

# Understanding the chemical reactivity of phenylhalocarbene systems: an analysis based on the spin-polarized density functional theory

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**Abstract** Global and local indices based on the spin-polarized density functional theory (SP-DFT) have been used to rationalize the philicity power and spin polarization pattern of a family of singlet substituted phenylhalocarbenes, (*p*YPhXC, Y = –NO<sub>2</sub>, –CN, –CHO, –F, –H, –CH<sub>3</sub>, –OH, –OCH<sub>3</sub>, –NH<sub>2</sub>; X = –F, –Cl, –Br). The local reactivity may be traced out by the simple condensed-to-atoms model for the SP-DFT Fukui functions, namely  $f_{NS,k}^+$  and  $f_{SS,k}^+$ . For the addition of some singlet phenylhalocarbenes on tetramethylethylene a linear correlation among the global ( $\omega_N$ ) and local electrophilicity index ( $\omega_{N,C}$ ), and the observed rate constants were found. This result supports a mechanistic model where the carbene adds to the olefin in a single step that is controlled by the carbene electrophilicity. These results emphasize the usefulness of general SP-DFT philicities in the rationalization of chemical reactivity at initial stages of reactions that could involve both charge transfer and spin polarization processes.

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## 1 Introduction

Density functional theory [1] (DFT) is a well-established tool to rationalize chemical reactivity [2]. Properties such as chemical potential [3], chemical hardness [4] and the Fukui function [5], allowing us to gain deep insights into the nature of chemical reactions, can be obtained on a ground theoretical basis. In addition, these properties have been related to well-known fundamental chemical concepts (like electronegativity, softness and hardness) and to empirical rules such as the hard and soft acids and bases (HSAB) [6–8] and the maximum hardness (MHP) [9,10] principles, providing a fruitful framework for the exploration of a theory of chemical reactivity. Within the context of an unified treatment of chemical reactivity and selectivity of systems, a generalized *philicity* index has been introduced by Chattaraj et al. [11]. The electrophilicity models of Parr et al. [12] and the Fukui function [5] were used to define such philicity descriptor, containing information about electrophilic, nucleophilic and radical reactive proclivities [11]. A regional philicity index has been tested for some systems in both gas and solution phases [13,14], intermolecular reactivity trends in carbonyl carbon systems [15], adsorption of small molecules in zeolites [16] and toxicity of chlorinated benzenes [17]. Roy et al. [18,19] have claimed, however, about the reliability of local and global electrophilicity descriptors, including the unified *philicity* index defined by Chattaraj et al. [11]. They have proposed [18,19] that such a *philicity* index is a better intermolecular reactivity

descriptor than an intramolecular one, claiming that relative electrophilicity and nucleophilicity descriptors are the most reliable intramolecular reactivity indices [20]. Relative electrophilicity ( $s_k^+/s_k^-$ ) and relative nucleophilicity ( $s_k^-/s_k^+$ ) introduced by Roy et al. [21] are defined in terms of electrophilic and nucleophilic softness and have been applied only to those sites presenting comparable and higher values of  $s_k^+$  and  $s_k^-$ . It is worth to mention that these relative local descriptors are not properly normalizable. In this sense these descriptors are less general than the local electrophilicity model introduced by Pérez et al. [22], which considers that the maximum electrophilicity power within molecules will be located at the softest site of the system. Additionally, a detailed discussion associated with the philicity concept and a clear demonstration that this concept is a better intermolecular reactivity descriptor than the relative nucleo(electro)philicity has been recently introduced [23]. On the other hand, Ayers et al. [24,25] have emphasized the perturbative nature of DFT chemical reactivity indices (i.e., responses of a system to a certain perturbation), focusing on global descriptors such as electrophilicity, nucleofugality and electrofugality [24,25] as well as its local counterparts applied to the study of regioselectivity. Recently, the nature of the electrophilicity concept provided by Parr et al. [12] and its wide range of applicability and predictive capacity has been reviewed by Chattaraj et al. [26]. These authors have stressed that electrophilicity contains information about structural, reactivity and selectivity patterns of many electron systems in both ground and excited electronic states [26]. Note, however, that a proper treatment of excited states is more complex within DFT because such a functional does not exist for all these states [27]. A discussion about the kinetic or thermodynamic character of such a concept can be explored in Ref. [28]. It must be appreciated that the Hohenberg–Kohn has been proven for certain classes of excited states only, i.e., for a lowest energetic state of a given symmetry and for ensemble of states with less than 50% contribution from the excited states [29].

Many chemical processes involve, however, transitions between two or more electronic states of different spin multiplicities. Understanding these mechanistic routes is of great interest from both a practical and a fundamental point of view as recently illustrated by Poli and Harvey [30] in the study of spin forbidden reactions in organometallic complexes, [31–37] and also in several chemical transformations in inorganic [38–48] and organic [49–53] chemistry. Exemplifying this type of reactivity proclivities, the divalent derivatives of carbon, carbenes, are for the most part, fleeting intermediates [54–56]. In the last 15 years, our understanding

of carbene chemistry has advanced dramatically [54] and more insights have also been gained for typical carbene reactivity, such as dimerization [57] and cyclopropanation [58]. The chemistry of these reactive intermediates has had an important role to a modern mechanistic and quantitative understanding of organic chemistry.

The factors governing chemical reactivity of carbene toward the addition reaction to a double bond remain the subject of fascinating discussions in the literature [59–69], and in particular, the addition to alkenes represents one of the most commonly investigated reactions of singlet carbenes and has been widely used for the synthesis of cyclopropanes [7]. The formation of two new  $\sigma$ -bonds proceeds via a concerted yet asynchronous pathway in which the carbene approaches the olefin in an asymmetric fashion [61–69]. Several studies using DFT and MP2 calculations support this asymmetric geometry for singlet addition [61–69] with the participation of the triplet electronic state [70]. From an experimental perspective, seminal experimental studies of Moss [71–73] about singlet carbenes (CXY) based on a kinetic model [70] and the frontier molecular orbital (FMO) were extensively applied in order to rationalize the selectivities presented in the addition of singlet CXY on ethylene to yield cyclopropanes. These studies allow classifying, within a unique scale also denominated philicity [71–75], the reactive nature of simple carbenes as electrophilic, nucleophilic and ambiphilic.

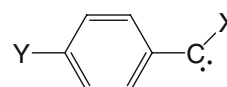
The divalent carbon atom of carbenes has only six electrons in its valence shell. Four of them are used to make  $\sigma$ -bonds with two substituents while two non-bonding electrons remain, and the ground state could be attained in a singlet or a triplet electronic state. The final spin multiplicity of the carbenes depends on the substituents bound to the carbenic atom [55,56]. In the 1980s, the phenylhalocarbenes (PhXC; X = F, Cl, Br) offered the advantage of determining the absolute rate constants for singlet arylcarbene/alkene addition reaction by nanosecond laser flash photolysis [76–79]. The singlet PhXCs are obtained by photolyzing under suitable conditions the corresponding diaziridines [77–80]. Recently, Sawaki et al. [81] have studied the oxygenation of singlet phenylhalocarbenes. These authors estimated the energy difference between the singlet and triplet states under the hypothesis of a singlet ground state of the PhXC equilibrated with its triplet state [81].

In the context of a fundamental theory to explain the reactivity pattern of carbene systems, involving both charge transfer and spin-polarization processes, the spin-polarized density functional theory (SP-DFT) provides a suitable and general framework to discuss chemical reactivity given an explicit consideration of both

electron and spin density. Galván and co-workers [82–85] have first presented a general treatment of chemical reactivity within a SP-DFT framework based on global and local electronic chemical reactivity descriptors. Global indices (i.e., describing global responses of a system to global perturbations) have been used to describe atomic systems [83], the chemical binding of homonuclear and simple heteronuclear polyatomic molecules [86], the charge redistribution between states of different multiplicities and the stability of half-filled shells in atoms [84] and the singlet-triplet gap in simple halocarbenes [85]. A comprehensive revision of these initial applications is available [86]. Recently, hardness and softness kernels have been introduced within SP-DFT [88,89] completing the hierarchy of reactivity descriptors and providing a formal framework. Recent applications of the SP-DFT descriptors have focused on the regioselectivity study of ring closures on alkyl and acyl substituted radicals [90], the hydrogenation reaction of the succinimidyl radical and the Bergman cyclization process [91], and the analysis of spin forbidden 1,2-cycloadditions of triplet methylene to ethylenes to form cyclopropanes, within the so-called two state reactivity model [70]. In addition, an extension of the nuclear reactivity descriptors within the SP-DFT framework has been discussed [92,93]. It has also presented an implementation of the generalized local Fukui functions within a condensed-to-atoms scheme, illustrating the usefulness of such a procedure for nitric oxide and some simple carbenes [93]. The conceptual implications of generalized philicities within such a SP-DFT framework have been discussed in detail [87].

Within an ongoing research concerning further exploring of a chemical reactivity theory based on SP-DFT, in the present work, and in order to explore computationally our model of global and local SP-DFT reactivity descriptors [86–88] we will study the electrophilicity patterns and spin polarization properties of a series of para-substituted phenylhalocarbenes, pYPhCX, above described (see Scheme 1). These systems represent a benchmark to test and discuss the performance of such SP-DFT descriptors [95] in dealing with spin polarization and substituent effects at the para-position of the aromatic ring and the halogen atom on the carbenic center. To contribute to a complete understanding of the addition of some pYPhCX species to alkenes, such as tetramethylethylene, we have also calculated the activation free energies for comparing with experimental results [78].

This work is organized as follows: theoretical model and computational details are summarized in Sect. 2 and 3, respectively. In Sect. 4, the results are reported, analyzed and discussed comparing with previous



X = F, Cl, Br

Y = NH<sub>2</sub>, OH, OCH<sub>3</sub>, CH<sub>3</sub>, F, H, CN, CHO, NO<sub>2</sub>

**Scheme 1** Phenylhalocarbenes systems studied in the present work

experimental works. The main conclusions are given in Sect. 5.

## 2 Theoretical background

Constrained philicities have been recently explored into a SP-DFT framework, extending the conceptual usefulness of the electrophilicity  $\omega$  index introduced first by Parr et al. [12]. A constrained electrophilicity (i.e., to constant spin number  $N_S$ ) have been defined as [95],

$$\omega_N \equiv \frac{(\mu_N)^2}{2\eta_{NN}} \quad (1)$$

where  $\mu_N$  and  $\eta_{NN}$  correspond to the constrained chemical potential and hardness [95].  $\omega_N$  measures the initial capability of a system to acquire electronic charge from the environment at constant spin number. In addition, the conceptual meaning of the previously defined spin-philicity  $\omega_S^+$  and spin-donicity  $\omega_S^-$ , descriptors [96,97] has been further clarified as a philicity measured of a given system to experience spin-polarization [95],

$$\omega_S^\pm \equiv \frac{(\mu_S^\pm)^2}{2\eta_{SS}} \quad (2)$$

where  $\mu_S$  and  $\eta_{SS}$  correspond to the spin potential and spin hardness, respectively [81]. In fact, the quantities in Eq. (2) have been found valuable to describe global chemical reactivity of reactive species [96] in the context of spin catalysis phenomena [98,99], and also in the study of the spin polarization reactivities of reactive species from IV [97] and V [98,100] groups. The corresponding local philicities can be mapped through the associated SP-DFT Fukui functions, namely [95],

$$\omega_N^\pm(\mathbf{r}) = \omega_N f_{NN}^\pm(\mathbf{r}) \quad \text{and} \quad \omega_S^\pm(\mathbf{r}) = \omega_S^\pm f_{SS}^\pm(\mathbf{r}). \quad (3)$$

where  $f_{NN}^\pm(\mathbf{r})$  is the electrophilic (–)/nucleophilic (+) SP-DFT Fukui function and  $f_{SS}^\pm(\mathbf{r})$  stands for the spin Fukui function in the direction of decreasing (–)/increasing (+) spin number. The first one gives the response of electron density to a constrained charge transfer processes, while the second measures the response of the spin density to undergo a spin polarization process.

### 3 Computational details

Full geometry optimizations of the whole series of para-substituted phenylhalocarbenes both in singlet (ground state) and triplet spin multiplicities, have been performed at the (U)B3LYP/6-31G(d) DFT level of theory using the Gaussian 98 package of programs [101]. Vibrational frequencies confirmed that all ground state structures correspond to true minima having no imaginary frequencies. The optimized transition structures for the addition of some singlet para-substituted phenylhalocarbenes on tetramethylethylene were also characterized by frequency calculations in order to verify that the only one imaginary frequency corresponds to this reaction mode. The SP-DFT operational formulae to obtain the chemical potentials and hardnesses, showed in Eqs. (1) and (2) were based on the well-known finite difference and frozen-core set of approximations [87],

$$\begin{aligned}\mu_N &\approx \frac{1}{2}(\mu_N^+ + \mu_N^-), \quad \eta_{NN} \approx (\mu_N^+ - \mu_N^-), \\ \eta_{SS}^{M \rightarrow M'} &\approx (\mu_S^{(M')-} - \mu_S^{(M)+}) / \Delta N_S\end{aligned}\quad (4)$$

where,

$$\begin{aligned}\mu_N^- &\approx \frac{1}{2}(\varepsilon_{\text{HOMO}}^\alpha + \varepsilon_{\text{HOMO}}^\beta), \\ \mu_N^+ &\approx \frac{1}{2}(\varepsilon_{\text{LUMO}}^\alpha + \varepsilon_{\text{LUMO}}^\beta), \\ \mu_S^- &\approx \frac{1}{2}(\varepsilon_{\text{HOMO}}^\alpha - \varepsilon_{\text{LUMO}}^\beta), \\ \mu_S^+ &\approx \frac{1}{2}(\varepsilon_{\text{LUMO}}^\alpha - \varepsilon_{\text{HOMO}}^\beta),\end{aligned}\quad (5)$$

are defined in terms of the one electron energies  $\varepsilon$  of the frontier molecular orbitals HOMO and LUMO of a given spin symmetry, for the system in the lower and upper M and M' spin multiplicities, respectively [96]. Comparison between frozen core and finite differences approximations (FDA) for the spin-dependent global and local reactivity indices has been recently discussed [102]. Both approximations have been applied to a substituted silylene [103] and carbene series [95] providing similar trends. Note that for a singlet ground state, these operational formulae for SP-DFT electrophilicities are equivalent to those of the spin-restricted case [95]. Also note that spin hardness,  $\mu_{SS}^{M \rightarrow M'}$ , has been calculated using the spin potentials  $\mu_S^{(M')-}$  evaluated at the geometry of the ground state corresponding to M and  $\Delta N_S$  corresponds to the change in the spin number between the M and M' multiplicity states. The local philicities at the carbenic site of the pYPhXCs have been obtained via Eq. (3) using a recently implemented

condensed-to-atoms scheme for the generalized SP-DFT Fukui functions [94].

### 4 Results and discussion

#### 4.1 Electrophilicity (global and local considerations)

Table 1 reports the constrained chemical potential  $\mu_N$ , hardness  $\eta_{NN}$ , electrophilicity  $\omega_N$  indices and the electrophilicity difference  $\Delta\omega_{N,Y=H}$  both for the singlet (ground) and triplet electronic states of the whole series of para-substituted phenylhalocarbenes studied in the present work. It may be seen that pYPhXCs substituted with groups classified as electron-releasing (Y = -CH<sub>3</sub>, -OCH<sub>3</sub>, -OH, -NH<sub>2</sub>) excepting the F substituent, (and taking Y = H as reference), present lower values in  $\omega_N$  than those species substituted by electron-withdrawing groups (Y = -CHO, -CN, -NO<sub>2</sub>). The presence of the strong electron-withdrawing groups at the para-position of the aromatic ring yields more electrophilic phenylhalocarbenes at their singlet ground state (i.e.,  $\omega_N = 5.78$  eV for NO<sub>2</sub>-PhBrC >  $\omega_N = 5.40$  eV for NO<sub>2</sub>-PhClC >  $\omega_N = 4.60$  eV for NO<sub>2</sub>-PhFC).

An analysis of the results reported in Table 1 shows that there is a regular pattern in the SP-DFT electrophilicity values for the three series: at the singlet ground state, the  $\omega_N$  values increase in the order Br > Cl > F when the aromatic ring is para-substituted by the same group. It is clear that the electron-withdrawing/electron-releasing effect through the aromatic ring is larger than the electronegativity of the halogen atoms directly bound to the carbenic center. The electronic donation by resonance from the halogen atom into the vacant p orbital on carbenic center, rather than its electronegativity is one of the dominant factors [104,105]. The presence of  $\pi$ -electron donating groups (i.e., -OH, -OCH<sub>3</sub>, -NH<sub>2</sub>) and the methyl substituent at para-position decreases the electrophilicity power due to a conjugation of its  $\pi$ -electrons with the aromatic ring and inductive effects, respectively. Electron-withdrawing groups increase the  $\omega_N$  values mentioned above due to the inductive and conjugation effects exerted through the aromatic ring [73]. On the other hand, in general, the electrophilicity  $\omega_N$  for the triplet state of phenylhalocarbenes is lower than those calculated at the singlet state, irrespective of the X atom at the carbenic site and the para-substituent at the aromatic ring. The origin of this behavior is the preferential interaction of phenyl substituents with the singlet state rather than with the corresponding triplet state. This difference is expected, while the singlet ground state of pYPhXC is conjugated to the  $\pi$  system via an empty p orbital, the triplet-excited



**Table 1** SP-DFT chemical potential  $\mu_N$ , chemical hardness  $\eta_{NN}$ , electrophilicity  $\omega_N$ , and the electrophilicity difference  $\Delta\omega_{N,Y=H}$ . Calculated values are shown for the singlet ground state and their triplet excited phenylhalocarbenes series

Y	2S + 1	X = F				X = Cl				X = Br			
		$\mu_N$	$\eta_{NN}$	$\omega_N$	$\Delta\omega_{N,R-H}$	$\mu_N$	$\eta_{NN}$	$\omega_N$	$\Delta\omega_{N,R-H}$	$\mu_N$	$\eta_{NN}$	$\omega_N$	$\Delta\omega_{N,R-H}$
NO <sub>2</sub>	1	-5.03	2.76	4.60	2.05	-5.11	2.42	5.40	2.07	-5.14	2.28	5.78	2.31
	3	-4.80	3.83	3.02	1.56	-4.80	4.02	2.86	1.39	-4.72	3.99	2.79	1.18
CN	1	-4.80	3.01	3.83	1.28	-4.94	2.56	4.77	1.44	-4.96	2.46	4.99	1.52
	3	-4.63	4.09	2.62	1.16	-4.36	4.61	2.06	0.59	-4.42	4.44	2.20	0.59
CHO	1	-4.69	2.90	3.80	1.25	-4.83	2.48	4.71	1.38	-4.83	2.39	4.88	1.41
	3	-4.52	3.54	2.89	1.43	-4.52	3.54	2.89	1.42	-4.34	3.90	2.41	0.80
F	1	-4.19	3.36	2.61	0.06	-4.40	2.87	3.38	0.05	-4.42	2.77	3.52	0.05
	3	-4.09	4.00	2.09	0.63	-4.25	4.05	2.23	0.76	-3.94	4.33	1.79	0.18
H	1	-4.11	3.32	2.55	0.00	-4.34	2.82	3.33	0.00	-4.35	2.73	3.47	0.00
	3	-3.62	4.49	1.46	0.00	-3.68	4.60	1.47	0.00	-3.76	4.41	1.61	0.00
CH <sub>3</sub>	1	-3.96	3.36	2.34	-0.21	-4.20	2.84	3.11	-0.22	-4.22	2.75	3.24	-0.23
	3	-3.83	4.02	1.82	0.36	-3.90	4.33	1.76	0.29	-3.68	4.35	1.56	-0.05
OH	1	-3.86	3.44	2.16	-0.39	-4.08	2.92	2.84	-0.49	-4.09	2.86	2.93	-0.54
	3	-3.71	3.71	1.86	0.40	-3.51	4.26	1.45	-0.02	-3.63	4.09	1.61	0.00
OCH <sub>3</sub>	1	-3.77	3.40	2.09	-0.46	-4.02	2.90	2.78	-0.55	-4.02	2.84	2.85	-0.62
	3	-3.33	4.07	1.36	-0.10	-3.43	4.24	1.39	-0.08	-3.58	4.07	1.57	-0.04
NH <sub>2</sub>	1	-3.51	3.41	1.81	-0.74	-3.73	2.96	2.35	-0.98	-3.76	2.88	2.45	-1.02
	3	-3.11	3.91	1.24	-0.22	-3.18	4.00	1.27	-0.20	-3.48	4.12	1.47	-0.14

$\Delta\omega_{N,Y=H} = \omega_N(pYPhXC) - \omega_N(PhXC)$ . See text for details. All values are given in eV units

state presents only a singly occupied p orbital to the  $\pi$  system [54] (see Table 1).

Aromatic ring substitution on phenylhalocarbenes does have a pronounced effect on the electrophilicity power. This fact is reflected in the  $\Delta\omega_{N,Y=H}$  values, which is defined as the electrophilicity difference between the para-substituted phenylhalocarbene and unsubstituted phenylhalocarbene at the same electronic state (see Table 1). We stress that the substituent effect on the electrophilicity also depends on the phenylhalocarbene electronic state. Electron-withdrawing groups (i.e.  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{CHO}$ ) have a larger effect on the  $\omega_N$  value in the singlet state than in the triplet state, as shown in the  $\Delta\omega_{N,Y=H}$  values. This effect is reflected by higher values of  $\Delta\omega_{N,Y=H}$  for the singlet state than for the triplet state, except in the case of Y = CHO substituent at the para-position in the pYPhFC and pYPhClC systems. Electron-releasing substituents (i.e.,  $-\text{F}$ ,  $-\text{CH}_3$ ,  $-\text{OCH}_3$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ ) decrease the electrophilicity of the singlet phenylhalocarbenes with respect to the unsubstituted one, with the only exception of fluorine atom, and therefore, negative values of  $\Delta\omega_{N,Y=H}$  are found. From the observed  $\Delta\omega_{N,Y=H}$  values, it is clear that in the triplet state, these substituents decrease their electron-releasing ability. In all cases,  $\Delta\omega_{N,Y=H}$  values are less negative in the triplet state than in the singlet state of the corresponding phenylhalocarbene. This behavior is consistent with the reactivity of the phenylhalocarbenes based upon molecular orbital arguments: the empty  $\pi$ -orbital

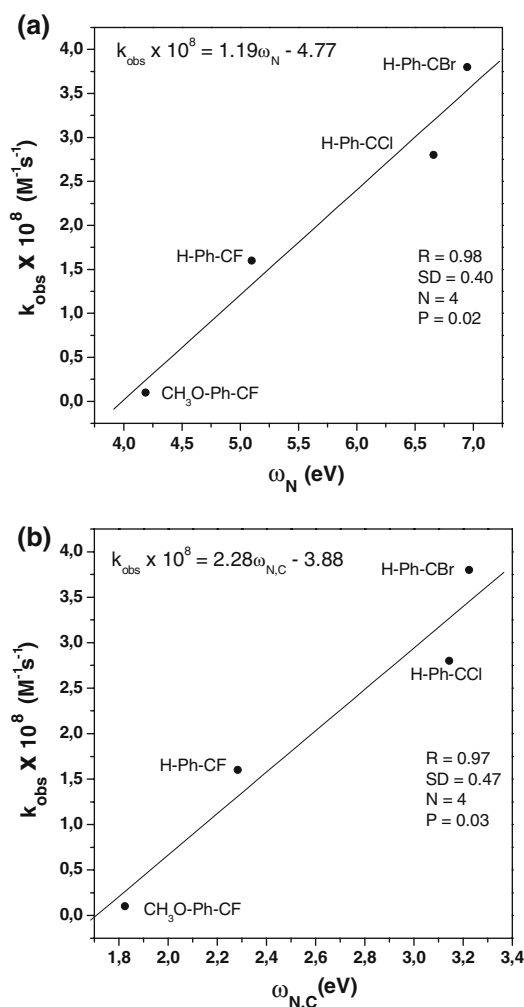
of the singlet carbenic atom should have a stronger interaction with the aromatic  $\pi$ -system than the singly occupied  $\pi$ -orbital of the triplet state in the same center. It is therefore expected that strong  $\pi$ -donors groups (i.e.,  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{OCH}_3$ ,  $-\text{CH}_3$ ,  $-\text{F}$ ) should preferentially decrease the electrophilic character of the singlet state relative to the triplet state, while  $\pi$ -acceptors ones (i.e.,  $\text{NO}_2$ ,  $\text{CN}$ ) will raise the electrophilic character of the singlet state. Although DFT calculations preclude an explanation based on a molecular orbital (MO) picture, our computational results using wavefunction models at the Hartree–Fock level, show that the DFT MOs are comparable in structure and topology [106,107].

The para-substitution by a fluorine atom on the aromatic ring of phenylhalocarbenes in the triplet state increases the electrophilicity relative to the unsubstituted phenylhalocarbene (i.e.  $\Delta\omega_{N,Y=H} = 0.63$  eV for F-PhFC,  $\Delta\omega_{N,Y=H} = 0.76$  eV for F-PhClC,  $\Delta\omega_{N,Y=H} = 0.18$  eV for F-PhBrC), indicating that its inductive electron-withdrawing effect is stronger than its mesomeric electron-releasing effect. A similar effect is observed for  $-\text{OH}$  and  $-\text{CH}_3$  groups on the PhFC. In the triplet state of PhClC and PhBrC systems, the inductive (electron-withdrawing) and resonant (electron-releasing) effects of the  $-\text{OH}$  and  $-\text{OCH}_3$  groups present opposite behaviors and an almost zero effect can be sensed.

A comparison between the electrophilicity index and the observed rate constant ( $k_{\text{obs}}$ ) for singlet

phenylhalocarbenes addition to tetramethylethylene (TME) [78] (see Figure 1a) reveals a linear correlation:  $k_{\text{obs}} \times 10^8 = 1.19\omega_{\text{N}} - 4.77$ . TME exhibits a higher reactivity in addition reactions to carbenes than other simple alkenes. Experimental results for comparison purposes are available [78]. It is interesting to note that the kinetic pattern of these specific addition reactions can be rationalized in terms of a single electronic-based index as the  $\omega_{\text{N}}$  is. The nature of the electrophilicity index as a kinetic or thermodynamic descriptor has been also recently addressed [28]. This result supports a mechanistic model where the carbene adds to the alkenes in a single step which is controlled by the electrophilicity of the carbene system [68, 73, 108]. In order to assess the addition mechanism of phenylhalocarbenes to TME, the transition structures and the corresponding activation free energy  $\Delta G^\ddagger$  for each addition reaction were calculated at the same level of theory. The theoretical  $\Delta G^\ddagger$  values obtained were: 5.3 kcal/mol (exp. 5.3 kcal/mol [78]) for PhBrC/TME; 9.0 kcal/mol (exp. 6.0 kcal/mol [78]) for PhClC/TME; 6.4 kcal/mol (exp. 6.0 kcal/mol [78]) for PhFC/TME and 7.9 kcal/mol (exp. 7.6 kcal/mol [78]) for CH<sub>3</sub>O-PhFC/TME. A reasonable agreement with the experimental  $\Delta G^\ddagger$  values is obtained. Henceforth, the associated theoretical rate constants reproduce consistently the experimental magnitude order of  $k_{\text{obs}}$  for the addition reactions [78]. This fact validates the use of the current level of theory for the evaluation of the electrophilicity indices, quantities that are well defined only within a chemical reactivity perturbative approximation. The low  $\Delta G^\ddagger$  values found in this series have been extensively discussed in the literature within the context of entropy-controlled processes [54, 68, 79]. Note also, from Fig. 1b, that the observed rate constant for singlet phenylhalocarbenes addition to TME nicely agrees with the activation of the electrophilicity power at the carbenic center  $\omega_{\text{N,C}}$  along the series. In other words, the local pattern of reactivity is correctly consistent with the kinetic data [78]. In the present case, the transition state stabilization energy for the cycloaddition depends inversely on the inductive effects of the halogen atom bounded to the carbenic center, in agreement with the regular pattern in the SP-DFT electrophilicity trend discussed recently [78]. It is interesting to note that both local and global electrophilicities are capable of explaining the kinetics. This proves that the global behavior originates from the corresponding local behavior.

The alkene electrophilic selectivity is dominated by an electronic donation from the alkene  $\pi$  orbital (HOMO) to the vacant p orbital (LUMO) of the singlet phenylhalocarbene. Our results show that the resonance donation from the fluorine atom to p



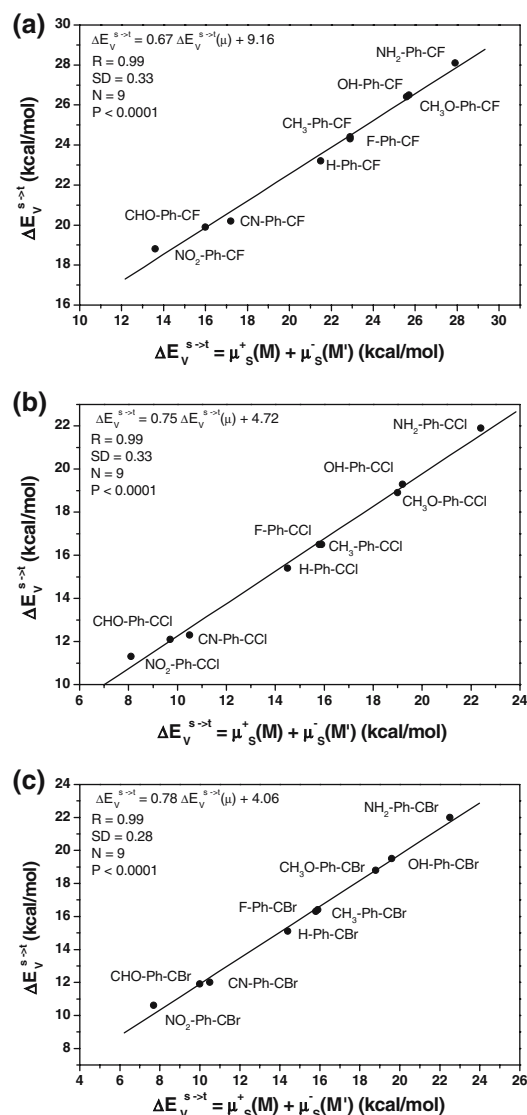
**Fig. 1** Linear correlation between the observed rate constants ( $k_{\text{obs}}$ ) of reaction for tetramethylethylene addition on some phenylhalocarbenes and **a** the SP-DFT electrophilicity  $\omega_{\text{N}}$  index, and **b** the condensed-to-atom SP-DFT local electrophilicity  $\omega_{\text{N,C}}$  index.  $R$  is the regression coefficient,  $N$  is the number of points and  $P$  is the probability that the observed correlation was randomly obtained. See text for details. Experimental rate constants were obtained from Ref. [78]

orbital of the carbenic carbon atom is strong enough to render PhFC a less electrophilic carbene than PhClC and PhBrC. Substitution on the phenylfluorocarbene by methoxy is accompanied by a decrease of the electrophilicity power (see Table 1), because the electron-releasing effect of CH<sub>3</sub>O-substituent stabilizes the phenylhalocarbene and decreases its reactivity toward the electron-rich alkenes as observed for tetramethylethylene [54]. Note that the electrophilicity index contains only information of the frontier molecular orbitals of the phenylhalocarbene systems (i.e.,  $\omega_{\text{N}}$  is defined within a perturbative approximation of chemical reactivity).

#### 4.2 Spin polarization singlet→triplet process (global and local considerations)

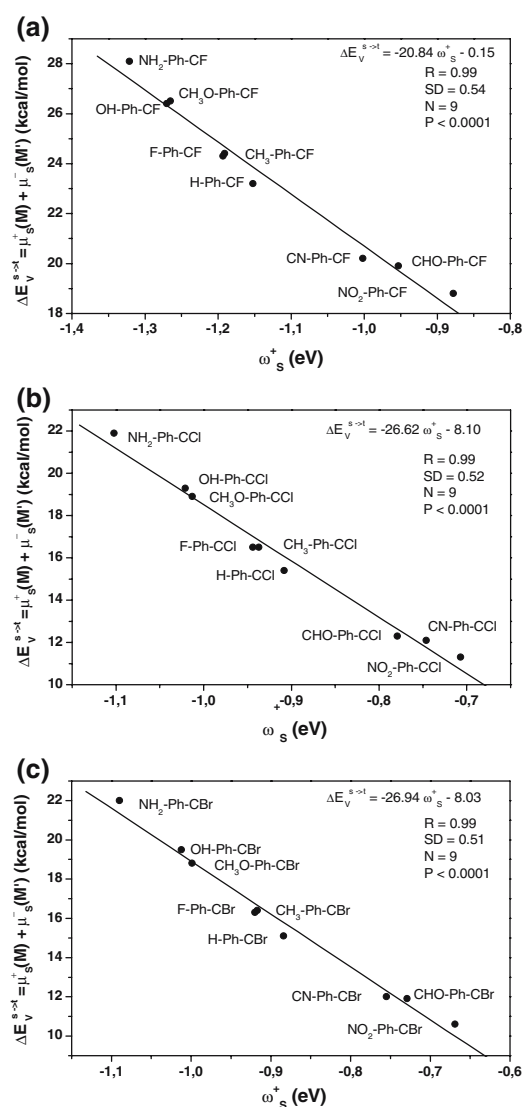
Table 2 summarizes the vertical singlet→triplet energies, spin potential ( $\mu_{\text{S}}^-, \mu_{\text{S}}^+$ ), spin hardness  $\eta_{\text{SS}}^{s \rightarrow t}$ , and the philicity  $\omega_{\text{S}}^+$ , values calculated for the three series of substituted phenylhalocarbenes. The vertical energies have been obtained from the total energy of the vertical triplet, i.e., a singlet point calculation at the triplet multiplicity using the optimized singlet ground state geometry (second column of Table 2), and from the expression:  $\Delta E_{\text{v}} = \mu_{\text{S}}^+(\text{M}) + \mu_{\text{S}}^-(\text{M}')$  [85]. The data are displayed in decreasing order of philicity  $\omega_{\text{S}}^+$  [97]. It can be noted that a direct  $\pi$  donation of the X substituent on the carbenic center increases the philicity for spin polarization character in the order  $\text{Br} > \text{Cl} > \text{F}$ . As for the electrophilicity reactivity, the electron-withdrawing/electron-releasing effects at the para-position in the aromatic ring become more important on the spin polarization trends than those due to the halogen atom directly bounded to the carbenic site. On the other hand, while functional groups with electron-withdrawing characteristics located at the para-position of the aromatic ring increase the  $\omega_{\text{S}}^+$  values ( $\text{Y} = -\text{NO}_2, -\text{CHO}$  and  $-\text{CN}$  groups), electron-releasing groups decrease the philicity character ( $\text{Y} = -\text{NH}_2, -\text{OCH}_3, -\text{OH}$  and  $-\text{F}$ ). Note from Fig. 2 that a linear relationship exists between the theoretical vertical singlet–triplet gaps evaluated from the total energy difference and from the SP-DFT chemical potentials,  $\Delta E_{\text{v}} = \mu_{\text{S}}^+(\text{M}) + \mu_{\text{S}}^-(\text{M}')$ , for the three substituted phenylhalocarbene series. As discussed recently [95], the philicity index  $\omega_{\text{S}}^+$  is related with the spin polarization at constant number of electrons in a vertical transition [93,94] and it is expected to correlate with the vertical singlet → triplet energies. This fact is in line with the fairly good correlations between  $\Delta E_{\text{v}} = \mu_{\text{S}}^+(\text{M}) + \mu_{\text{S}}^-(\text{M}')$  and  $\omega_{\text{S}}^+$  displayed in Fig. 3 for the three para-substituted phenylhalocarbene families studied here.

Tables 3 and 4 show that the  $f_{\text{NS},k}^+$  and  $f_{\text{SS},k}^+$  Fukui functions at the carbenic center can be used to discuss the charge and spin reorganization under the spin number changes [94]. Specifically,  $f_{\text{NS},k}^+$  measures the initial response of the charge density changes at site  $k$  caused by spin polarization. Calculated  $f_{\text{NS},k}^+$  values at the carbenic site for each phenylhalocarbene show negative values (see Table 3), following the order  $\text{F} > \text{Cl} > \text{Br}$  (for instance,  $f_{\text{NS},k}^+ = -0.1707$  for  $\text{NO}_2\text{-PhFC}$ ,  $f_{\text{NS},k}^+ = -0.1255$  for  $\text{NO}_2\text{-PhClC}$ ,  $f_{\text{NS},k}^+ = -0.0966$  for  $\text{NO}_2\text{-PhBrC}$  and  $f_{\text{NS},k}^+ = -0.2498$  for  $\text{NH}_2\text{-PhFC}$ ,  $f_{\text{NS},k}^+ = -0.1775$  for  $\text{NH}_2\text{-PhClC}$ ,  $f_{\text{NS},k}^+ = -0.1512$  for  $\text{NH}_2\text{-PhBrC}$ ), implying that a depletion of charge



**Fig. 2** Linear correlation between the vertical singlet→triplet energy from total energies,  $\Delta E_{\text{v}}^{s \rightarrow t}$ , and the vertical singlet–triplet energy from  $\Delta E_{\text{v}}^{s \rightarrow t} = \mu_{\text{S}}^+(\text{M}) + \mu_{\text{S}}^-(\text{M}')$  for **a** substituted singlet phenylfluorocarbenes, **b** substituted singlet phenylchlorocarbenes and **c** substituted singlet phenylbromocarbenes

density occurs at this center under a spin polarization process [93,94]. It may be also seen that electron-withdrawing groups like  $\text{NO}_2, -\text{CHO}$  and  $-\text{CN}$  present highest depletion along the halogen series, on going from  $\text{X} = \text{F}, \text{Cl}$  and  $\text{Br}$ . As it has been observed for other simple carbenes, chemical substitution resulting in a large electron withdrawing effect on the carbon atom increases the spin philicity at this position [93,94]. The associated changes in the spin density at site  $k$  upon a spin polarization process [94] can be traced out by the  $f_{\text{SS},k}^+$  Fukui function. As shown in Table 4, these values are always predicted to be positive (i.e., accumulation) whatever



**Fig. 3** Linear correlation between the vertical singlet→triplet energy ( $\Delta E_V^{s \rightarrow t} = \mu_S^+(M) + \mu_S^-(M')$ ) and the philicity  $\omega_S^+$  values for **a** substituted singlet phenylfluorocarbenes, **b** substituted singlet phenylchlorocarbenes and **c** substituted singlet phenylbromocarbenes

be the X and Y substituents. Such accumulation of spin charge density increases in the order of halogen electronegativity,  $F > Cl > Br$ , for a given Y substituent along the series. As it has also been discussed recently [93], the SP-DFT reactivity descriptors correctly incorporate both the inductive and conjugation effects exerted by substituents.

## 5 Concluding remarks

Both *electrophilicity* and *philicity for spin polarization* processes in singlet phenylhalocarbenes can be

**Table 2** Vertical singlet–triplet energies, spin potential ( $\mu_S^-, \mu_S^+$ ), spin hardness  $\eta_{SS}$ , and the philicity  $\omega_S^+$  values calculated for the series of substituted phenylhalocarbenes

X = F						
Y	$\Delta E_V^{s \rightarrow t}$	$\Delta E_V^{s \rightarrow t}$	$\mu_S^-$	$\mu_S^+$	$\eta_{SS}$	$\omega_S^+$
NO <sub>2</sub>	18.8	13.6	-0.79	1.38	-1.08	-0.88
CHO	19.9	16.0	-0.76	1.45	-1.10	-0.95
CN	20.2	17.2	-0.76	1.51	-1.13	-1.00
H	23.2	21.5	-0.73	1.66	-1.19	-1.15
CH <sub>3</sub>	24.4	22.9	-0.69	1.68	-1.18	-1.19
F	24.3	22.9	-0.69	1.68	-1.19	-1.19
OCH <sub>3</sub>	26.5	25.7	-0.58	1.70	-1.14	-1.27
OH	26.4	25.6	-0.61	1.72	-1.17	-1.27
NH <sub>2</sub>	28.1	27.9	-0.50	1.71	-1.10	-1.32
X = Cl						
Y	$\Delta E_V^{s \rightarrow t}$	$\Delta E_V^{s \rightarrow t}$	$\mu_S^-$	$\mu_S^+$	$\eta_{SS}$	$\omega_S^+$
NO <sub>2</sub>	11.3	8.1	-0.86	1.21	-1.03	-0.71
CHO	12.1	9.7	-0.82	1.24	-1.03	-0.75
CN	12.3	10.5	-0.83	1.28	-1.05	-0.78
H	15.4	14.5	-0.78	1.41	-1.10	-0.91
CH <sub>3</sub>	16.5	15.8	-0.73	1.42	-1.08	-0.94
F	16.5	15.9	-0.74	1.43	-1.09	-0.94
OCH <sub>3</sub>	18.9	19.0	-0.63	1.45	-1.04	-1.01
OH	19.3	19.2	-0.63	1.46	-1.05	-1.02
NH <sub>2</sub>	21.9	22.4	-0.51	1.48	-1.00	-1.10
X = Br						
Y	$\Delta E_V^{s \rightarrow t}$	$\Delta E_V^{s \rightarrow t}$	$\mu_S^-$	$\mu_S^+$	$\eta_{SS}$	$\omega_S^+$
NO <sub>2</sub>	10.6	7.7	-0.81	1.14	-0.97	-0.67
CHO	11.9	10.0	-0.76	1.19	-0.98	-0.73
CN	12.0	10.5	-0.78	1.23	-1.00	-0.76
H	15.1	14.4	-0.74	1.36	-1.05	-0.88
CH <sub>3</sub>	16.4	15.9	-0.69	1.38	-1.03	-0.92
F	16.3	15.8	-0.70	1.39	-1.04	-0.92
OH	18.8	18.8	-0.61	1.43	-1.02	-1.00
OCH <sub>3</sub>	19.5	19.6	-0.57	1.42	-0.99	-1.01
NH <sub>2</sub>	22.0	22.5	-0.47	1.44	-0.95	-1.09

Triplet–singlet energy values are given in kcal/mol; values of  $\mu_S^-, \mu_S^+, \eta_{SS}$  and  $\omega_S^+$  values are given in eV units.  $\Delta E_V^{s \rightarrow t} = \text{Total Energy}(M') - \text{Total Energy}(M)$ ; Total Energy ( $M'$ ) was evaluated at the geometry of the ground state corresponding to  $M$ .  $\Delta E_V^{s \rightarrow t} = \mu_S^+(M) + \mu_S^-(M')$ ;  $\mu_S^-(M')$  values were evaluated at the geometry of the  $M$  ground state. See text for details

rationalized within the context of SP-DFT. These species are correctly predicted to be electrophilic species showing high values of  $\omega_N$ , whatever be the nature of Y and X substituents (singlet ground state). Our SP-DFT based model descriptors predict that electron-withdrawing groups at para-position of the phenylhalocarbenes yield an increase in the electrophilicity values. A linear correlation between the electrophilicity index  $\omega_N$  and the observed rate constants  $k_{\text{obs}}$  for the addition of some singlet phenylhalocarbenes on tetramethylethylene was found. This result agrees with a mechanistic



**Table 3** Spin Fukui function  $f_{NS,k}^+$ , at the carbenic site of singlet phenylhalocarbenes

X	F	Cl	Br
Y	$f_{NS,k}^+$		
NO <sub>2</sub>	-0.1707	-0.1255	-0.0966
CHO	-0.1533	-0.1159	-0.0781
CN	-0.1631	-0.1172	-0.0864
H	-0.1575	-0.1125	-0.0826
CH <sub>3</sub>	-0.1559	-0.1078	-0.0790
F	-0.1564	-0.1080	-0.0782
OH	-0.1975	-0.1414	-0.1121
OCH <sub>3</sub>	-0.2216	-0.1603	-0.1280
NH <sub>2</sub>	-0.2498	-0.1775	-0.1512

**Table 4** Spin Fukui function  $f_{SS,k}^+$ , at the carbenic site of singlet phenylhalocarbenes

X	F	Cl	Br
Y	$f_{SS,k}^+$		
NO <sub>2</sub>	0.5927	0.5643	0.5261
CHO	0.6058	0.5724	0.5446
CN	0.5987	0.5723	0.5352
H	0.6010	0.5748	0.5399
CH <sub>3</sub>	0.6037	0.5798	0.5430
F	0.6018	0.5790	0.5414
OH	0.5626	0.5444	0.5072
OCH <sub>3</sub>	0.5380	0.5239	0.4901
NH <sub>2</sub>	0.5106	0.5074	0.4699

model where the carbene adds to the olefin in a single step that is controlled by the electrophilicity of the carbene system. This fact is emphasized by the low values of the activation free energy obtained for a series of phenylhalocarbene/alkene additions, in association with increasing electrophilicity power at the carbenic site as predicted by the  $\omega_{N,C}$  index along the series. On the other hand, the philicity for spin polarization character of these systems has been discussed in terms of the  $\omega_S^+$  index. A linear relationship between such descriptor and the vertical singlet–triplet energies is found for the whole series. As it is clear from the available experimental and theoretical evidence reported for these systems, both under charge transfer and spin polarization processes, in the singlet ground state, the carbenic center reactivity is more strongly affected by the para-substituent on the aromatic ring than by the halogen species directly bounded to it. This behavior may be traced out by our simple condensed-to-atoms model for the SP-DFT Fukui functions, namely  $f_{NS,k}^+$  and  $f_{SS,k}^+$ . These results further stress and clarify the usefulness of general SP-DFT derived philicities in the rationalization of chemical reactivity in the initial stages of reactions that

could involve both charge transfer and spin polarization processes.

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