond transmissions), which is delicate to account for. We have chosen instead another popular $\sigma-\pi$ separation approach, proposed by Swain and Lupton.[4] Its key idea is to associate with 4-substituted benzene a carefully chosen "molecular bridge" with ideally (i) equal distances between the substituent X and the functional center FC (to assume almost identical inductive effects) and (ii) saturated aliphatic chains in the molecular bridge to (partly) switch off π contributions. No molecular bridge can exactly fulfill these criteria,[36] and one has to resort to the best compromise; the most common choice is a bicyclo-[2.2.2]-octane skeleton or closely related compounds like quinuclidines[35] and cyclohexanes.[37]

The comparison of ρ_I^{4*} for **6** and **6bis** is insightful. Corresponding curves are displayed in Figure 2. The aromatic compound **6** exhibits a higher sensitivity, respectively, -24.8 vs -17.2 kcal$\cdot$mol$^{-1}\cdot$au^{-1}, leading to an estimate of 30% for the π-inductive effect. Thus, the contribution of π electrons in the transmission of inductive effects is significant. Interestingly enough, a much lower value (10%) is obtained with a similar procedure for vibrational frequencies of 4-substituted benzonitriles.[38]

Concluding Remarks

In this work, fictitious hydrogen atoms (H*) were used to investigate inductive-only substituent effects on proton affinities of a family of aromatic compounds. In spite of their overall regularity, the sensitivity is highly modulated by the softness of the functional center. Both the property of interest and the functional center play a major role that could hardly be neglected if we are hoping to derive a sound foundation of substituent effects.

In the same way that the several components of the global substituent effect need to be considered separately, a solid understanding of inductive contributions probably requires a distinction between different mechanisms of transmission.

Acknowledgment. This work was supported by a grant of supercomputer time by the *Centre de Calcul Recherche et Enseignement* (CCR) from the University Paris VI. E.D. thanks Dr. Pierre-François Loos and Prof. Xavier Assfeld for their helpful comments on the manuscript.

References and Notes

(1) Krygowski, T. M.; Stephien, B. T. *Chem. Rev.* **2005**, *105*, 3482.
(2) Hammett, L. P. *Trans. Faraday Soc.* **1938**, *34*, 156.
(3) Taft, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 1045.
(4) Swain, C. G.; Lupton, E. C. J. *J. Am. Chem. Soc.* **1968**, *90*, 4328.
(5) (a) Wiberg, K. B.; Hadad, C. M.; Rablen, P. R. *J. Am. Chem. Soc.* **1992**, *114*, 8644. (b) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1992**, *115*, 9234.
(6) Monaco, R. R.; Gardiner, W. C. *J. Phys. Org. Chem.* **1995**, *8*, 629.
(7) Jug, K.; Koster, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 6772.
(8) Janesko, B. G.; Gallek, C. J.; Yaron, D. *J. Phys. Chem. A* **2003**, *107*, 1655.
(9) Linares, M.; Humbel, S.; Braïda, B. *Faraday Discuss.* **2007**, *135*, 273.
(10) Dumont, E.; Chaquin, P. J. *Mol. Struct. (Theochem)* **2004**, *680*, 99.
(11) Dumont, E.; Chaquin, P. J. *Mol. Struct. (Theochem)* **2005**, *756*, 161.
(12) Dumont, E.; Chaquin, P. *Chem. Phys. Lett.* **2007**, *435*, 354.
(13) Exner, O.; Böhm, S. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3864.
(14) Wiberg, K. B. *Collect. Czech. Chem. Commun.* **2004**, *69*, 2183.
(15) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785.
(16) Becke, A. D. *J. Chem. Phys.* **1993**, *96*, 5648.
(17) Vessecchi, R.; Galembeck, S. E. *J. Phys. Chem. A* **2008**, *112*, 4060–4066.
(18) Frisch, M. J. et al. *Gaussian 03*, Rev. C.02; Gaussian, Inc.: Wallingford, CT, 2004.
(19) NIST Chemistry webbook (www.nist.gov). The proton affinity data were compiled in the following: Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Data.* **1998**, *27*, 413.
(20) Lee, G. Y.; Lee, H. M. *J. Korean Chem. Soc.* **1998**, (1), 42.
(21) Morgon, N. H. *Int. J. Quantum Chem.* **2006**, *106*, 2658.
(22) Exner, O.; Böhm, S. *J. Org. Chem.* **2002**, *67*, 6320.
(23) (a) Exner, O.; Naus, P. *J. Phys. Org. Chem.* **2000**, *13*, 693. (b) Exner, O.; Böhm, S. *Chem. Eur. J.* **2002**, *8*, 5147.
(24) Vianello, R.; Maksic, Z. B. *J. Phys. Org. Chem.* **2005**, *18*, 699.
(25) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1993**, *115*, 614.
(26) Pearson, R. G. *Science* **1966**, *151*, 172.
(27) Ayers, P. W. *Faraday Discuss.* **2007**, *135*, 161.
(28) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.
(29) Jaffé, H. H. *Chem. Rev.* **1953**, *53*, 191.
(30) Perez, P.; Toro-Labbé, A.; Contreras, R. *J. Phys. Chem. A* **2000**, *104*, 11993.
(31) Headley, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 2347.
(32) Exner, O. *J. Phys. Org. Chem.* **1999**, *12*, 265.
(33) Exner, O. *Collect. Czech. Chem. Commun.* **1966**, *31*, 65.
(34) Decouzon, M.; Exner, O.; Gal, J.-F.; Maria, P.-C. *J. Phys. Org. Chem.* **1994**, *7*, 615.
(35) Exner, O.; Böhm, S. *Chem. Eur. J.* **1997**, *9*, 4718.
(36) Grob, C. A.; Schlageter, M. G. *Helv. Chim. Acta* **1971**, *59*, 264.
(37) Swain, C. G.; Unger, S. H.; Rosenquist, N. R.; Swain, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 492.
(38) Dumont, E. Ph.D. Thesis, University Paris VI.

JP806871R