Nucleophilicity and electrophilicity of silylenes from a molecular electrostatic potential and dual descriptor perspectives

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ABSTRACT

Nucleophilicity and elecrophilicity of mono and disubstituted silylenes are analyzed using the molecular electrostatic potential and the dual descriptor $\Delta f(\vec{r})$, defined within the so called conceptual DFT. A set of 32 compounds has been chosen which can be classified into 4 groups or families based on a linear relationship between the molecular electrostatic potential measured in the electrophilic (empty $3p_z$ orbital) V_A and nucleophilic (lone pair) V_{min} regions around of the silicon atom. The electrophilic and nucleophilic character of silylenes given by $|V_A - V_{min}|$ is connected to the orbital-resolved dual descriptor Δf_{3p_z} through the π-electron donating property of the substituent.

1. Introduction

Silylenes, RR′Si, are divalent silicon species analogous to carbenes. Most of them are only known as reactive intermediates in thermal and photochemical reactions. Their existence has been proved by forming adducts with trapping agents while in recent years several stable species have been isolated [1–3]. In general, silylenes prefer a singlet configuration in their ground state. Several factors associated to the stabilization of singlet ground state silylenes are well-known, the π-electron donating ability from the substituent to the formally empty $3p_z$ orbital of silicon being the most important one. Other factors are the aromaticity, and ring stress in the case of cyclic compounds [4–7].

The reactivity and stability patterns of silylenes have been studied intensively, both experimentally and theoretically [1–10]. These aspects are strongly related: unstable silylenes show a strong electrophilic character whereas the stable species are highly nucleophilic. The most reactive center, in both cases, corresponds to the silicon atom. As can be seen from Scheme 1, singlet silylenes present two characteristic regions: region **A** corresponds to the empty $3p_z$ orbital of the silicon atom, which is perpendicular to the molecular plane and responsible for the electrophilic character of these compounds. In region **B** a lone pair of electrons is localized in a σ-orbital which accounts for the nucleophilic character of the singlet silylenes. It has been shown that substituents with π-electron donating properties like –NH$_2$, –SH, and –OH groups confer stability to the silicon center favouring the singlet electronic state.

The particular situation that in silylenes electrophilic and nucleophilic regions are localized on the same atom, but in different directions incited various researchers to explore the merits of electrophilicity and nucleophilicity descriptors, traditionally used to differentiate between parts of molecular systems located on different atoms, to describe this 'one center' problem. In this context, some of the present authors have established a unified picture between reactivity indices and stability for silylenes in their ground states as a function of the π-electron donating ability of the substituent (see Scheme 4 in Ref. [11]). Density Functional Theory (DFT)-based reactivity descriptors were used in conjunction with the molecular electrostatic potential ($V(\vec{r})$) as measures of chemical reactivity, whereas the reaction enthalpy for isodesmic reaction (RR′Si + SiH$_4$ → RR′SiH$_2$ + H$_2$Si), the dimerization energy (RR′Si + RR′Si → RR′Si=SiRR′), and the singlet–triplet energy difference were used as measures of stability.

An interesting result from this study is a connection of electrophilicity and nucleophilicity with the $3p_z$ electron population of the silicon atom governed by the π-donating character of the substituents: increasing π-electron donating capability of the substituents increases the population of the $3p_z$ orbital of the Si atom which is reflected in a less positive electrostatic potential in region **A** yielding a lower electrophilicity. On the other hand, a diminishing electrophilic power is accompanied by an increasing nucleophilicity in the lone pair region possibly associated with an electron delocalization effect between the $3p_z$ and σ orbitals of Si atom.

In the present Letter we elaborate on this remarkable property of silylenes probing the different reactivity in different directions on a single center through a combined use of the molecular electrostatic potential and conceptual DFT based descriptors.

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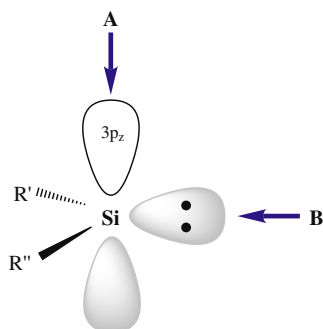
Scheme 1. Definition of electrophilic (A) and nucleophilic (B) regions around the silicon atom in silylenes.

The molecular electrostatic potential (MEP) originally invoked to study electrophilic reactivity [12], later on nucleophilic [13] has also been successfully correlated which a variety of atomic and molecular properties such as energy, covalent and ionic radii and electronegativity [14–17]. In this context, it is interesting to mention the complementarity between the electrostatic potential and the local ionization potential to analyze and predict the reactive behavior of a molecular system [18]. Moreover, some of the present authors have recently proposed a plausible link between the local ionization potential with the Fukui function showing that both local properties convey similar information concerning some aspect of the reactive behavior within a molecular system [19]. Of primary importance however here is that its topography has been widely used for the characterization of reactive regions for electro-

philic and nucleophilic ones within a molecular system [20,21], in the case of charge controlled reactions.

The Fukui function ($f(\vec{r})$), defined in the so called conceptual DFT, turns out to be a relevant reactivity descriptor when some degree of charge transfer or orbital overlap is involved either for an electrophilic ($f^-(\vec{r})$) or nucleophilic ($f^+(\vec{r})$) attack. Conceptual DFT provides sharp definitions of a set of global, local, and non-local energy derivatives as reactivity descriptors, which can be interpreted as the response of the total energy when the number of electrons N and/or external potential $\upsilon(\vec{r})$ are altered. They have been applied in different subfields of chemistry to gain understanding on the reactive behavior of atoms, molecules, clusters, surface, etc. [22–25]. Recently Morell et al. [26,27] concentrated on the N-derivative of the Fukui function $\left(\frac{\partial f(\vec{r})}{\partial N}\right)$ the dual descriptor $\Delta f(\vec{r})$. It was shown that it contains information about the susceptibility for both electrophilic and nucleophilic attacks of various parts within a molecule. It has been successfully applied in the study of aromatic electrophilic substitution reactions, in investigations of the stereoselectivity in the Dunitz–Burgi attack of carbonyl compounds [26], and lately in reformulating the Woodward–Hoffmann rules in an orbital free context [28,29].

Both $V(\vec{r})$ and $\Delta f(\vec{r})$ are one-shot tools where both electrophilic and nucleophilic regions in a molecular regions can be identified. In general, the electrostatic potential and the dual descriptor complement each other quite effectively for processes that involve electrophilic and nucleophilic attack, in the sense that the former describes the charge control whereas the second describes the orbital controlled aspects of the reactive attack. In the present study the capability of the dual descriptor in describing single center regioselectivity is investigated for the first time. A combined perspective is given through simultaneous use of the molecular
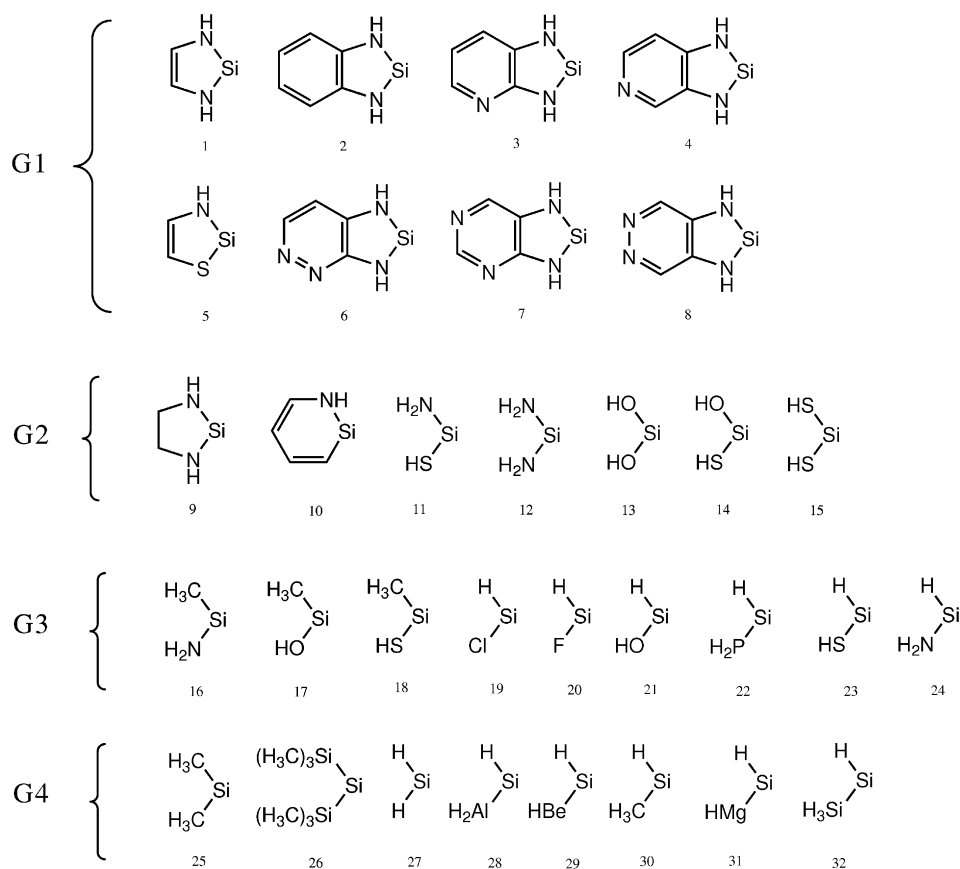
Scheme 2. Set of silylenes studied.

electrostatic potential and the dual descriptor. For this purpose a set of 32 mono- and disubstituted silylenes in their singlet ground state is considered with different π-electron donating and accepting character and electronegativity (see Scheme 2).

2. Theoretical background

The Fukui function, $f(\vec{r})$ was introduced by Parr and Yang as the derivative of the chemical potential (μ) with respect to the external potential, or equivalently as the derivative of the total electron density $\rho(\vec{r})$ upon a changes in the total number of electrons [30]:

$$f(\vec{r}) = \left(\frac{\delta\mu}{\delta\upsilon(\vec{r})} \right)_N = \left(\frac{\partial\rho(\vec{r})}{\partial N} \right)_{\upsilon(\vec{r})}. \tag{1}$$

Due to the discontinuity of the derivative on the right-hand of Eq. (1) at an integer value of N, three $f(\vec{r})$ can be defined at the point $\vec{r}$: $f^+(\vec{r})$, $f^-(\vec{r})$, and $f^0(\vec{r})$ which governing the nucleophilic, electrophilic, and radical attacks, respectively. These functions can be condensed on atoms or functional groups, k. In this sense, a scheme based on the finite difference approximation and population analysis was proposed by Yang and Mortier [31]:

$$f_k^+ \approx [N_k(N+1) - N_k(N)],$$
$$f_k^- \approx [N_k(N) - N_k(N-1)], \tag{2}$$

where N_k corresponds to the electronic population on the site k for the systems with $(N-1), (N)$, and $(N+1)$-electrons evaluated at the same geometry with N-electron system.

The Dual Descriptor, $\Delta f(\vec{r})$ was recently defined by Morell et al. [26,27] in term of the variation of chemical hardness (η) with respect to the external potential or through the Maxwell relation as the variation of the $f(\vec{r})$ upon a changes in the total number of electrons:

$$\Delta f(\vec{r}) = \left(\frac{\delta\eta}{\delta\upsilon(\vec{r})} \right)_N = \left(\frac{\partial f(\vec{r})}{\partial N} \right)_{\upsilon(\vec{r})}. \tag{3}$$

Using the well-known finite difference approximation, $\Delta f(\vec{r})$ can be written as the difference between nucleophilic and electrophilic Fukui functions:

$$\Delta f(\vec{r}) \approx f^+(\vec{r}) - f^-(\vec{r}). \tag{4}$$

Eq. (4) nicely shows why the dual descriptor allows to identify simultaneously the nucleophilic and electrophilic regions within a molecule. $\Delta f(\vec{r}) > 0$ at the point $\vec{r}$ implies that the site is more favourable for a nucleophilic attack, whereas for $\Delta f(\vec{r}) < 0$ the electrophilic attack is favoured. Therefore, positive values of Δf_k define electrophilic regions within a molecular system whereas negative values will define the nucleophilic regions, and a favourable chemical event occurs when electron accepting regions ($\Delta f(\vec{r}) > 0$) are aligned with electron donating regions ($\Delta f(\vec{r}) < 0$).

The Molecular Electrostatic Potential, $V(\vec{r})$ that is created at a point $\vec{r}$ by electrons and nuclei of a molecules is given as:

$$V(\vec{r}) = \sum_A \frac{Z_A}{|R_A - \vec{r}|} - \int \frac{\rho(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r} \tag{5}$$

where Z_A is the charge on nucleus A, located at R_A, and $\rho(\vec{r}')$ is the molecule's electron density. The projection of MEP onto an electronic isodensity molecular surface, $V_S(\vec{r})$, is particularly useful in the interpretation of a molecule's reactive behavior. The most negative values of the surface, which are known as the local minima $V_{S,min}(\vec{r})$, are associated with the lone pairs of electronegative atoms and the π-electrons of unsaturated hydrocarbons. While the most positive values $V_{S,max}(\vec{r})$ are localized close to hydrogen atoms bonded to electronegative atoms [20,21,18]. On the other hand, a significantly positive electrostatic potential on the outer side of

covalently bonded atoms from group V–VII has been recently observed by Politzer and collaborators [32,33].

3. Computational details

For the series of compounds given in Scheme 2 geometry optimizations and frequency calculations were done using the GAUSSIAN03 program [34] at DFT level with the hybrid B3LYP functional [35,36] combined with a split-valence triple-zeta plus diffuse and polarization basis set, 6-311+G** [37,38].

The electronic populations N_k to compute the Fukui indices as indicated by Eq. (2) used to calculate the dual descriptor were obtained by the natural population analysis (NPA) [39] at the same level of theory using the NBO program implemented in GAUSSIAN03.

The molecular electrostatic potential was computed in regions **A** (V_A) at 2 Å from the Si atom perpendicular to the molecular plane of the silylenes whereas in region **B**, corresponding to the lone pair region of the silicon, the minimum of the electrostatic potential (V_{min}) was determined.

4. Results and discussion

The values of molecular electrostatic potential calculated in both regions **A** and **B**, V_A and V_{min}, the condensed Fukui functions on the silicon atom, f_{Si}^+ and f_{Si}^-, and the corresponding dual descriptor, Δf_{Si}, are collected in Table 1. In the following paragraphs we will investigate in the first part the relationship between nucleophilic and electrophilic character of silylenes based on the MEP and accordingly classify the set of 32 compounds in four distinct

Table 1
Molecular electrostatic potential calculated at the point **A** (V_A) and **B** (V_{min}) as displayed in Scheme 1. Silicon condensed Fukui functions, f_{Si}^+ and f_{Si}^-, and the dual descriptor, Δf_{Si}. The MEP values are given in au.

System	R	R'	V_A	V_{min}	f_{Si}^+	f_{Si}^-	Δf_{Si}
1			0.004	−0.037	0.746	0.335	0.411
2			0.017	−0.030	0.639	0.247	0.392
3			0.024	−0.025	0.596	0.243	0.352
4			0.028	−0.021	0.642	0.237	0.405
5			0.019	−0.024	0.650	0.310	0.340
6			0.037	−0.014	0.584	0.183	0.401
7			0.035	−0.016	0.607	0.281	0.326
8			0.039	−0.012	0.652	0.165	0.486
9			0.013	0.043	0.793	0.227	0.565
10			0.013	−0.048	0.523	0.596	−0.072
11	−NH$_2$	−SH	0.025	−0.025	0.703	0.543	0.160
12	−NH$_2$	−NH$_2$	0.013	−0.047	0.807	0.710	0.097
13	−OH	−OH	0.039	−0.020	0.867	0.675	0.192
14	−OH	−SH	0.043	−0.015	0.752	0.530	0.222
15	−SH	−SH	0.043	−0.010	0.662	0.466	0.195
16	−NH$_2$	−CH$_3$	0.029	−0.050	0.779	0.626	0.153
17	−OH	−CH$_3$	0.045	−0.036	0.824	0.603	0.220
18	−SH	−CH$_3$	0.047	−0.030	0.728	0.530	0.199
19	−H	−Cl	0.068	−0.014	0.858	0.513	0.345
20	−H	−F	0.069	−0.016	0.954	0.622	0.332
21	−H	−OH	0.052	−0.029	0.915	0.630	0.285
22	−H	−PH$_2$	0.052	−0.028	0.772	0.484	0.287
23	−H	−SH	0.051	−0.027	0.784	0.551	0.233
24	−H	−NH$_2$	0.033	−0.043	0.857	0.653	0.204
25	−CH$_3$	−CH$_3$	0.053	−0.0496	0.816	0.628	0.188
26	−Si(CH$_3$)$_3$	−Si(CH$_3$)$_3$	0.058	−0.046	0.765	0.518	0.247
27	−H	−H	0.069	−0.033	1.032	0.725	0.307
28	−H	−AlH$_2$	0.067	−0.030	0.870	0.591	0.279
29	−H	−BeH	0.069	−0.039	0.927	0.749	0.178
30	−H	−CH$_3$	0.060	−0.042	0.912	0.653	0.259
31	−H	−MgH	0.067	−0.04	0.856	0.666	0.190
32	−H	SiH$_3$	0.071	−0.028	0.863	0.583	0.280
33	−CF$_3$	−CF$_3$	0.094	–	0.894	0.552	0.342
34	−Cl	−Cl	0.068	–	0.751	0.444	0.307
35	−F	−F	0.068	–	0.918	0.717	0.202

groups. In a second part the connection between the molecular electrostatic potential and the dual descriptor of the Si atom and its orbital component will be given.

4.1. Relation between nucleophilicity and electrophilicity based on $V(\vec{r})$

In Fig. 1 V_{min} is plotted against V_A for all silylenes. V_{min} is related to the lone pair region in Scheme 1. These values are conjectured to be indicative of the σ-donor property of the substituent whereas V_A is related to the formally empty $3p_z$ orbital of Si atom. A less positive value can be interpreted as a measure of the electronic population of the $3p_z$ orbital due to the π-electron donating character of the substituent. On the other hand, notice that the range of V_A is slightly greater than of V_{min} which suggests that upon variation of a substituent the σ-donor property possibly plays a smaller role than the π-electron donor character in determining the variation of reactivity.

On the basis of our analysis we can classify all silylenes whose molecular structures are shown in Scheme 2 into 4 groups or families as displayed in Fig. 1. The first group (**G1**) is formed by cyclic and annellated silylenes; **G2** is formed by 2 cyclic and simple –OH, –NH$_2$, and –SH disubstituted compounds; **G3** includes RR′Si systems where R = –CH$_3$, –H and R′ = –NH$_2$, –OH, –SH, –Cl, –F, and –PH$_2$; **G4** is formed by molecules where R = –CH$_3$, –Si(CH$_3$)$_3$, –H, and R′ = –CH$_3$, –Si(CH$_3$)$_3$, –H, –AlH$_2$, –BeH, –MgH, and –SiH$_3$. Notice that **G1** and **G2** are characterized by the presence of a lone pair of electrons in both Si neighbour atoms whereas the systems included in **G3** only one of the neighbour atoms contains a lone pair and in **G4** the neighbour atoms do not contain a lone pair of electrons and some of the substituents are more electropositive while other present an inductive effect donor. Although the classification of two cyclic compound (**9** and **10**) in **G2** might be not evident (see Fig. 1) the criterion of structural similarity was combined with that of the best correlation coefficient to make a final judgement. For each family a good linear relationship between V_{min} and V_A was found (the correlation coefficient is equal to 0.98 for the first three

groups and 0.88 for **G4**), which allows to find a connection between the electrophilic and nucleophilic character of the silylenes in accordance with the π- and σ-electron donating ability of the substituent in each group. As can be seen the presence of strong π-donor substituents like –NH$_2$, –OH, –SH (especially in **G1** and **G2**) will increase the electronic population of the $3p_z$ orbital in the Si atom and consequently the electrophilic character of silylenes will decrease whereas a σ-donor substituent like –CH$_3$ (for instance, the system **16** in **G3** and **25** in **G4**) increases the nucleophilic character of the silylenes as can be seen in Fig. 1. However in these families the electrophilic character is also increased, indicating that the electrophilic/nucleophilic character of silylenes is determined by the electron population of the $3p_z$ orbital. To put it in other words, the reactivity can be modulated by the electron population of the $3p_z$ orbital.

4.2. Dual descriptor, $\Delta f(\vec{r})$

For some representative silylenes, the extreme and middle members of each family defined in Fig. 1, a $\Delta f(\vec{r})$ map was computed as displayed in Fig. 2. These were obtained from the frontier molecular orbital densities differences. The dual descriptor can indeed be approximately written as: $\Delta f(\vec{r}) \approx \rho(\vec{r})_{LUMO} - \rho(\vec{r})_{HOMO}$ (frozen core approximation) [26,27]. These molecular surfaces allow us to confirm that the reactive region both for a nucleophilic and an electrophilic attack is centered on the silicon atom where the electrophilic activity is controlled by the formally empty $3p_z$ orbital (region **A** in Scheme 1) whereas the nucleophilicity is driven by the lone pair of electrons (region **B** in Scheme 1). It is interesting to note in these maps the quick evolution of the lone pair region (in blue) from **G1** to **G2**, whereas in the two other families its topography is nearly constant. The condensed values reported in Table 1 show that $\Delta f_{Si} > 0$, except in system **10** where it is slightly negative, suggesting that the electrophilic proclivity dominates over the nucleophilic proclivity in the set of silylenes studied. Notice that –NH$_2$, –OH, and –SH type disubstituted compounds (see **G2** in Table 1) show the lowest values of Δf_{Si} suggesting that the elec-
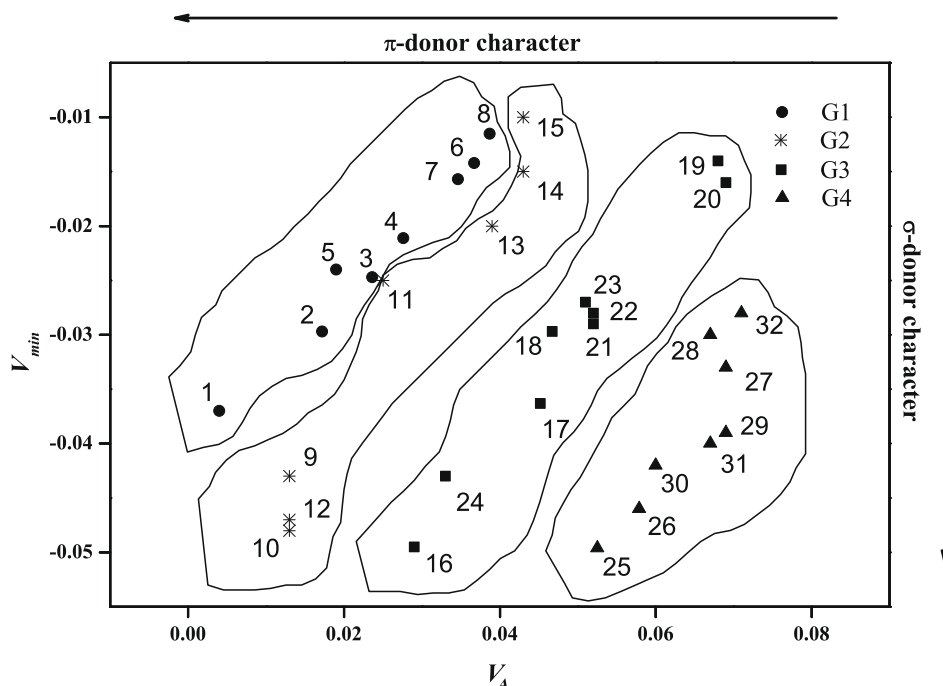

Fig. 1. Relationship between the minimum of the molecular electrostatic potential calculated in the lone pair region (V_{min}) of silylenes vs the molecular electrostatic potential in the region of the empty orbital of the silicon atom.

trophilic proclivity is decreasing and the nucleophilic proclivity is increasing with respect to other substituents. This is an indication that these silylenes turn out to be ambiphilic as was pointed out recently by Oláh et al. [11].

It has widely been accepted that $V(\vec{r})$ values provide information about the regions where an electrophile or nucleophile is likely to approach whereas the Fukui functions, $f^-(\vec{r})$ and $f^+(\vec{r})$, carry information on the tendency for electronic rearrangement in those regions in the case of the electrophilic attack or nucleophilic

attack. In this context, we have tried to find the connection between the dual descriptor of the Si atom with a similar descriptor based on the $V(\vec{r})$ values. This latter has been defined following Eq. 4 where the reactivity upon a nucleophilic attack is measured with respect to the reactivity upon an electrophilic attack, i.e. $|V_A - V_{min}|$. As can be seen in Fig. 3 when Δf_{Si} is plotted vs $|V_A - V_{min}|$ it is not possible to find a clear-cut relationship between both descriptors because we tried to find a link between a descriptor computed in different directions of one center, $|V_A - V_{min}|$, with
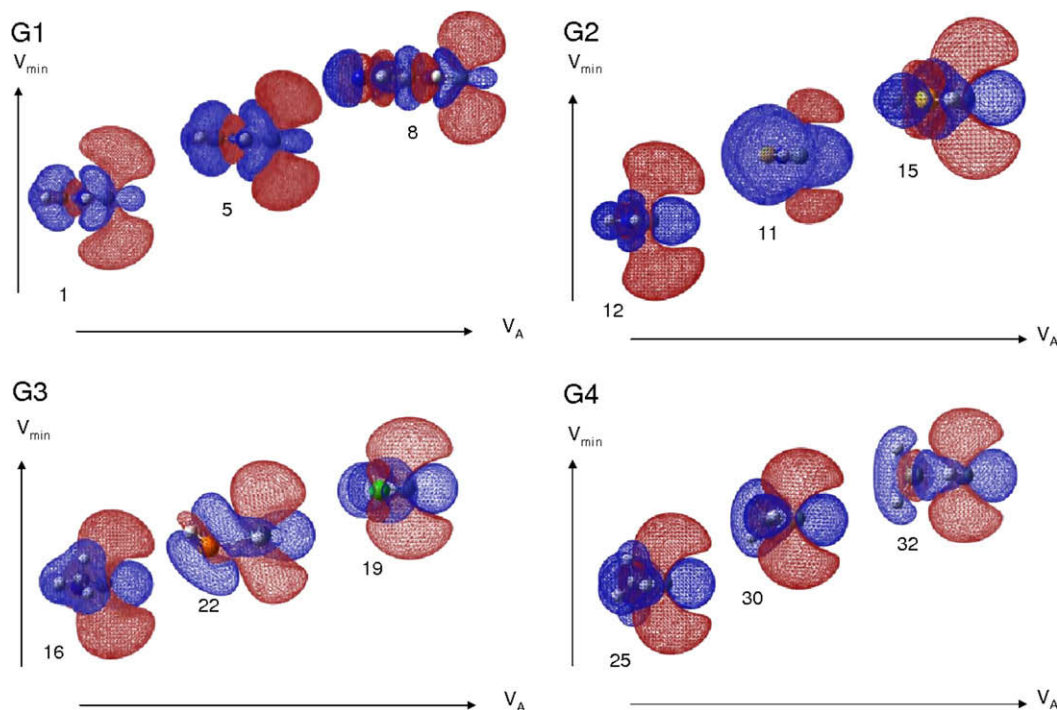

Fig. 2. $\Delta f(\vec{r})$ map for silylenes of each family (compound numbering according to Scheme 2). Electrophilic regions ($\Delta f(\vec{r}) > 0$) are indicated in red and the nucleophilic regions ($\Delta f(\vec{r}) > 0$) are given in blue.
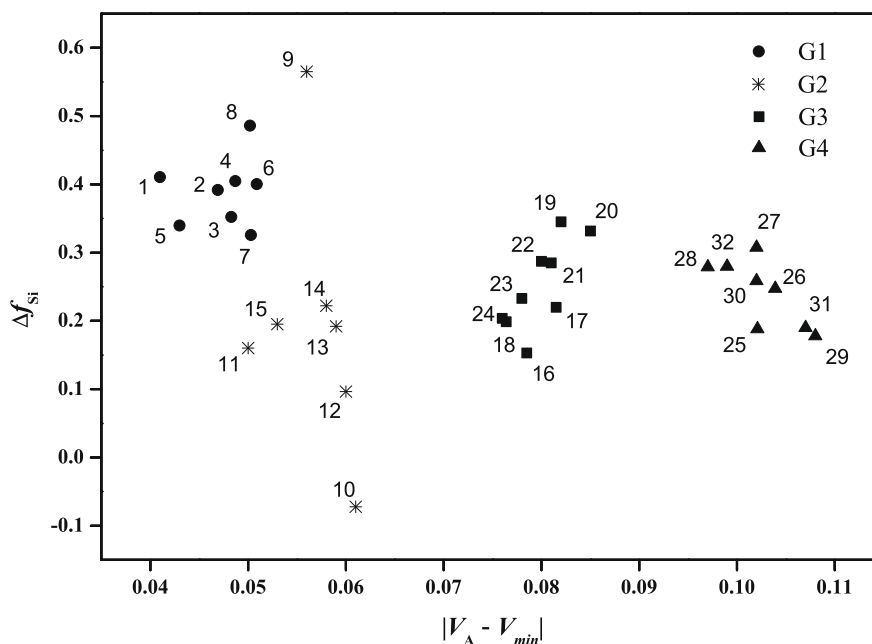

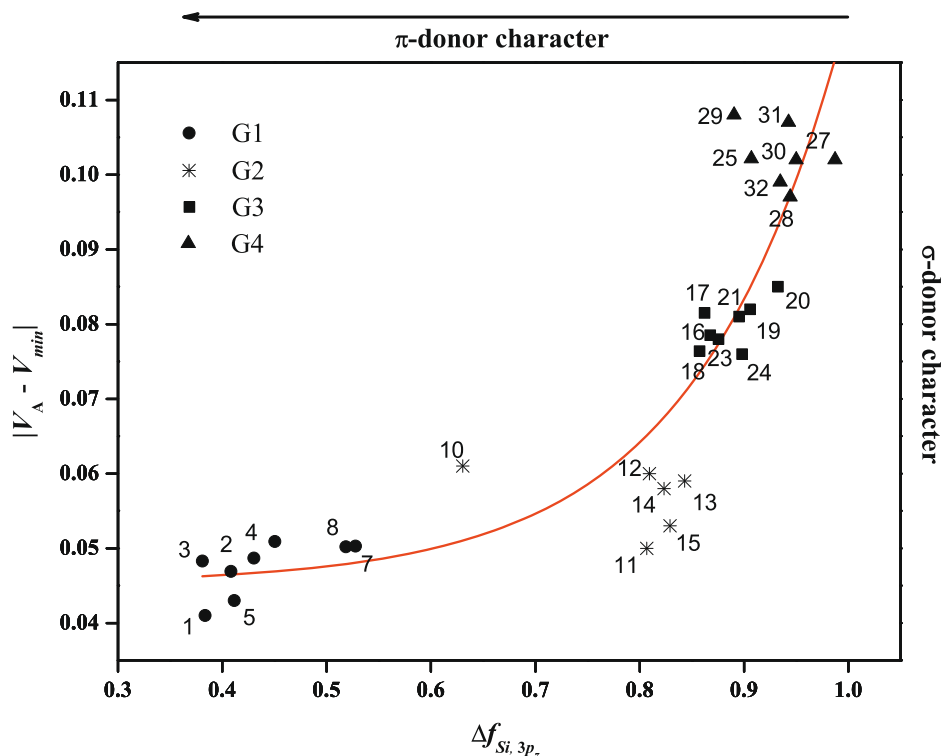**Fig. 3.** Si dual descriptor against $|V_A - V_{min}|$ for the complete set of silylenes.

Fig. 4. $|V_A - V_{min}|$ connection with $3p_z$ orbital-resolved dual descriptor, $\Delta f_{Si,3p_z}$.

one that contains the information around every direction of one center, Δf_{Si}. However, the different groups previously defined can be identified.

4.3. Relationship between electrophilicity and nucleophilicity $|V_A - V_{min}|$ with orbital-resolved dual descriptor $\Delta f_{Si,3p_z}$

Considering the fact that the reactivity of silylenes is controlled by the $3p_z$ orbital of Si atom, we introduce and define the orbital dual descriptor as:

$$\Delta f_{Si,3p_z} \equiv f^+_{Si,3p_z} - f^-_{Si,3p_z}. \tag{6}$$

Using the finite difference approximation, $\Delta f_{Si,3p_z}$ can be written as:

$$\Delta f_{Si,3p_z} = [N_{Si,3p_z}(N+1) - N_{Si,3p_z}(N)] - [N_{Si,3p_z}(N) - N_{Si,3p_z}(N-1)]. \tag{7}$$

From Eq. (7) it is possible to analyze the silylenes which are substituted by π-electron donors. For a π-electron poor donor a high value of $|V_A - V_{min}|$ is observed (see Fig. 3), concomitantly the $3p_z$ orbital electronic populations are expected to be close to 1 for the $(N+1)$-electron system and close to 0 for both the (N)- and $(N-1)$-electron systems. Therefore in this limit one expects that $\Delta f_{3p_z} \to 1$. For a π-electron rich donor it is seen that the magnitude of $|V_A - V_{min}|$ is smaller than in the previous situation and the orbital electron populations are not easy to predict. However, in the limit it can be expected that it is higher than 1 for the $(N+1)$-system, close to 1 for the (N)–system, and higher than 0 for the $(N-1)$-electron system. Therefore in the limit of a very strong π-electron donor substituent it can be expected that $\Delta f_{3p_z} \to 0$.

We have plotted in Fig. 4 the orbital dual descriptor Δf_{3p_z} vs. $|V_A - V_{min}|$ for the set of silylenes. Notice that a nice relation is found which is agreement with the previous discussion presenting further evidence that the $3p_z$ orbital electronic population is controlling the reactivity in this type of compounds.

5. Concluding remarks

In this study, we have carried out an analysis of the nucleophilic and electrophilic character of silylenes in terms of the molecular electrostatic potential and the dual descriptor and its orbital-resolved form introduced here in a set of 32 compounds. A linear relationship between the molecular electrostatic potentials measured in the region of the $3p_z$ orbital (V_A) and the σ lone pair (V_{min}) was found, which allows us to classify the set considered into 4 families or groups, as well as to find an inverse relation between the nucleophilic and electrophilic character of silylenes. Finally, we have found a relation between the orbital dual descriptor Δf_{3p_z} and $|V_A - V_{min}|$ illustrating the key role played by the $3p_z$ orbital in the in balance of electrophilic and nucleophilic reactivity in different directions from a single center, the Si atom.

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