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Substituent effects on the intramolecular proton transfer in the ground and lowest-lying singlet excited states of salicylaldimine

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Abstract

The effects of chemical substitution on the photophysical and photochemical properties of salicylaldimine (2-iminomethylphenol) have been studied by replacing the hydrogen atom of the imino group in salicylaldimine by SiH_3, CH_3, NH_2, COH, NO, CF_3, and CN. For the different derivatives of salicylaldimine, we have computed geometries and potential energy curves for the intramolecular proton transfer in their ground states along with the Franck–Condon energy curves for their three lowest-lying singlet excited states. Our results show that the intramolecular hydrogen bond in the enol form is weakened by the presence of the NH_2, NO, CF_3, and CN substituents. This weaker bond causes an increase of the energy barrier for the ground state proton transfer that converts the enol form to the keto tautomer. Moreover, the keto form becomes unstable in the ground state when the CH_3, NH_2, CF_3, or CN substituents are present in the molecule. Finally, whereas the $1\pi\pi^*$ state remains almost unaltered by the effect of the substituent, the $n\pi^*$ excited state is stabilized in the SiH_3, COH, and NO derivatives. This fact is especially true for NO, where the $n\pi^*$ state becomes the first excited state. The results have been rationalized by taking into account the different electronic effects of each substituent. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Salicylaldimine derivatives; Intramolecular proton transfer; Potential energy curves; Franck–Condon energy curves; Substitution effects

1. Introduction

The molecules that contain both an acidic and a basic group in close proximity may rearrange via an intramolecular proton transfer upon photoexcitation, a process usually referred to as excited-state intramolecular proton transfer (ESIPT). ESIPT processes have attracted considerable attention due to their implication in biology [1], their role in many laser dyes [2–5], in materials able to store information at the molecular level [6], in high-energy radiation detectors [7,8], and in fluorescent probes. One of the molecules that exhibits ESIPT is salicylaldimine (R = H according to Fig. 1) and related compounds [9–16]. In the gas phase, the most stable isomer of these molecules in the ground state is the enol form, which has an N···H–O intramolecular hydrogen bond connecting the acidic hydroxyl group and the basic nitrogen atom. Photoexcitation of the enol form to the first singlet excited state is followed by transformation to the phototautomer. In the excited

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state, the keto form is often more stable than the enol form and, thus, the emission of these molecules is largely red-shifted [9–32].

The phototautomeric behavior of molecules exhibiting ESIPT is associated with a difference of electron charge distribution between the ground and the excited states. The proton donor and acceptor groups connected by the intramolecular hydrogen bond become more acid and basic, respectively, in some excited states with respect to the ground state [9,27,33–37]. Therefore, the intramolecular hydrogen bond is stronger in these excited states and the ESIPT process is favored. The electronic and structural reorganization of the molecule upon photoexcitation depends strongly on its specific molecular composition and on the nature of the solvent [24,26,27,38–41]. Substitution of a seemingly irrelevant group of the molecule can strongly modify its photophysical and photochemical properties [42,43]. The significance of a certain substituent on the ESIPT process depends on both its position and its chemical properties in the molecule. For instance, introduction of a *tert*-butyl group *ortho* to the phenolic OH group in 2-(2′-hydroxyphenyl)benzotriazole prevents the intramolecular hydrogen bond from being broken [39]. Likewise, a bromine atom in the *meta* position with respect to the OH group in 2-(2′-hydroxyphenyl)iminomethyl-benzimidazole impedes the breaking of the intramolecular hydrogen bond by polar solvents in the excited state [44]. On the other hand, the stronger electron-donating ability of methoxy as compared to hydrogen explains the disappearance of ESIPT in salicylic acid when hydrogen is replaced by methoxy at the *para* position with respect to the phenolic OH [45]. Moreover, because of their electron-withdrawing character, the COOH and $COOCH_3$ substituents prevent one of the two possible ESIPTs from taking place in (2,2′-bipyridyl)-3,3′-diol when they are placed in a specific position of the molecule [46]. In yet another case, substitution of hydrogen by a methyl group at the 1-position of 2-(2′-hydroxyphenyl)benzimidazole has more influence on its photochemical properties than when it is located at the 5′-position [28,47].

Interestingly, because of the critical role that some specific chemical groups may play in a molecule, it was suggested that the photophysical and photochemical properties of ESIPT-prone molecules may be changed in a desirable and predictable way by specific chemical modifications [48,49]. It is, thus, of great interest to have a thorough understanding of the detailed mechanism by which a substituent can modulate the ESIPT behavior of a molecule [50]. One of our previous studies addressed this point by analyzing the influence of fluorosubstitution on the ESIPTs of salicylaldimine (R = H in Fig. 1) as a function of the position of fluorine in the molecule [11]. We now extend this study to the analysis of the effects that different substituents joined to a specific position, N_1 (Fig. 1), have on the photophysical and photochemical properties of this molecule. In particular, in this work two questions are addressed: (a) how substitution influences the intramolecular hydrogen bond and the intramolecular proton transfer in the ground state? and (b) which are the effects of chemical substitution in the lowest-lying singlet excited states of salicylaldimine? The results obtained in the present work have been rationalized by taking into account the different electronic effects of each substituent.

2. Computational details

We have studied seven derivatives of salicylaldimine which have been obtained by substitution of the hydrogen atom of the imine group in salicylaldimine by the SiH_3, CH_3, NH_2, COH, NO, CF_3, and CN groups. In the forthcoming text, all derivatives will be referred to by the corresponding substituent name. To our knowledge, the species with $R = CH_3$ and NH_2 have been already synthesized. The synthesis of the SiH_3, COH, and CN compounds should be possible from the attack of the silylamine, formamide, and cyanamide to salicyaldehyde, while the NO and CF_3 species may be more difficult to achieve, but are interesting to include in the study because of their particular chemical effects.

The potential energy curve (PEC) for the ground-state proton transfer of each salicylaldimine derivative has been calculated using the reaction coordinate method. We have computed 11

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points along the reaction coordinate, as defined by the difference between the N_1–H_6 and H_6–O_5 bond lengths. In some cases, a few additional points have been calculated to locate a minimum for a specific excited state. Each point has been obtained freezing the $r(N_1–H_6)$ bond distance and optimizing the rest of the geometrical parameters.

It is well established that an accurate evaluation of the ground state intramolecular proton transfer (GSIPT) requires the inclusion of electron correlation effects [51–54]. One of the methods being able to provide fairly good geometry and energy parameters for the ground state is MP2 [55]. Furthermore, the use of a basis set large enough is also necessary. In particular, inclusion of polarization functions in the basis set is essential to obtain a reliable description of the proton transfer [56]. By contrast, diffuse functions have little effect on the results [55,57–59]. For these reasons, the MP2 method together with the Dunning and Hay double-ζ basis set with polarization functions (D95**) [60] have been employed for the optimizations of the different systems in the ground state.

The PECs for the proton transfer of the three first singlet excited states have been built as Franck–Condon curves (FCCs) computed at the CIS/D95** level [61] from the corresponding MP2/D95** GSIPT curve. Given the deficient treatment of electron correlation at the CIS level [57] and the lack of geometry optimization in the excited states, the FCCs obtained in this way represent a rough estimation of the correct PECs. However, one may reasonably expect that the qualitative conclusions reached by comparing the different derivative FCCs will be unaltered in a meaningful way by the use of more sophisticated approaches. All computations have been carried out with the GAUSSIAN 94 program [62].

3. Results and discussion

3.1. Geometries

Fig. 1 depicts the hydroxy and oxo tautomeric forms of salicylaldimine, together with the substituents chosen for the present study, plotted in the spatial orientation resulting in the most stable conformer for each enol tautomer. It is worth noting that the NO substituent adopts the conformation shown in Fig. 1 in order to minimize repulsions between the lone pair electrons of N_1 and those of the N atom of NO. Furthermore, the NH_2 group in the enol form reaches a conforma-

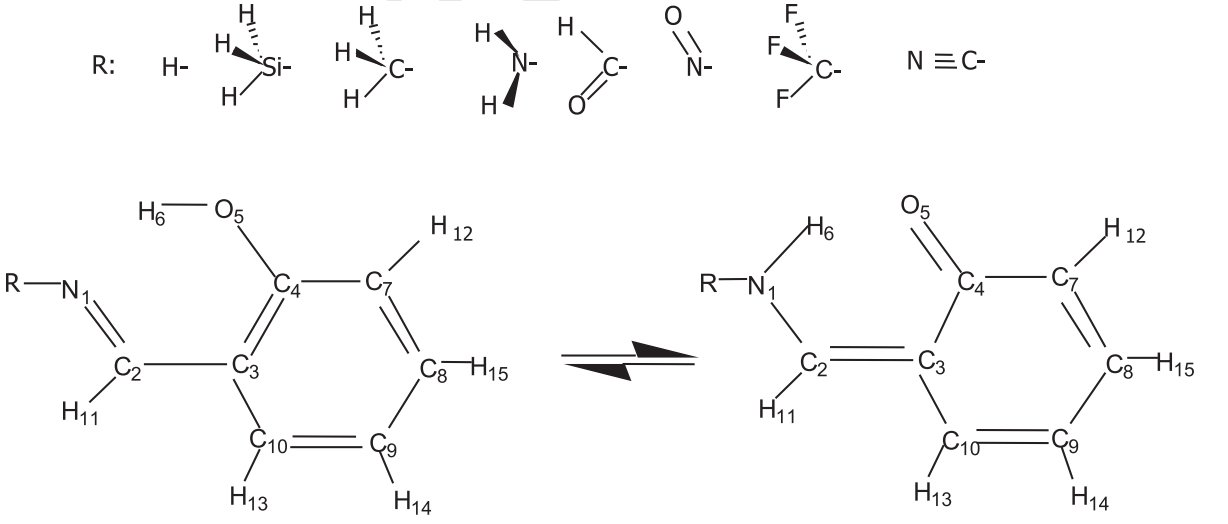

Fig. 1. Scheme with atom numbers of the enol and keto tautomers of the salicylaldimine derivatives. The most stable conformation adopted by each substituent in the enol tautomer is given.

tion where the two hydrogen atoms lie in the same side of the molecular plane. Thus, the lone pair of the NH_2 group is perpendicular to the lone pair of N_1, and parallel to the π-system of the molecule. The seven spatial arrangements shown in Fig. 1 remain unaltered along the reaction coordinate except for NH_2. During the transfer of H_6 from O_5 to N_1, the lone pair of N_1 becomes perpendicular to the molecular plane, and the NH_2 substituent rotates aligning its lone pair with the molecular plane in order to minimize repulsions.

Table 1 lists the bond lengths of the OCCCN structure for each compound in the ground state. The unsubstituted and SiH_3- and CH_3-substituted enol forms have nearly the same bond lengths. The other enol structures exhibit some differences with salicylaldimine, mainly for the N_1–C_2 and C_2–C_3 bond lengths, yet never larger than 0.02 Å. Therefore, one can conclude that the geometry of the OCCCN backbone in the enol form of salicylaldimine is remarkably insensitive to any substituent bonded to N_1. A similar behavior is found for the OCCCN backbone of the keto form. It is worth noting that the keto tautomers corresponding to the CH_3, NH_2, CF_3, and CN substituents are not stable in the ground state and so they do not appear in Table 1.

Since the intramolecular hydrogen bond plays an important role in the proton transfer, it is interesting to examine how the geometrical parameters most involved in this bond are affected by the presence of a substituent in the molecule. Results in Table 2 show that in the enol form of the NH_2, NO, CF_3, and CN compounds, the $N_1\cdots H_6$ and $N_1\cdots O_5$ distances are larger, whereas the H_6–O_5 bond length and the $\theta(N_1H_6O_5)$ angle are smaller, when compared to the corresponding values of the enol form of the unsubstituted salicylaldimine. In many cases, there is a clear relationship between these parameters and the strength of the hydrogen bond. The smaller the N···H and N···O distances and the larger the H–O bond length and the θ(NHO) angle in the enol tautomer, the stronger the intramolecular hydrogen bond [9–11,57,59,63–65]. Hence, the aforementioned set of chemical groups weaken the intramolecular hydrogen bond in the enol form. This effect is also shown in the keto form of NO and COH. Moreover, the hydrogen bond in the enol form is hardly affected by the presence of the SiH_3, CH_3, and COH groups.

Table 1
Selected bond lengths (Å) for the enol and keto tautomers of salicylaldimine derivatives in the ground state

	N_1–C_2	C_2–C_3	C_3–C_4	C_4–O_5
Enol				
H	1.302	1.462	1.421	1.353
SiH_3	1.303	1.460	1.422	1.351
CH_3	1.298	1.461	1.421	1.353
NH_2	1.304	1.460	1.400	1.359
COH	1.310	1.445	1.424	1.348
NO	1.312	1.444	1.424	1.350
CF_3	1.301	1.451	1.422	1.352
CN	1.311	1.446	1.423	1.352
Keto				
H	1.332	1.404	1.462	1.278
SiH_3	1.341	1.403	1.463	1.279
COH	1.359	1.385	1.478	1.265
NO	1.360	1.382	1.482	1.262

Table 2
Geometrical parameters (in Å and degrees) most involved in the intramolecular hydrogen bond of the ground-state salicylaldimine derivatives

	$N_1\cdots H_6$	H_6–O_5	$N_1\cdots O_5$	$\theta(N_1H_6O_5)$
Enol				
H	1.724	0.994	2.620	148.0
SiH_3	1.710	0.999	2.624	150.3
CH_3	1.710	0.997	2.618	149.4
NH_2	1.767	0.987	2.651	147.3
COH	1.717	0.995	2.617	148.4
NO	1.771	0.989	2.644	145.3
CF_3	1.774	0.987	2.651	146.1
CN	1.783	0.985	2.657	145.8
	N_1–H_6	$H_6\cdots O_5$		
Keto				
H	1.046	1.647	2.534	139.6
SiH_3	1.061	1.595	2.541	146.5
COH	1.035	1.736	2.589	137.0
NO	1.036	1.808	2.597	129.8

3.2. Energies

3.2.1. Hydrogen bond strength

The stability (E_{HB}) caused by the intramolecular hydrogen bond of the enol form can be estimated through the difference in energy between the structure containing the hydrogen bond (closed

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Table 3
Parameters for the inductive field (σ_F), resonance (σ_R), polarizability (σ_α), and electronegativity (σ_χ) effects,[a] and the ground state intramolecular hydrogen bond energies for each substituted salicylaldimine derivative

Enol	σ_F	σ_R	σ_α	σ_χ	E_{HB}[b]
H	0.00	0.00	0.00	0.00	16.4
SiH_3	−0.02[c]	0.02[c]	−0.35[d]	−0.24[e]	16.8
CH_3	0.00	−0.08	−0.35	0.00	17.0
NH_2	0.14	−0.52	−0.16	0.33	13.7
COH	0.31	0.19	−0.46	−0.05	16.0
NO	0.41	0.26	−0.25	0.39	14.2
CF_3	0.44	0.07	−0.25	0.02	13.3
CN	0.60	0.10	−0.46	0.30	12.0

[a] Values taken from Ref. [67], except for SiH_3. The hydrogen atom is taken as a reference.
[b] In kcal mol^{-1}.
[c] Same value as $Si(CH_3)_3$ [67].
[d] Same value as CH_3.
[e] Value estimated from the correlation between the H natural atomic charge in the H–R compounds and the σ_χ of each substituent (CH_3 has been excluded from the correlation analysis).

form) and that in which the $C_3C_4O_5H_6$ dihedral angle is rotated to 180° (open form) without further geometry optimization [11,57,59,63–65]. Table 3 reports this energy difference for each salicylaldimine derivative. The SiH_3, CH_3, and COH derivatives have nearly the same E_{HB} as the unsubstituted system; thus, confirming that these substituents have a small influence on the hydrogen bond of salicylaldimine. In agreement with the geometry parameters, the rest of the substituents weaken the intramolecular hydrogen bond by 2.2–4.4 kcal mol^{-1}.

Because of the small size of all substituents, one can reasonably assume that the influence of each substituent on the chemical properties of salicylaldimine will be due mainly to their different electronic effects, rather than to essentially different steric effects. The electronic effects of the different substituents can be conveniently discussed by using the model proposed by Taft and coworkers [66,67]. In that model, the electronic effects are divided into four main contributions, namely the field (F), electronegativity (E), resonance (R), and polarizability (P) effects. These four effects were parameterized [66,67] for different substituents, taking the hydrogen atom as the reference substituent. For the present work, the values for the seven substituents studied have been gathered in Table 3. From these four parameters, one finds that substituents with a positive σ_F value tend to weaken the intramolecular hydrogen bond. The main difference between the closed and open enol forms is the position of H_6; since this atom is positively charged, destabilization by a substituent with positive σ_F in the open form is smaller than in the closed structure. Therefore, the H-bond strength, computed as the difference in energy between these two forms, is reduced. Moreover, π-acceptor ($\sigma_R > 0$) and electronegative ($\sigma_\chi > 0$) substituents contribute to reduce the basicity of N_1 in the enol form (vide infra) and thus, weaken the hydrogen bond [49].

The system with $R = NH_2$ deserves a more detailed discussion. The effect of NH_2 on the hydrogen bond strength is comparable to the other strongly electronic withdrawing groups (CF_3, CN, and NO) despite the fact that it has a large donating resonance parameter that should increase the density on the imino group, thus, increasing the hydrogen bond strength. Two factors account for this unexpected behavior. First, the π-electron donation in the enol form of NH_2 is partially inhibited by the strong π-electron donor character of the hydroxyl group. Second, NH_2 is an electronegative substituent that acts as a σ-acceptor weakening the hydrogen bond. The combined inhibition of π-donation and the large electronegativity effect explain the reduction of the hydrogen bond strength in NH_2.

3.2.2. Enol–keto stability

Fig. 2 shows the PEC describing the displacement of the hydrogen atom along the reaction coordinate in the ground state and the FCCs for the three lowest excited singlet states for each salicylaldimine derivative. Let us, first, focus our attention on the ground state PEC of salicylaldimine. Such a curve is characterized by the existence of two energy minima, one for the enol structure and another for the keto tautomer that is higher in energy. The same result was found earlier with the Hartree–Fock method [9]. The origin of the larger stability of the enol form was found in the increased aromaticity of the six-membered ring

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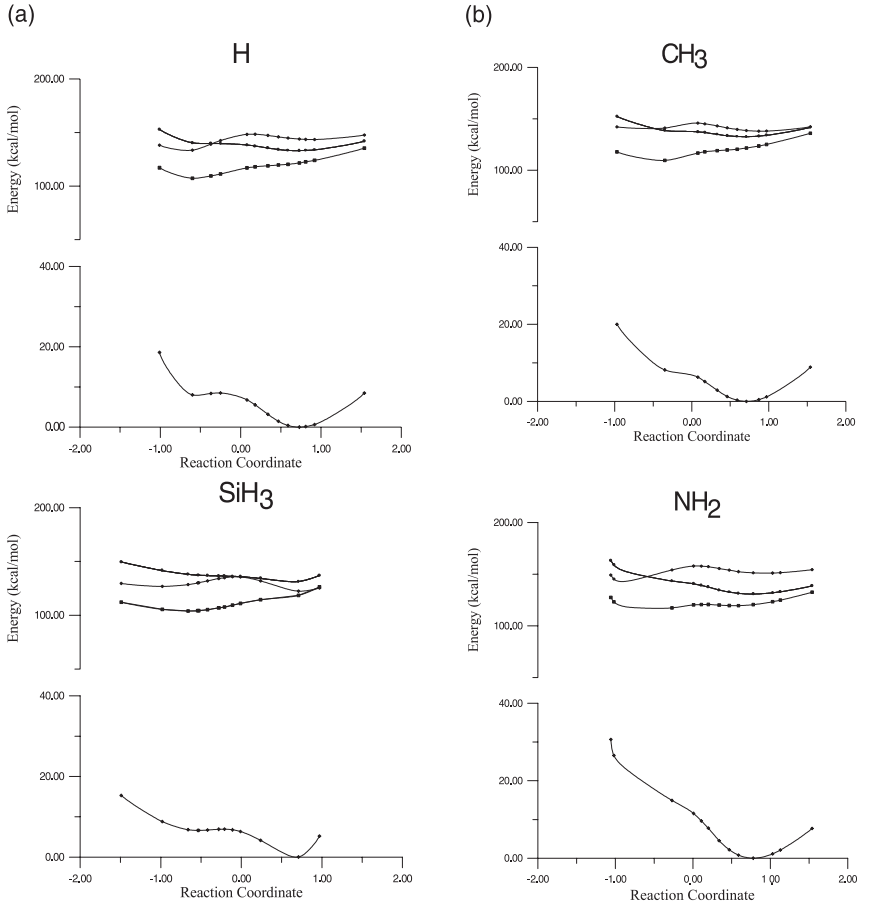

Fig. 2. GSIPT curves obtained from the MP2/D95** optimized structures and FCCs for the three lowest singlet excited states calculated at the CIS/D95** level using the ground state MP2 optimized geometries. In the case of NO, the fourth excited state ($2n\pi^*$) is also showed. Energy values are referred to the ground state enol form of each substituent.

of this tautomer, as compared to that of the keto structure [9]. Regarding the CH_3, NH_2, CF_3, and CN compounds, an energy minimum for the keto form has not been found, thus, indicating that introduction of any of the mentioned substituents in salicylaldimine makes the keto form unstable. This effect is especially important for NH_2, whereas the other derivatives exhibit a fairly flat curve in the keto zone. We must note that the CH_3 compound has been studied experimentally [12]. It was found that, although the enol form is the dominant tautomer in the ground state, the keto form was also present in CH_3CN [12] and methanol [13] solutions. Although, we have not found a minimum for the keto form of this compound in the gas phase, its PEC shows a quite flat profile near the keto zone; moreover, a stabilization of the keto form in polar solvents can be expected due to the higher dipole moment of the keto form with respect to the enol form for this kind of compounds [40]. [1] Therefore, an increase of the stability of the keto form in polar solvents is expected to occur, in agreement with the experimental results. Finally, one can say that the SiH_3, COH, and NO substituents do not exert any qualitative change on the ground-state PEC of salicylaldi-

[1] The dipole moment of salicylaldimine is 2.95 and 4.05 D for the enol and keto tautomers, respectively.

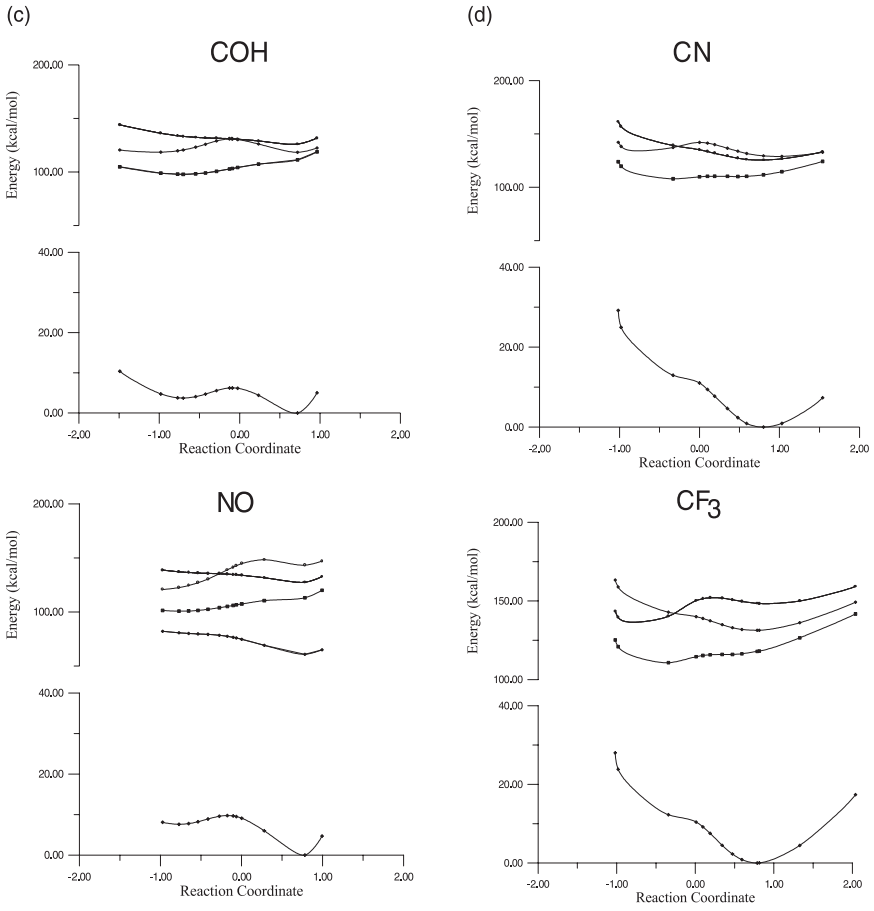

Fig. 2. (*continued*).

mine, both tautomers of their corresponding derivatives being stable in the ground state.

The addition of a substituent to the salicylaldimine molecule leads to some redistribution of the electron density near the substitution site, which affects the relative stability of the two tautomers. The natural atomic charges [68–70] of the substituent (*R*) and N_1 (Table 4) in the salicylaldimine derivatives are helpful to understand the electron density changes in the molecule due to chemical substitution. The electron-donor/acceptor ability of a substituent can be related to its resonance and electronegativity parameters. In the case of SiH_3, there is a transfer of electronic charge from SiH_3 to N_1, which is due to the electropositive character of SiH_3. The positive and negative charge of *R* and N_1 in the enol form is, thus, increased by 0.164 and decreased by 0.203 a.u., re-

Table 4
Natural atomic charges (in a.u.) for selected atoms of the ground-state enol and keto tautomers

	Enol		Keto	
	R[a]	N_1	R[a]	N_1
H	0.376	−0.699	0.411	−0.744
SiH_3	0.540	−0.902	0.573	−0.943
CH_3	0.216	−0.513	0.254	−0.550
NH_2	0.085	−0.308	0.068	−0.382
COH	0.177	−0.637	0.154	−0.656
NO	−0.008	−0.422	−0.158	−0.426
CF_3	0.178	−0.624	0.215	−0.697
CN	0.092	−0.579	0.118	−0.655

[a] Total charge of the substituent.

spectively, with respect to the charges of the unsubstituted salicylaldimine. By contrast, the CH_3 group acts as an electron acceptor with respect to H, which can be attributed partially to negative hyperconjugation effects [71]. Specifically, a natural bond orbital (NBO) [69,70,72,73] analysis reveals that there is a favorable interaction between the lone pair of N_1 and the σ^* orbital corresponding to the C–H bond of the CH_3 placed in the molecular plane. Moreover, there is an interaction between the σ^* orbital corresponding to the other two C–H bonds of CH_3 and the π orbital of the N_1–C_2 bond. These interactions agree with the smaller charge transfer found for CH_3 than that from H. In the case of NH_2, the π-electron donation is difficulted in the keto form due to the perpendicular orientation of the lone pair orbital of NH_2 and the π system of the molecule, and is partially inhibited in the enol form because of the π-electron donor character of the hydroxyl group. As compared to the hydrogen atom, the large electronegativity effect of this substituent prevails over the π-electron donor influence, and as a result there is a smaller flow of electron charge from NH_2 to the rest of the molecule. NO and CN act as σ and π electron acceptors having as a whole a behavior similar to that of NH_2. Moreover, the smaller resonance and electronegativity effects of COH and CF_3 translate into a smaller electron accepting character of the substituent, as compared to NH_2, NO and CN.

When the negative charge of N_1 increases by the effect of the substituent, the basic imino group in the enol form becomes stronger and the acid amino group in the keto form becomes weaker, the keto structure being favored as compared to the enol form. This happens to the SiH_3 derivative, as can be seen from the relative energies of the two tautomers collected in Table 5. An opposite behavior is found for the NH_2, CF_3, and CN derivatives. In all these compounds, there is a smaller electron transfer from the substituent to the molecule, as compared to the transfer in the unsubstituted salicylaldimine; this fact favors the enol form with respect to the keto form. Another factor that may play a relevant role in the relative stability of the two tautomers is the field effect; substituents having a large positive value of σ_F stabilize the lone pair of N_1 in the enol form and destabilize the positive charge of H_6 in the keto form. As mentioned above, combination of the electron charge redistribution and the σ_F effects makes the keto form unstable for the NH_2, CF_3, and CN derivatives. Although the keto form is also unstable for CH_3, the energy difference between the enol structure and a keto form optimized by constraining the N_1–H_6 bond length to 1.7 Å is nearly the same as the enol–keto energy difference of unsubstituted salicylaldimine (Table 5). This result, together with the flatness of the PEC around the keto form (Fig. 2) indicates that the keto form in CH_3 is not as unfavored as the NH_2, CF_3, and CN keto forms, as one could expect from the zero σ_F and σ_χ values of the CH_3 substituent.

Table 5
MP2/D95** relative energies (kcal mol^{-1}) of the ground-state keto structures as compared to the enol forms, alongwith energy barriers for the proton transfer interconverting both tautomers

	ΔE_{K-E}	$\Delta E^{\ddagger}$
H[a]	8.0	8.5
SiH_3	6.6	6.9
CH_3[b]	8.6	8.6
NH_2[b]	15.9	15.9
COH	3.7	6.2
NO	7.6	9.8
CF_3[b]	12.5	12.5
CN[b]	13.5	13.5

[a] ΔE_{K-E} and $\Delta E^{\ddagger}$ values are 6.8 and 14.4 kcal mol^{-1} at the HF level [9].
[b] The keto form has been obtained by freezing the $H_6\cdots O_5$ bond distance to 1.7 Å, while the rest of the geometrical parameters have been fully optimized.

Compared to salicylaldimine, the relative stability of the two tautomers of NO is almost the same, while the keto form is stabilized with respect to the enol form in COH. COH and NO are those substituents having the largest π-electron acceptor character. Although this effect contributes to increase the acidity of NH in the keto form, it can also exercise a stabilizing effect on this tautomer with respect to the enol form. As compared to the unsubstituted salicylaldimine, there is a larger increase of π conjugation in the keto form than in the enol form for the COH and NO compounds. This fact is proved by the behavior of the bond

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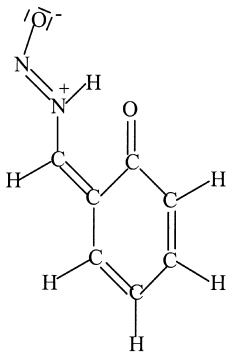

Scheme 1.

lengths, the single N_1–N bond being 0.066 Å shorter and the double N–O bond being 0.013 Å larger in the keto form than in the enol form of the NO derivative (in the case of the COH the differences being 0.034 and 0.001 Å), thus, indicating a larger contribution of the valence bond structure shown in Scheme 1 in the wave function of the keto form. In COH, the stabilizing resonance effect for the keto form dominates over the charge redistribution effect favoring the keto structure, while the effects are almost compensated in NO. Remarkably, for all systems, the behavior of the energy barrier follows that of the H-bond strength in the enol form: a weakening of the H-bond implies an increase of the energy barrier [9,57–59].

3.2.3. ESIPT processes

Let us now turn our attention to the three lowest-lying singlet excited states of the studied systems. For all compounds, we have analyzed the same electronic transitions. When transferring one electron from the HOMO to the LUMO, the state of the molecule changes to $1\pi\pi^*$. The second $2\pi\pi^*$ excited state is in turn a combination of the HOMO-1/LUMO and HOMO/LUMO+2 electronic transitions. The remaining excited state ($n\pi^*$) results of a promotion of an electron from the HOMO-2 to the LUMO. Earlier, CIS calculations showed that the lowest excited state of the enol form of salicylaldimine (R = H in Fig. 1) is $1\pi\pi^*$ [9]. When the enol form is excited to this state, an ESIPT takes place giving rise to the phototautomer form, which is more stable than the photoenol. These results indicated that the next state higher in energy for the enol tautomer is $n\pi^*$, which crosses with the $2\pi\pi^*$ PEC twice along the reaction coordinate [9]. The energy barrier for the intramolecular proton transfer in the $n\pi^*$ excited state was found to be higher than that in the $2\pi\pi^*$ state. The FCCs of salicylaldimine (Fig. 2) qualitatively reproduce the features shown by the ESIPT curves [9]. We must point out, however, that the agreement between PECs and FCCs is not complete. For instance, the PEC of the $1\pi\pi^*$ state of salicylaldimine has minima both for the keto and the enol tautomers, while the FCC for the same state only shows a minimum corresponding to the keto tautomer. Further, the value of the reaction coordinate for the keto form in the $1\pi\pi^*$ state of salicylaldimine is -0.601 for the FCC and -0.981 in the PEC. [2] Therefore, the geometry relaxation is relevant, particularly for those parameters that are most involved in the intramolecular hydrogen bond. Despite these differences, we must say that the energy barrier for the enol to keto conversion in the $1\pi\pi^*$ state of salicylaldimine obtained from the PEC is only 1.5 kcal mol^{-1} at the CIS/D95** level [9], and therefore, qualitatively the PEC and FCC lead to the same conclusion: an ESIPT takes place in the $1\pi\pi^*$ state after photoexcitation from the ground state enol tautomer. Therefore, we expect that the FCCs of the different salicylaldimine derivatives will be adequate approximations to the real ESIPT curves and we assume that the FCCs are a rational choice to perform a comparative analysis of the substitution effects on the photophysical and photochemical properties of salicylaldimine [50].

The FCCs of the three lowest-lying singlet excited states for the CH_3, NH_2, CF_3, and CN compounds look qualitatively very similar to those of the reference molecule. Among these species, the only remarkable difference corresponds to the enol form of CH_3 and CN in the $1n\pi^*$ state, which is stabilized with respect to the keto form. The behavior of the FCCs of SiH_3 and COH deviates

[2] An equivalent behavior has been found for the COH substituent, with two minima in the PEC and only a minimum corresponding to the keto form in the FCC.

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Table 6
$1n\pi^*$ and $1\pi\pi^*$ vertical excitation energies (kcal mol^{-1}) from the ground-state enol form of the different salicylaldimine derivatives studied

	$S_0 \rightarrow 1n\pi^*$	$S_0 \rightarrow 1\pi\pi^*$
H	144.0	121.6
SiH_3	122.5	118.5
CH_3	138.6	121.6
NH_2	151.3	120.5
COH	118.4	111.3
NO	60.8	113.2
CF_3	148.5	117.9
CN	129.5	111.7

from that of the H, CH_3, NH_2, CF_3, and CN FCCs in the fact that the $n\pi^*$ state is lower in energy than the $2\pi\pi^*$ state, excepting for some points near the TS of the $n\pi^*$ state, where both states take the same energy values, yet no crossing between these two excited states is found. This fact indicates that the $n\pi^*$ state is stabilized by the SiH_3 and COH substituents. In particular, the stabilization is fairly large for the enol form, which has nearly the same energy as the keto form in the COH derivative and is the most stable tautomer in the SiH_3 derivative. Interestingly, this pattern is much more pronounced in the NO system, the $n\pi^*$ state being the first excited state and the enol form becoming the only tautomeric structure stable in this excited state. The values of the enol $n\pi^*$ vertical excitation energies, obtained in Table 6, confirm the stabilization of this tautomer in the $n\pi^*$ state by the effect of COH, SiH_3, and NO substitution in salicylaldimine, and to a lesser extent, by substitution by CH_3 and CN.

The substituents with positive σ_F values stabilize the ground state to a larger extent than the $n\pi^*$ excited state, as compared to salicylaldimine, due to a larger stabilization of the lone pair of the enol form in the ground state by the presence of the substituent. On the contrary, the π-acceptor effect of the substituent stabilizes the $n\pi^*$ excited state to a larger extent than the ground state because the electron transfer to the LUMO is favored by π-conjugation. Catalán et al. found a similar influence of these effects on the $n\pi^*$ excitation for a similar system [50]. The fact that NO has the largest positive σ_R value among the seven substituents correlates well with the fact that the $n\pi^*$ excited state of this compound is the most stabilized state. The next lowest singlet states of NO are the $1\pi\pi^*$ and $2\pi\pi^*$ states. Both states show a behavior similar to those of salicylaldimine. Nevertheless, $2\pi\pi^*$ has the particularity of crossing with a fourth excited state ($2n\pi^*$), which is the third excited state for negative values of the reaction coordinate. Not surprisingly, the $2n\pi^*$ singlet excited state is especially stabilized in NO for the same reasons explaining the stabilization of its $1n\pi^*$ excited state.

The shape of the FCC of the $1\pi\pi^*$ excited state is nearly unaffected by substitution effects, all derivatives showing either a single energy minimum corresponding to the keto form or a small energy barrier for the conversion of the enol to the keto structure. Hence, the ESIPT process takes place when the enol form is excited to this state for all derivatives of salicylaldimine. In the case of CH_3, the ESIPT reaction in the $1\pi\pi^*$ excited state has already been observed experimentally [12]. Table 6 also collects the enol $1\pi\pi^*$ vertical excitation energies for all compounds. In all cases, they have a value smaller than that of salicylaldimine, except for CH_3, which has the same value. The experimental value for the $1\pi\pi^*$ electronic transition in the CH_3 compound is 91.6 kcal mol^{-1} to be compared with the theoretical estimation of 121.6 kcal mol^{-1}. This large difference is not unexpected, since it is well known that the CIS method overestimates the $1\pi\pi^*$ excitation energies by about 30 kcal mol^{-1} [57,74–76]. The effect of substitution on the $1\pi\pi^*$ electronic transition is much less significant than on the $n\pi^*$ transition. The nature of the orbitals involved in the $1\pi\pi^*$ electron excitation is similar and, thus, the substituent effects on the $1\pi\pi^*$ state are less important.

4. Conclusions

The NH_2, NO, CF_3, and CN substituents weaken the intramolecular hydrogen bond of salicylaldimine when they are bonded to the imine group of this molecule. In consequence, the ground-state energy barrier for the proton transfer from the enol to the keto form increases. In the

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case of the SiH_3, CH_3, and COH compounds, the intramolecular hydrogen bond strength is similar to that in salicylaldimine.

Substitution of the hydrogen atom of the imino group in salicylaldimine by SiH_3 leads to a large charge transfer from this substituent to the molecule, due to the electropositive character of this substituent. Therefore, the basicity of the imino group in the enol form increases and the acidity of the amino group in the keto form decreases, which translates into a stabilization of the keto form with respect to the enol structure of salicylaldimine. On the contrary, the NH_2, CF_3, and CN substituents destabilize the keto form with respect to the enol form. This fact arises from the combined electronegative, resonance, and field effects of the substituent. Furthermore, there is a larger stability for the enol form than for the keto form in COH, with respect to the unsubstituted salicylalimine which has been attributed to the stabilizing π-acceptor resonance effects.

The features of the $1\pi\pi^*$ ESIPT in salicylaldimine are not qualitatively modified by the presence of any of the studied substituents. The FCCs of the $1\pi\pi^*$ excited state show either a single minimum corresponding to the keto tautomer or an small energy barrier for the conversion of the enol to the keto tautomer. Thus, one can predict that after excitation to the $1\pi\pi^*$ state, an ESIPT should take place in all salicylaldimine derivatives studied. This kind of ESIPT process had already been found experimentally for CH_3. Concerning the excited $n\pi^*$ state, it is stabilized in SiH_3, COH, or NO derivatives. $n\pi^*$ is the second excited state in SiH_3 and COH, whereas it turns out to be the first excited state in NO. This kind of effect has been attributed to favorable resonance effects.

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References

[1] A. Sytnik, J.C. Del Valle, J. Phys. Chem. 99 (1995) 13028.
[2] P.T. Chou, D. McMorrow, T.J. Aartsma, M. Kasha, J. Phys. Chem. 88 (1984) 4596.
[3] D.A. Parthenopoulos, D. McMorrow, M. Kasha, J. Phys. Chem. 95 (1991) 2668.
[4] A.U. Acuña, A. Costela, J.M. Muñoz, J. Phys. Chem. 90 (1986) 2807.
[5] A.U. Acuña, F. Amat, J. Catalán, A. Costela, J.M. Figuera, J.M. Muñoz, Chem. Phys. Lett. 132 (1986) 567.
[6] T. Nishiya, S. Yamauchi, N. Hirota, M. Baba, I. Hanazaki, J. Phys. Chem. 90 (1986) 5730.
[7] P.T. Chou, M.L. Martínez, Radiat. Phys. Chem. 41 (1993) 373.
[8] L.A. Harrah, C.L. Renschler, Nucl. Instrum. Meth. Phys. Rev. 90 (1985) 5730.
[9] M. Forés, M. Duran, M. Solà, Chem. Phys. 234 (1998) 1.
[10] M. Forés, M. Duran, M. Solà, L. Adamowicz, J. Phys. Chem. A 103 (1999) 4413.
[11] M. Forés, S. Scheiner, Chem. Phys. 246 (1999) 65.
[12] A. Grabowska, K. Kownacki, L. Kaczmarek, Acta Phys. Pol. A 88 (1995) 1081.
[13] H. Lee, T. Kitagawa, Bull. Chem. Soc. Jpn. 59 (1986) 2897.
[14] A. Grabowska, K. Kownacki, J. Karpiuk, S. Dobrin, L. Kaczmarek, Chem. Phys. Lett. 267 (1997) 132.
[15] K. Kownacki, A. Mordzinski, R. Wilbrandt, A. Grabowska, Chem. Phys. Lett. 227 (1994) 270.
[16] A. Grabowska, K. Kownacki, L. Kaczmarek, J. Lumin. 60/61 (1994) 886.
[17] D.L. Willians, A. Heller, J. Phys. Chem. 74 (1970) 4473.
[18] A. Mordzinski, A. Grabowska, Chem. Phys. Lett. 90 (1982) 122.
[19] T. Arthen-Engeland, T. Bultmann, N.P. Ernsting, Chem. Phys. 163 (1992) 43.
[20] G.J. Woolfe, M. Melzig, S. Schneider, F. Dörr, Chem. Phys. 77 (1983) 213.
[21] M.A. Ríos, M.C. Ríos, J. Phys. Chem. 99 (1995) 12456.
[22] R.S. Becker, C. Lenoble, A. Zein, J. Phys. Chem. 91 (1987) 3509.
[23] C.A.S. Potter, R.G. Brown, Chem. Phys. Lett. 153 (1988) 7.
[24] H. Sinha, S.K. Dogra, Chem. Phys. 102 (1986) 337.
[25] K.K. Kalnin'sh, D.N. Glebovskii, M.E. Bedrina, E.K. Roschina, J. Struct. Chem. 33 (1992) 636.
[26] K. Das, D. Majumdar, K. Bhattacharyya, Chem. Phys. Lett. 198 (1992) 443.
[27] K. Das, N. Sarkar, A.K. Ghosh, D. Majumdar, D.N. Nath, K. Bhattacharyya, J. Phys. Chem. 98 (1994) 9126.
[28] A. Douhal, F. Amat-Guerri, M.P. Lillo, A.U. Acuña, J. Photochem. Photobiol. A: Chem. 78 (1994) 127.

UNCORRECTED PROOF

[29] M. Mosquera, J.C. Penedo, M.C. Ríos Rodríguez, F. Rodríguez-Prieto, J. Phys. Chem. 100 (1996) 5398.
[30] M. Kondo, Bull. Chem. Soc. Jpn. 51 (1978) 3027.
[31] F. Rodríguez-Prieto, M.C. Ríos Rodríguez, M. Mosquera González, M.A. Ríos, M.A. Fernández, J. Phys. Chem. 98 (1994) 8666.
[32] M. Bräuer, M. Mosquera, J.L. Pérez-Lustres, F. Rodríguez-Prieto, J. Phys. Chem. A 102 (1998) 10736.
[33] P.M. Felker, W.R. Lambert, A.H. Zewail, J. Chem. Phys. 77 (1982) 1603.
[34] J.L. Herek, S. Pedersen, L. Bañares, A.H. Zewail, J. Chem. Phys. 97 (1992) 9046.
[35] A. Douhal, F. Lahmani, A. Zehnacker-Rentien, Chem. Phys. 178 (1993) 493.
[36] E. Bosch, M. Moreno, J.M. Lluch, Chem. Phys. 159 (1992) 99.
[37] A. Douhal, F. Lahmani, A.H. Zewail, Chem. Phys. 207 (1996) 477.
[38] G.S. Denisov, N.S. Golubev, V.M. Schreiber, Sh.S. Shajakhmedov, A.V. Shurukhina, J. Mol. Struct. (Theochem) 436 (1997) 153.
[39] J. Catalán, P. Pérez, F. Fabero, J.F.K. Wilshire, R.M. Claramunt, J. Elguero, J. Am. Chem. Soc. 114 (1992) 964.
[40] M. Forés, M. Duran, M. Solà, M. Orozco, F.J. Luque, J. Phys. Chem. A 103 (1999) 4525.
[41] K.C. Hass, W.F. Schneider, C.M. Estévez, R.D. Bach, Chem. Phys. Lett. 263 (1996) 414.
[42] J.C. Del Valle, J. Catalán, C. Foces-Foces, A.L. Llamas-Saiz, J. Elguero, D. Sanz, J. Dotor, R.M. Claramunt, J. Lumin. 75 (1997) 17.
[43] C. Foces-Foces, A.L. Llamas-Saiz, R.M. Claramunt, P. Cabildo, J. Elguero, J. Mol. Struct. (Theochem) 440 (1998) 193.
[44] I.A.Z. Al-Ansari, J. Lumin. 71 (1997) 83.
[45] F. Lahmani, A. Zehnacker-Rentien, J. Phys. Chem. A 101 (1997) 6141.
[46] P. Borowicz, A. Grabowska, A. Les, L. Kaczmarek, B. Zagrodzki, Chem. Phys. Lett. 291 (1998) 351.
[47] F. Rodríguez-Prieto, J.C. Penedo, M. Mosquera, J. Chem. Soc. Faraday Trans. 94 (1998) 2775.
[48] H.J. Heller, Eur. Polym. J. Suppl. (1969) 105.
[49] J. Catalán, C. Díaz, J. Phys. Chem. A 102 (1998) 323.
[50] J. Catalán, J. Palomar, J.L.G. De Paz, J. Phys. Chem. A 101 (1997) 7914.
[51] S. Scheiner, Acc. Chem. Res. 18 (1985) 174.
[52] M. Kieninger, S. Suhai, Int. J. Quant. Chem. 92 (1994) 465.
[53] J.G.C.M. Van Duijneveldt-van de Rijdt, F.B. Van Duijneveldt, J. Chem. Phys. 97 (1992) 5019.
[54] A. Laforgue, C. Brucena-Grimbert, D. Laforgue-Kantzer, G. Del Re, V. Barone, J. Phys. Chem. 86 (1986) 4436.
[55] V. Barone, C. Adamo, J. Chem. Phys. 105 (1996) 11007.
[56] A.L. Sobolewski, L. Adamowicz, Chem. Phys. 213 (1996) 193.
[57] M. Forés, M. Duran, M. Solà, L. Adamowicz, J. Comp. Chem. 21 (2000) 257.
[58] K. Luth, S. Scheiner, J. Phys. Chem. 98 (1994) 3582.
[59] K. Luth, S. Scheiner, J. Phys. Chem. 99 (1995) 7352.
[60] T.H.J. Dunning Jr., P.J. Hay, in: H.F. Schaefer III (Ed.), Methods of Electronic Structure Theory, vol. 3, Plenum Press, New York, 1977.
[61] J.B. Foresman, M. Head-Gordon, J.A. Pople, M.J. Frisch, J. Phys. Chem. 96 (1992) 135.
[62] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheesman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomerts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94, Revision B.2, Gaussian, Pittsburgh, PA, 1995.
[63] M.C. Rovira, S. Scheiner, J. Phys. Chem. 99 (1995) 9854.
[64] S. Scheiner, T. Kar, M. Cuma, J. Phys. Chem. A 101 (1997) 5901.
[65] M. Cuma, C. Thompsom, S. Scheiner, J. Comp. Chem. 19 (1998) 129.
[66] C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 91 (1991) 165.
[67] R.W. Taft, R.D. Topsom, Prog. Phys. Org. Chem. 16 (1987) 1.
[68] J.P. Foster, F. Weinhold, J. Am. Chem. Soc. 102 (1980) 7211.
[69] A.E. Reed, F. Weinhold, J. Phys. Chem. 83 (1985) 1736.
[70] A.E. Reed, F. Weinhold, R.B. Weinstock, J. Chem. Phys. 83 (1985) 735.
[71] W.F. Schneider, B.I. Nance, T.J. Wallington, J. Am. Chem. Soc. 117 (1995) 478.
[72] F. Grein, P. Delongchamps, Can. J. Chem. 70 (1992) 604.
[73] E.A. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.
[74] D.E. Love, D. Nachligallova, K.D. Jordan, J.M. Lawson, M.N. Paddon-Row, J. Am. Chem. Soc. 118 (1996) 1235.
[75] C.M. Hadad, J.B. Foresman, K.B. Wiberg, J. Phys. Chem. 97 (1993) 4293.
[76] T. Kar, S. Scheiner, M. Cuma, J. Chem. Phys. 111 (1999) 849.

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