Spin-Philicity and Spin-Donicity of Substituted Carbenes, Silylenes, Germylenes, and Stannylenes

Julianna Oláh,[†,‡] Frank De Proft,[†] Tamás Veszprémi,[‡] and Paul Geerlings*[,†]

Eenheid Algemene Chemie (ALGC), Vrije Universiteit Brussel (VUB), Pleinlaan 2, B-1050, Brussels, Belgium, and Inorganic Chemistry Department, Budapest University of Technology and Economics (BUTE), Szent Gellért tér 4, H-1521, Budapest, Hungary

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Spin potential, spin hardness, spin-philicity, and spin-donicity indices have been extensively studied on a large set of carbenes, silylenes, germylenes, and stannylenes at the B3LYP/6-31G(d) level. The effect of the substituents and that of the central atom have been investigated. The sum of the spin potentials calculated in the singlet and triplet states correlates excellently with the vertical singlet−triplet energy gap. A very good quadratic relationship between the spin-philicity and spin-donicity indices and the vertical singlet−triplet energy gaps is obtained. The analogy of the spin-philicity and spin-donicity indices with the electrophilicity index is discussed in detail.

1. Introduction

Conceptual DFT[1] provides precise definitions of well-known, but historically often vaguely defined chemical properties such as the hardness[2] or the electronegativity.[3] However, new quantities have been introduced as well to better understand and describe atomic and molecular interactions and properties. An important step along this way was among others the definition of the electrophilicity index (ω)[4,5] of a given ligand. Parr et al. suggested a model in which the ligand is embedded in an ideal zero-temperature free electron sea of zero chemical potential. In this case, the ligand A will be filled with electrons up to the point that its chemical potential becomes equal to that of the sea implying:

$$\mu_A = \left(\frac{\partial E_A}{\partial N}\right)_v = 0 \tag{1}$$

as the chemical potential is defined as $\mu = (\partial E/\partial N)_v$[3] with E the energy of the system and N the number of electrons. The energy change of the ligand (ΔE_A) up to second order due to electron flow (ΔN) from the free electron sea is (the index A will be dropped from now on) is

$$\Delta E = \mu \Delta N + 1/2\eta(\Delta N)^2 \tag{2}$$

where $\eta = (\partial^2 E/\partial N^2)_v$ is the chemical hardness of the ligand.[2]

Minimizing ΔE with respect to ΔN yields the optimal ΔN for the ligand, for which the energy change then becomes:

$$\Delta E = -\frac{\mu^2}{2\eta} \tag{3}$$

It was then proposed to call the quantity $\omega = \mu^2/2\eta$ the electrophilicity of the ligand, where it was shown that it depends on both the ionization potential and the electron affinity of ligand. Moreover, as intuitively expected, the electrophilicity index was shown to increase with increasing electron affinity.

Very recently Chattaraj et al. have introduced a generalized concept of philicity.[6] They claim that this generalized philicity is even a more powerful index than the global electrophilicity of Parr et al.,[5] as it contains information both on the Fukui function and the global electrophilicity of the atom or molecule.

The spin-philicity and spin-donicity indices[7] have been defined by using similar arguments within the context of spin-polarized DFT. Spin-polarized DFT[8] allows one to get some insight into the chemical properties related to the change in spin number. Vargas et al. used the spin potentials in the analysis of the singlet−triplet gap of a small set of halocarbenes and found that the sum of the spin potentials correlates linearly with the vertical singlet−triplet energy gap.[9] Recent work by Pérez et al.[7] demonstrated the applicability of the spin-related DFT indices in the interpretation of spin-catalysis phenomena.[10] For a small set of di- and triatomic molecules these authors showed that the spin-philicity and -donicity indices qualitatively account for their observed spin-catalytic effect and that the spin potentials quantitatively define the direction and magnitude of the spin transfer process involved in spin-catalysis phenomena. This phenomenon is induced by both magnetic and nonmagnetic (exchange) interactions.[10] It operates in triads of spin carriers (the simplest case being three radicals); pairwise exchange between either of the partners of the pair and a third spin carrier induces the spin conversion in the pair of selected spin carriers (e.g. radical pair); the latter acts as a spin catalyst that transforms nonreactive spin states of the pair into the reactive one. Overall this physical phenomenon manifests itself in chemical reactions of radicals, ions, carbenes, and high-spin molecules and strongly affects their reaction rates and competition of reaction channels.

However, so far, no detailed investigation has been performed on a large set of molecules confirming the usefulness of spin-philicity and spin-donicity. Substituted divalent forms of the Group 14 elements constitute a suitable set of molecules to be

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* Corresponding author. E-mail: pgeerlin@vub.ac.be. Phone: +32.2.629.33.14. Fax: +32.2.629.33.17.

[†] Vrije Universiteit Brussel.

[‡] Budapest University of Technology and Economics.

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examined. The ground state of the carbenoid compounds varies with the atomic number of the central atom and with the substituents attached to it. While the ground state of CH_2 and most of its derivatives is a $^3B_1$ triplet, the ground state of SiH_2, GeH_2, and SnH_2 is a closed shell, $^1A_1$ singlet. In the case of the carbene, coulomb repulsion between the electrons constrained to the carbon-centered HOMO is large, and although some energy must be surmounted to separate the electrons to different molecular orbitals, this energy is largely compensated by the accompanying decrease of electron−electron repulsion. Furthermore, the triplet configuration is additionally stabilized by relief of "exchange repulsion". In the case of the heavier hypovalent species the energy difference between the similar orbitals is larger; furthermore, less energy is gained upon relief of the electron−electron repulsion energy. Thus the heavier hypovalent species favor the closed shell, singlet state with increasing atomic number of the central atom.[11] The effect of the substituent on the ground state of carbenes[12] and silylenes[12b,13] has been extensively studied and it has been shown that the most important factor in the stabilization of the singlet carbenoids is the π-electron donation from the substituent to the central atom, while the triplet state can be stabilized with electropositive subtituents. A convenient way to examine and quantify the effect of substitution on the stability of carbenoid compounds (carbenes, silylenes, etc.) is the calculation of isodesmic reaction energies (ΔH_i). In these reactions (see (4) for a prototype of these) the number and type of bonds is equal on both sides of the equation allowing the comparison of the stability of the differently substituted species.

$$\mathrm{RR'X(singlet)} + \mathrm{XH_4} \rightarrow \mathrm{H_2XRR'} + \mathrm{XH_2}\ \mathrm{(singlet)} \qquad (\mathrm{X} = \mathrm{C, Si, Ge, Sn}) \quad (4)$$

The aim of our work is the study of the spin-related DFT-based indices, such as the spin potentials, spin hardness, spin-philicity, and spin-donicity numbers, to give a sound basis to these indices and to clarify their interpretation. Therefore it is tempting to explore how these indices change within a given group of the periodic table with the increasing atomic number of the central atom and with the different substituents. Although several papers have used the spin potentials, only one very recent contribution deals with the spin-philicity and spin-donicity numbers leaving in our view several open questions. (1) Conceptually, in which sense are these indices similar to the electrophilicity index? On the other hand we think it would be useful to clarify issues such as the following: (2) Does the spin-philicity/spin-donicity number describe ground-state or excited-state properties? (3) How is it related to the energy change when the system acquires a given spin number? To answer these questions we made a thorough investigation of the spin-related indices of an elaborate series of carbenes, silylenes, germylenes, and stannylenes substituted with first- and second-row elements. In this sense this work is in line with previous studies of our group on the evolution of DFT-related concepts (electronegativity, hardness, softness, etc.) in a given group or column throughout the periodic table[1b,d,14] and recent work of our group on the use of DFT descriptors in Sn-containing compounds.[15] In the set NH_2, OH, F, SH, and Cl disubstituted species have been considered as well. As it is always desirable to connect the theoretical results with the experimental data, we also included some well-known already synthesized or predicted to be synthesizable compounds in our set (see Chart 1). **1** (with X = C and R = adamantyl) was the first bottleable carbene synthesized by Arduengo et al. in 1989.[16] Not much later the corresponding silylene[17] and germylene[18] were synthesized as well. A few years later **2**[19] (with X = Si), the saturated form of **1**, was synthesized and proved to be stable. The R-substituted form of **3** (X = C), a thiazol ylidene, was the first non-diamino-substituted synthesized carbene. Finally **4**[20] is a possible target of silylene synthesis, as it was predicted with appropriate bulky groups to be as stable as **2**.

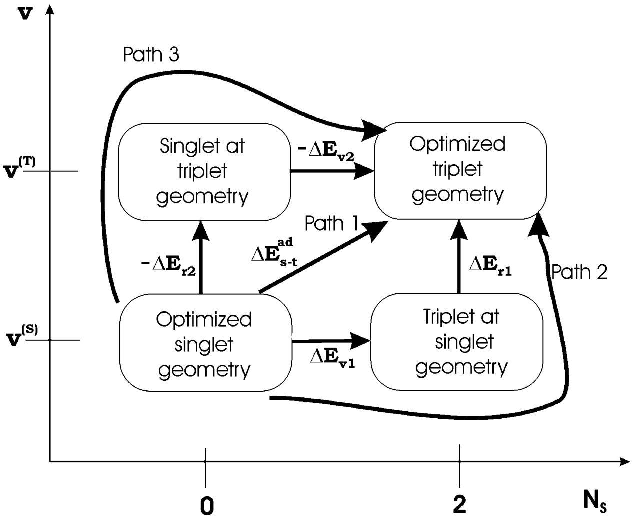
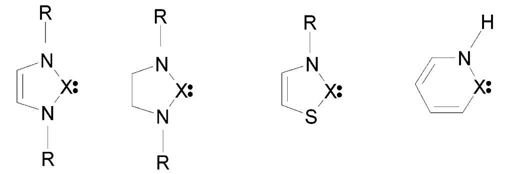


Figure 1. External potential (v) vs spin number (N_S): different pathways of calculation of $\Delta E^{\mathrm{ad}}_{\mathrm{s-t}}$ (for the explanation of all the quantities see text).

CHART 1



1 **2** **3** **4**

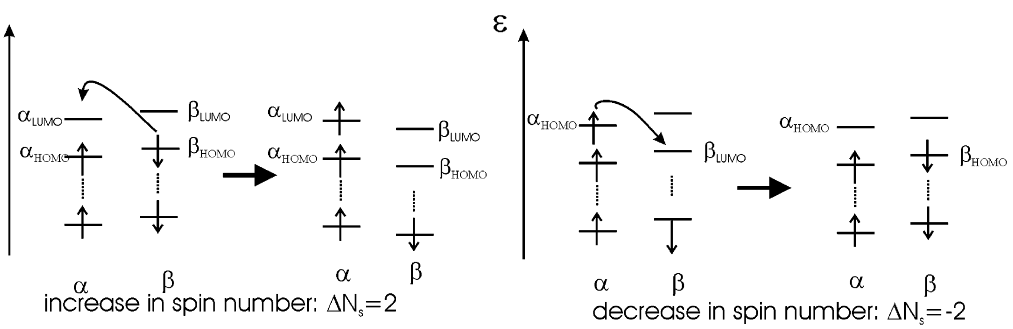
2. Theory and Computational Details

As the abovementioned DFT-based and spin-related indices were defined at constant external potential, comparison should be made with vertical singlet−triplet energy gaps. In Figure 1, which can be considered as an extension of Figure 1 in ref 9, three different methods are presented to calculate the adiabatic singlet−triplet energy separation ($\Delta E^{\mathrm{ad}}_{\mathrm{s-t}}$). $\Delta E^{\mathrm{ad}}_{\mathrm{s-t}}$, the usual singlet−triplet energy separation is the energy difference between the lowest lying triplet and singlet states of the molecule, both at their equilibrium geometry. Path 1 corresponds to the adiabatic excitation energy, being negative if the triplet state is more stable than the singlet. Path 2 corresponds to the case of those molecules with a singlet ground state. The adiabatic singlet−triplet energy separation can be calculated as the sum of the "vertical" singlet−triplet energy separation (ΔE_{v}) calculated at the singlet optimized geometry and the "relaxation energy" (ΔE_{r}). Path 3 shows the similar path for molecules with triplet ground state. Thus we get:

$$\Delta E^{\mathrm{ad}}_{\mathrm{s-t}} = \Delta E_{\mathrm{v1}} + \Delta E_{\mathrm{r1}} = -\,(\Delta E_{\mathrm{v2}} + \Delta E_{\mathrm{r2}}) \qquad (5)$$

Note that (ΔE_{v1}) is calculated as the energy of the system in the triplet state at the optimized singlet geometry minus the energy of the system in the singlet state, and (ΔE_{v2}) is calculated as the energy of the system in the singlet state at the optimized triplet geometry minus the energy of the system in the triplet state.

CHART 2



The energy change (ΔE_v) due to a change in spin number (ΔN_S) at constant external potential (v) and number of electrons (N) can be expanded in a Taylor series around a reference point; in the $\{N,N_S\}$ representation of spin-polarized DFT[21] we get:

$$\Delta E_{v,N} = \mu_s^0 \Delta N_S + \frac{1}{2}\eta_{ss}^0 (\Delta N_S)^2 \tag{6}$$

where μ_s^0 is the spin-potential[8c,22] and η_{ss}^0 the spin hardness.[9] As the energy is not an analytical function of the spin number (N_S), and has noncontinuous first partial derivatives with respect to the spin number evaluated at integer values of N_S (when the total number of electrons is kept fixed), μ_s^0 always must be calculated in a given direction, i.e., toward increasing (μ_s^+) or decreasing (μ_s^-) multiplicities.

As stated, the spin potential is defined as the first-order partial derivative of the energy E with respect to the spin number (N_S). It describes the energy required to change the spin multiplicity of an electronic state at constant external potential (v) and electron number (N). The value of the spin potential can be evaluated by using the finite difference formulas proposed by Galvan et al.[9,22] as

$$\mu_s^- = \left(\frac{\partial E}{\partial N_S}\right)^-_{N,v} \cong \frac{(\epsilon_H^\alpha(M') - \epsilon_L^\beta(M'))}{2} \tag{7}$$

$$\mu_s^+ = \left(\frac{\partial E}{\partial N_S}\right)^+_{N,v} \cong \frac{(\epsilon_L^\alpha(M) - \epsilon_H^\beta(M))}{2} \tag{8}$$

These expressions contain the one-electron energies of the HOMO and LUMO orbitals for the system in lower (M) and upper (M') spin multiplicities, respectively. These formulas can be easily understood within the Koopmans approximation in a UHF scheme. For the transition of a system from lower multiplicity M to a higher multiplicity M', one has to remove one electron from the β_{HOMO} orbital of the system and place it in the α_{LUMO} orbital. In the case of decreasing multiplicity one removes one electron from the α_{HOMO} orbital of the system and places it in the β_{LUMO} orbital (Chart 2).

The spin hardness (η_{ss}^0) is related to the second partial derivative of the energy with respect to the spin coordinates and can be calculated from the spin potentials:

$$\eta_{ss}^0 = \left(\frac{\partial^2 E}{\partial N_S^2}\right)_{v,N} \cong \frac{\mu_s^- - \mu_s^+}{2} \tag{9}$$

It measures the concavity of the E versus N_S curve in the given interval.

The spin-philicity power (ω_s^+) and the spin-donicity number (ω_s^-) were defined similarly to the electrophilicity. Considering a "sea of spins" on the basis of (6) with a simple variational calculation as used for the derivation of the electrophilicity index, Perez et al. arrived at the following formula for the maximal energy change:[7]

$$\Delta E_{\max,v,N} = -\frac{(\mu_s^0)^2}{2\eta_{ss}^0} \tag{10}$$

In the direction of increasing spin multiplicity $(\Delta N_S > 0)$, they suggested using this energy difference as the spin-philicity index of the system:

$$\omega_s^+ \equiv -\frac{(\mu_s^+)^2}{2\eta_{ss}^0} \tag{11}$$

The spin-donicity number is defined in the direction of decreasing multiplicity $(\Delta N_S < 0)$ and the reference state is μ_s^-:

$$\omega_s^- \equiv -\frac{(\mu_s^-)^2}{2\eta_{ss}^0} \tag{12}$$

The analogy between the electrophilicity and spin-philicity is clear with the exception of the negative sign in the spin-philicity index, which yields a difference in the interpretation. If we consider the electrophilicity values, (e.g. as in ref 5) we see that a large positive electrophilicity index corresponds to a large energy difference between the neutral and the lower lying negatively charged system, and a small electrophilicity index is obtained in the case of smaller energy changes. Thus we can say that a molecule with a large electrophilicity index "likes" to receive electrons, i.e., it is a good "electrophile".

However the spin-philicity index was introduced as the energy change itself, and not the negative of the energy change. As a result, a large spin-philicity index is expected if the energy difference between the higher and lower spin states is large, and a small index occurs in the case of small differences. This is somewhat contradictory with chemical intuition, since the name "spin-philic" suggests that the energy difference between the higher and lower spin states is small compared to the less "spin-philic" species. Therefore we propose that not the energy change but its negative should be used to define the spin-philicity index of a given species, similarly to the definition of Parr et al. for the electrophilicity index.

$$\omega_s^+ \equiv \frac{(\mu_s^+)^2}{2\eta_{ss}^0} \tag{13}$$

In this case, if the energy change between the higher and lower spin states is large, one gets a large negative number for the spin-philicity index, and if the energy difference is small the result is a small negative spin-philicity index. Applying this definition to the results obtained by Vargas et al. in ref 6, this would mean that molecules with large negative spin-philicity values are good spin catalysts.

In the case of the spin-donicity index we also propose to use the negative of the energy change as the index on the basis of a similar reasoning as used in the case of the spin-philicity index.

$$\omega_s^- \equiv \frac{(\mu_s^-)^2}{2\eta_{ss}^0} \tag{14}$$

If a system has a triplet ground state and the singlet state lies much higher in energy, we expect a small spin-donicity number. This means that the triplet state is energetically favored, i.e., the system does not want to decrease its spin number. If the energy difference between triplet and singlet states is smaller, a large spin-donicity number is to be expected.

All the structures treated in this work were fully optimized in both their singlet and triplet states at the (U)B3LYP level of theory with the 6-31G(d) basis set, using the Gaussian 98 program.[23] This basis set has been shown to be appropriate for the qualitative analysis of singlet−triplet energy gaps.[24] For Sn, the LANL2DZ[25] basis set was used augmented with a d-type polarization function.[26] This basis set has proved to be of great value in recent studies of the HSAB principle on tin-containing molecules.[15] Analytical second derivative calculations were performed to ensure that all the stationary points were real minima on the potential energy surface. Although at the DFT level one has no wave function, the S^2 expectation value of the Slater determinant constructed from the Kohn−Sham orbitals is frequently used as a probe of the UKS scheme. In our case the S^2 values for the triplets were always very close to 2, implying that the contamination with higher spin states is negligible. Single-point calculations were performed in the triplet state on the geometry corresponding to the singlet state and vice versa to evaluate the vertical singlet−triplet energy separations.

3. Results and Discussion

Table 1 contains the calculated adiabatic singlet−triplet energy separations, vertical singlet−triplet gaps, spin potential (μ_s^+, μ_s^-) values, spin-hardnesses (η_{ss}^0), spin-philicity/spin-donicity numbers, and maximal spin acceptance/spin release values($\Delta N_{S,\max}$). The spin-related indices are only presented for the corresponding *ground* state, i.e., for molecules with a singlet ground state μ_s^+, ω_s^+, η_{ss}^0, and $\Delta N_{S,\max}^+$, and for molecules with a triplet ground state only μ_s^-, ω_s^-, η_{ss}^0, and $\Delta N_{S,\max}^-$ are presented. It is self-evident that for molecules in the singlet ground state no spin-donicity should be calculated, as there is no lower lying spin state. For molecules with triplet ground state, all of these indices can be calculated μ_s^-, ω_s^- in the direction of the singlet state and μ_s^+, ω_s^+, and $\Delta N_{S,\max}^+$in the direction of the quintet state, but as we are only interested in the ground state properties for these molecules only μ_s^-, ω_s^-, $\Delta N_{S,\max}^-$have been considered. Note that in general these indices can be used to describe ground- and excited-state properties as well.

Adiabatic and Vertical Singlet−Triplet Energy Separations. It has been shown that the evaluation of accurate quantitative singlet−triplet energy gaps requires precise, highly sophisticated MRCI calculations with large basis sets.[27] However, it is also known that the main sources of errors do not change significantly with the method,[28] Mendez et al., e.g., found that the B3LYP/6-31G(d) values were systematically lower by 2−4 kcal/mol than the experimental ones.[24] Therefore we can assume that our values will exhibit the correct qualitative trends.

As can be seen from the comparison of the data, the stabilization of the singlet state increases with increasing atomic number of the central atom for all the substituents except for the examined ring compounds. In the stabilization of the singlet state the difference between the C and Si compounds is much larger (15−35 kcal/mol) than that between the Si and Ge or Sn compounds, which is in accordance with the somewhat different behavior of the first-row elements, as compared to the elements of higher periods.

The vertical energies have been evaluated at two geometries: at the optimized singlet (ΔE_{v1}) and triplet (ΔE_{v2}) geometries. Evidently, the vertical energies are always larger than the adiabatic singlet−triplet gaps as they do not include the energy decrease due to geometry relaxation (in this sense ΔE_{v2} is larger than ΔE_{t-s}^{ad}, the energy difference calculated as the energy of the optimized singlet state minus the energy of the optimized triplet state; as $\Delta E_{t-s}^{ad} = -\Delta E_{s-t}^{ad}$, this implies that ΔE_{v2} is larger than $-\Delta E_{s-t}^{ad}$). This "relaxation energy" is large if the optimized singlet and triplet geometries are considerably different. The difference is most pronounced in the case of $HCNH_2$ and $HCPH_2$ (and also in their corresponding silylenes). In these molecules, the N and P atoms are strongly pyramidalized in the triplet state, while the N atom is planar and the P is almost planar in the singlet state. The degree of the planarity of the heteroatom in the singlet state decreases with the atomic number of the central atom.

Let us consider the cycle depicted in Figure 1 (Path 2 and in the reverse direction Path 3). On the basis of the signs of the vertical excitation energies three energetically different cycles exist (see Figure 2). Molecules with a highly stable triplet ground state behave as shown in the first cycle. Molecules with singlet and triplet states of similar stability behave according to cycle 2. Molecules with a highly stable singlet state act as shown in cycle 3. When going down the carbon group, the compounds shift toward categories 2 and 3. Furthermore, the molecules shift toward categories 2 and 3 with increasing capability of substituents to stabilize the singlet state.

In Figure 3 the vertical energies are plotted against ΔE_{s-t}^{ad} for carbenes (similar curves have been found in the case of silylenes, germylenes, and stannylenes as well). Vargas et al. found that for a limited series of halocarbenes, these two values differed only by a constant.[9] This is, however, not true for our set, as it exhibits much broader structural variety, but the linear relationship still holds. The correlation is much better for ΔE_{v1} than for ΔE_{v2}; this may be due to the fact that ΔE_{v2} is calculated from an excited state, as most of the molecules exhibit a singlet ground state. Similar curves exist for silylenes, germylenes, and stannylenes.

Spin-Related Conceptual DFT Indices. Comparison of the numerical data for the four molecular groups shows that with the increasing atom number of the central atom the spin hardness slightly increases (becomes less negative). This is in contrast with the changing of the hardness of the molecule: the hardness decreases with the atomic number of the central atom. The spin-philicity and spin-donicity numbers decrease (become more negative) with the increasing atomic number of the central atom for a given substituent. Similar trends cannot be observed in the case of the spin potential values.

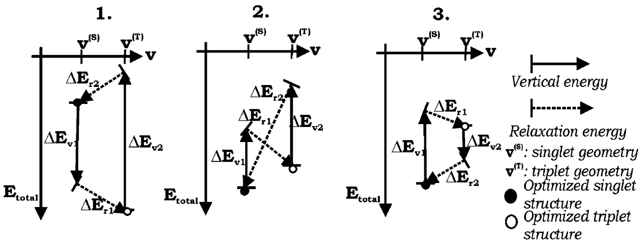
TABLE 1: Ground State Multiplicity (singlet or triplet), Adiabatic Singlet−Triplet Energy Separation (ΔE^{ad}_{s-t}), Vertical Energies (ΔE_{v1}, ΔE_{v2}), Spin Potentials (μ_s^+/μ_s^-), Spin Hardness (η^0_{SS}), Spin-Philicity/Spin-Donicity (ω_s^+/ω_s^-) Numbers, and Maximal Spin Acceptance ($\Delta N^+_{S,max}/\Delta N^-_{S,max}$) for the Investigated Compounds[a]

molecule	GS mult[b]	ΔE^{ad}_{s-t}	ΔE_{v1}	ΔE_{v2}	μ_s^+/μ_s^-	ω_s^+/ω_s^-	η^0_{ss}	$\Delta N_{S,max}$	molecule	GS mult[b]	Δ	$E^{ad}_{s-t}\Delta E_{v1}$	ΔE_{v2}	μ_s^+/μ_s^-	ω_s^+/ω_s^-	η^0_{ss}	$\Delta N_{S,max}$
a. carbene compounds (X = C)																	
HXH	t	−13.7	−1.4	27.2	−2.28	−1.53	−1.69	−1.35	HXCl	s	2.2	10.9	9.5	1.70	−1.00	−1.45	1.18
HXLi	t	−32.1	−32.1	32.1	−1.64	−1.14	−1.17	−1.40	$X(NH_2)_2$	s	52.1	89.5	4.2	3.40	−3.96	−1.46	2.33
HXBeH	t	−34.2	−29.9	34.5	−2.14	−1.58	−1.45	−1.48	$X(OH)_2$	s	56.6	75.2	−2.4	3.18	−3.27	−1.55	2.06
$HXCH_3$	t	−6.9	11.2	21.1	−2.02	−1.30	−1.57	−1.29	$X(SH)_2$	s	24.4	37.8	20.8	2.10	−1.76	−1.26	1.67
$HXNH_2$	s	31.5	53.8	47.2	2.62	−2.36	−1.45	1.80	XF_2	s	52.2	60.4	−40.8	2.99	−2.67	−1.67	1.79
HXOH	s	23.4	34.2	16.5	2.27	−1.70	−1.52	1.49	XCl_2	s	16.6	24.7	−5.6	1.90	−1.34	−1.35	1.41
HXF	s	12.1	19.4	−1.3	2.02	−1.29	−1.59	1.27	H_2NXOH	s	54.3	79.8	−4.6	3.22	−3.50	−1.48	2.17
HXNa	t	−26.1	−18.3	33.1	−1.12	−0.70	−0.89	−1.25	H_2NXSH	s	38.9	64.1	10.6	2.76	−2.80	−1.36	2.03
HXMgH	t	−32.3	−23.7	34.8	−2.04	−1.50	−1.38	−1.47	HOXSH	s	35.7	49.1	21.1	2.47	−2.20	−1.39	1.78
$HXAlH_2$	t	−21.3	−20.0	22.3	−1.71	−1.08	−1.36	−1.26	**1**	s	82.1	99.7	−39.2	3.38	−4.43	−1.29	2.62
$HXSiH_3$[c]									**2**	s	69.4	89.9	−23.2	3.35	−3.97	−1.41	2.37
$HXPH_2$	s	6.6	51.3	38.0	2.37	−2.31	−1.22	1.95	**3**	s	66.2	77.5	−42.7	2.89	−3.41	−1.22	2.36
HXSH	s	13.8	32.8	35.2	2.09	−1.62	−1.34	1.55	**4**	s	38.2	52.4	−16.9	1.91	−2.09	−0.88	2.19
b. silylene compounds (X = Si)																	
HXH	s	20.1	29.3	−8.8	1.68	−1.34	−1.05	1.60	HXCl	s	33.7	38.4	−26.2	1.81	−1.68	−0.98	1.85
HXLi	t	−6.8	−1.9	16.2	−1.11	−0.75	−0.82	−1.35	$X(NH_2)_2$	s	55.6	86.1	−12.0	2.93	−3.95	−1.08	2.70
HXBeH	t	0.0	9.5	11.0	−1.17	−0.73	−0.94	−1.25	$X(OH)_2$	s	66.4	80.4	−44.0	2.85	−3.63	−1.12	2.55
$HXCH_3$	s	22.3	30.1	−12.2	1.68	−1.37	−1.03	1.63	$X(SH)_2$	s	43.1	57.9	−8.9	2.19	−2.56	−0.94	2.34
$HXNH_2$	s	41.0	59.2	−6.4	2.27	−2.58	−1.00	2.27	XF_2	s	75.6	79.4	−70.9	2.90	−3.52	−1.20	2.42
HXOH	s	39.9	47.3	−21.3	2.04	−2.05	−1.02	2.00	XCl_2	s	53.0	56.9	−47.6	2.24	−2.48	−1.01	2.22
HXF	s	39.1	43.1	−32.6	1.97	−1.87	−1.04	1.90	H_2NXOH	s	60.1	80.5	−27.8	2.81	−3.67	−1.08	2.61
HXNa	t	−3.8	−1.2	10.2	−0.81	−0.46	−0.71	−1.14	H_2NXSH	s	50.1	72.6	−10.3	2.55	−3.29	−0.99	2.58
HXMgH	t	−0.7	5.7	10.8	−1.10	−0.69	−0.88	−1.25	HOXSH	s	51.9	68.7	−24.7	2.48	−3.08	−1.00	2.49
$HXAlH_2$	s	3.9	16.7	15.1	1.27	−0.90	−0.90	1.41	**1**	s	59.3	76.6	−37.5	2.41	−4.03	−0.72	3.35
$HXSiH_3$	s	13.45	22.7	−1.9	1.45	−1.10	0.95	1.52	**2**	s	75.5	82.1	−65.1	2.69	−3.82	−0.95	2.84
$HXPH_2$	s	22.4	39.6	−2.4	1.79	−1.73	−0.92	1.93	**3**	s	56.6	73.6	−34.5	2.32	−3.84	−0.70	3.32
HXSH	s	32.9	48.9	−7.7	2.05	−2.13	−0.99	2.07	**4**	s	60.3	69.0	−44.0	2.32	−3.16	−0.85	2.73
c. germylene compounds (X =Ge)																	
HXH	s	26.3	36.2	−14.2	1.71	−1.59	−0.92	1.86	HXCl	s	41.3	45.1	−34.3	1.83	−1.97	−0.85	2.15
HXLi	t	−5.8	−1.3	18.1	−1.13	−0.92	−0.69	−1.63	$X(NH_2)_2$	s	55.8	91.6	−17.3	2.86	−4.43	−0.93	3.10
HXBeH	s	1.5	11.6	13.4	1.12	−0.73	−0.87	1.29	$X(OH)_2$	s	70.7	83.6	−47.5	2.80	−3.98	−0.98	2.84
$HXCH_3$	s	27.3	35.4	−16.4	1.68	−1.56	−0.91	1.85	$X(SH)_2$	s	48.8	63.4	−18.8	2.20	−2.95	−0.82	2.68
$HXNH_2$	s	43.9	64.8	−13.4	2.29	−2.96	−0.89	2.58	XF_2	s	82.7	85.9	−78.2	2.91	−4.06	−1.04	2.79
HXOH	s	44.7	51.7	−27.6	2.04	−2.28	−0.91	2.24	XCl_2	s	62.7	66.1	−57.4	2.28	−3.06	−0.85	2.68
HXF	s	45.4	48.6	−39.3	1.97	−2.13	−0.91	2.16	H_2NXOH	s	62.3	84.5	−32.0	2.79	−4.06	−0.96	2.91
HXNa	t	−2.2	−0.3	8.6	−0.76	−0.44	−0.67	−1.14	H_2NXSH	s	53.4	89.2	−17.9	2.54	−5.39	−0.60	4.24
HXMgH	s	1.5	7.4	10.7	0.95	−0.58	−0.77	1.23	HOXSH	s	57.3	73.9	−31.7	2.46	−3.50	−0.87	2.84
$HXAlH_2$	s	6.7	20.0	14.3	1.26	−0.98	−0.81	1.55	**1**	s	50.4	64.5	−34.3	2.17	−3.17	−0.74	2.92
$HXSiH_3$[c]									**2**	s	67.9	77.1	−52.2	2.44	−3.82	−0.78	3.13
$HXPH_2$	s	26.3	38.9	−8.4	1.67	−1.70	−0.82	2.04	**3**	s	49.0	64.1	−32.6	2.11	−3.21	−0.69	3.05
HXSH	s	38.9	55.0	−16.0	2.08	−2.46	−0.88	2.37	**4**	s	58.8	68.3	−38.7	2.25	−3.28	−0.77	2.92
d. stannylene compounds (X = Sn)																	
HXH	s	26.6	34.5	−16.4	1.65	−1.49	−0.91	1.81	HXCl	s	40.4	43.9	−34.1	1.79	−1.89	−0.85	2.11
HXLi	t	−0.7	2.4	8.5	−0.87	−0.52	−0.72	−1.20	$X(NH_2)_2$	s	50.7	81.6	−18.4	2.53	−3.59	−0.89	2.84
HXBeH	s	7.1	15.0	4.1	1.14	−0.80	−0.82	1.40	$X(OH)_2$	s	63.9	74.4	−44.7	2.56	−3.39	−0.97	2.65
$HXCH_3$	s	26.9	33.6	−17.9	1.61	−1.46	−0.89	1.81	$X(SH)_2$	s	46.5	59.1	−22.9	2.09	−2.68	−0.82	2.56
$HXNH_2$	s	40.8	58.4	−16.3	2.13	−2.56	−0.88	2.41	XF_2	s	74.2	77.2	−69.7	2.70	−3.45	−1.05	2.56
HXOH	s	41.7	47.4	−27.9	1.91	−2.05	−0.89	2.15	XCl_2	s	60.4	63.5	−55.7	2.22	−2.87	−0.86	2.58
HXF	s	43.1	46.1	−37.6	1.88	−1.99	−0.89	2.11	H_2NXOH	s	55.4	75.0	−31.0	2.55	−3.45	−0.95	2.70
HXNa	s	1.2	2.5	3.5	0.74	−0.44	−0.62	1.19	H_2NXSH	s	49.6	70.7	−20.9	2.36	−3.26	−0.85	2.77
HXMgH	s	6.0	10.7	3.1	0.97	−0.65	−0.73	1.34	HOXSH	s	51.7	61.9	−33.0	2.19	−2.80	−0.86	2.56
$HXAlH_2$	s	9.8	22.0	7.0	1.25	−1.02	−0.77	1.64	**1**	s	54.4	64.9	−38.8	2.08	−3.21	−0.67	3.09
$HXSiH_3$	s	20.6	28.2	−10.4	1.43	−1.25	−0.82	1.75	**2**	s	49.0	58.0	−37.5	1.95	−2.82	−0.67	2.90
$HXPH_2$	s	26.4	35.8	−12.8	1.56	−1.54	−0.79	1.98	**3**	s	35.6	46.6	−26.2	1.76	−2.18	−0.71	2.48
HXSH	s	37.8	50.2	−19.4	1.96	−2.18	−0.88	2.23	**4**	s	38.5	51.6	−26.3	1.79	−2.55	−0.63	2.85

[a] Adiabatic singlet−triplet energy separation and vertical energies in kcal/mol, spin potential values in V, spin-hardness in V/spin units, spin-philicity and spin-donicity values in eV, maximal spin acceptance in spins. [b] Singlet = s; triplet = t. [c] No stable species has been found at the B3LYP level of theory.

Vargas et al. showed that the energy difference estimated on the basis of the sum of the spin potentials μ_s^+ and μ_s^- calculated in the singlet and triplet state correlates very well with the vertical singlet−triplet energy gap.[9] We have confirmed this ($R^2 > 0.99$ in all cases) for all the compounds (Figure 4). It is worth noting that the parameters of the linear fit are the same for all carbenoid compounds and do not depend on the ground state of the molecules.

An interesting feature of the spin potential μ_s^+ is that it gives information on the stability of carbene type compounds. In Figure 5, the changes of ΔE^{ad}_{s-t}, μ_s^+, and ΔH_i (isodesmic reaction energy for reaction 4, calculated at the B3LYP/6-31G(d) level taken from ref 29) are plotted for the silylenes substituted by first- and second-row elements. As mentioned earlier the isodesmic reaction energy can be used to quantitatively compare the stabilities of similar molecules, e.g. that of



	1.	2.	3.
X=C	HXH, HXLi, HXBeH, HXNa, HXMgH, HXAlH$_2$	HXCH$_3$, HXNH$_2$, HXOH, HXPH$_2$, HXSH, HXCl, HX(NH$_2$)$_2$	Everything else
X=Si, X=Ge	HXLi, HXNa	HXBeH, HXMgH, HXAlH$_2$	Everything else
X=Sn		HXLi, HXBeH, HXNa, HXMgH, HXAlH$_2$	Everything else

Figure 2. Total energy (E_{total}) vs the external potential (v). Relative stability of singlet and triplet states.

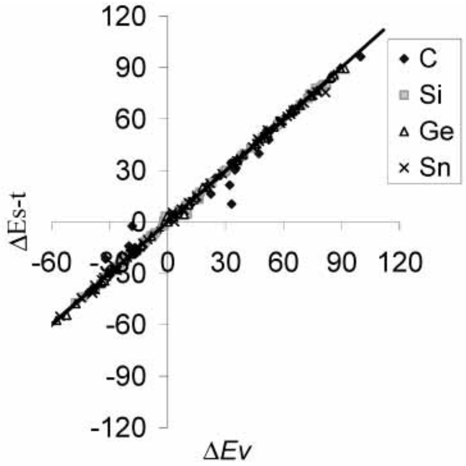


Figure 3. The estimated singlet−triplet gap (in kcal/mol) on the basis of the sum of the spin-potentials ($\mu_s^+ + \mu_s^-$) plotted against the corresponding vertical singlet−triplet energy separations (ΔE_{v1} at the singlet geometry and ΔE_{v2} at the triplet geometry (in kcal/mol)) for the investigated carbenes, silylenes, germylenes, and stannylenes.

the substituted carbenes or silylenes. From Figure 5 it can be seen that all three quantities predict the same ordering for the stabilization effect of the different substituents. It must be noted that the approximate formula for μ_s^+ corresponds to twice the hardness of the singlet molecule; it is known that large HOMO−LUMO differences, thus a large hardness, imply high stability, due to the maximum hardness principle.[30] It is worth noting that in a spin-polarized case (e.g. in the triplet state) the relationship between the HOMO−LUMO gap and the stability of the molecule is not straightforward, as in open-shell cases the LUMO is not well-defined and may lie below the HOMO.[31] In Figure 6 the maximal spin acceptance ($\Delta N_{\text{S,max}}^+$) of the molecules is plotted against the vertical energies for carbenes with singlet ground state and the maximal spin release ($\Delta N_{\text{S,max}}^+$) for carbenes with triplet ground state. It shows that molecules with larger vertical energies are able to accept more spins from the “sea” or donate more spins to the “sea”. This seems to be in contrast with intuition; one would expect a system with a stable singlet state to take fewer spins from the sea. This is, however, similar in the case of spin catalysis. Pérez et al. found that molecules with larger vertical energies are proven to be experimentally better spin catalysts.[7] A possible explanation for this fact is that one is describing an energetically unfavorable process; molecules with singlet ground state accept spins from the sea and molecules with triplet ground state donate spins to the sea. The larger the energy difference between the two states, the larger the destabilization of the molecule and the more spins it can accept or donate. The more destabilized molecule can more easily convert the spin state of the reactants during the catalytic process.

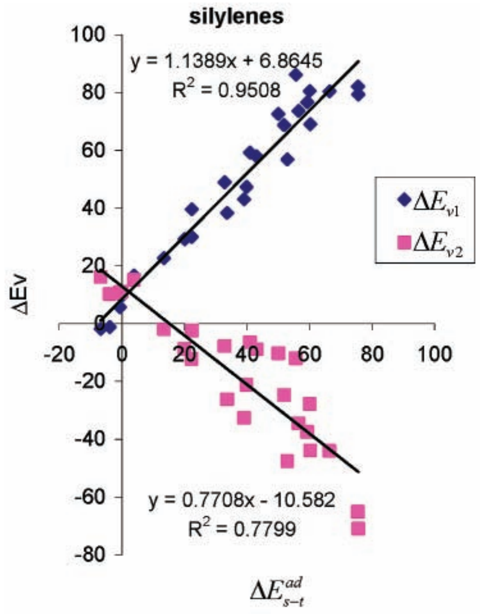


Figure 4. The calculated vertical singlet−triplet energy separations (ΔE_{v1} and ΔE_{v2} (in kcal/mol)) as a function of the adiabatic singlet−triplet energy separation ($\Delta E_{\text{s-t}}^{\text{ad}}$ (in kcal/mol)) for the investigated silylenes.

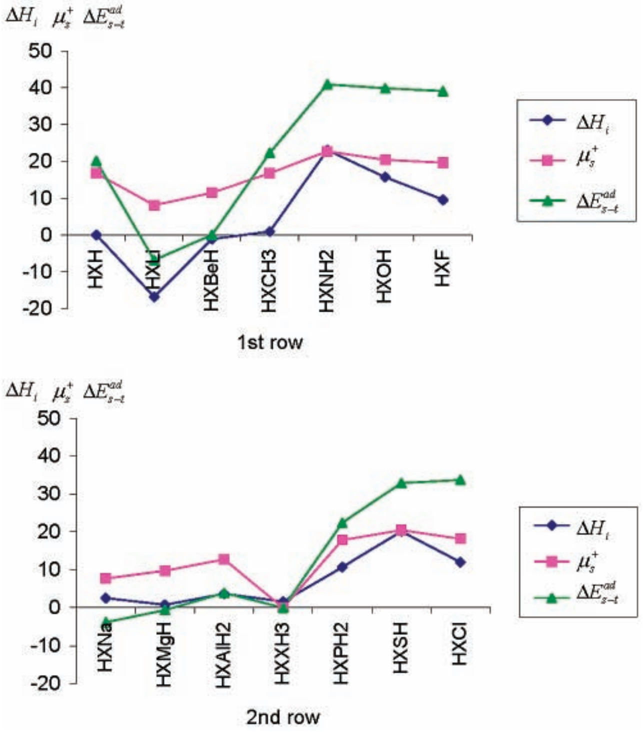


Figure 5. Comparison of the isodesmic reaction energy (ΔH_i) (eq 4) (in kcal/mol), spin potential (μ_s^+) (in 10^{-1} V), and adiabatic singlet−triplet gap $\Delta E_{\text{s-t}}^{\text{ad}}$ (in kcal/mol) in the first and second row substituted silylenes (isodesmic reaction energy taken from ref 29 at the B3LYP/6-31G(d) level).

Figure 7 shows the dependence of the spin-philicity index on the vertical energy gap. As we are interested in the singlet and triplet states, spin-philicities are presented only for molecules with singlet ground state. Although the correlation

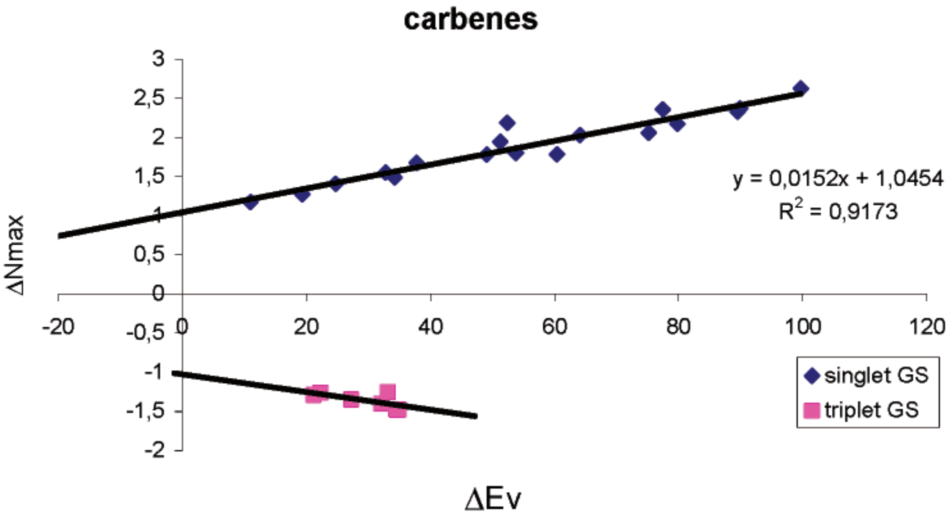


Figure 6. Linear relationship between the maximal spin acceptance $\Delta N^{+}_{S,\max}$(in spins) and the ΔE_{v1} (in kcal/mol) for molecules with singlet ground state and maximal spin release $\Delta N^{-}_{S,\max}$ (in spins) plotted against ΔE_{v2} (in kcal/mol) for molecules with triplet ground state.

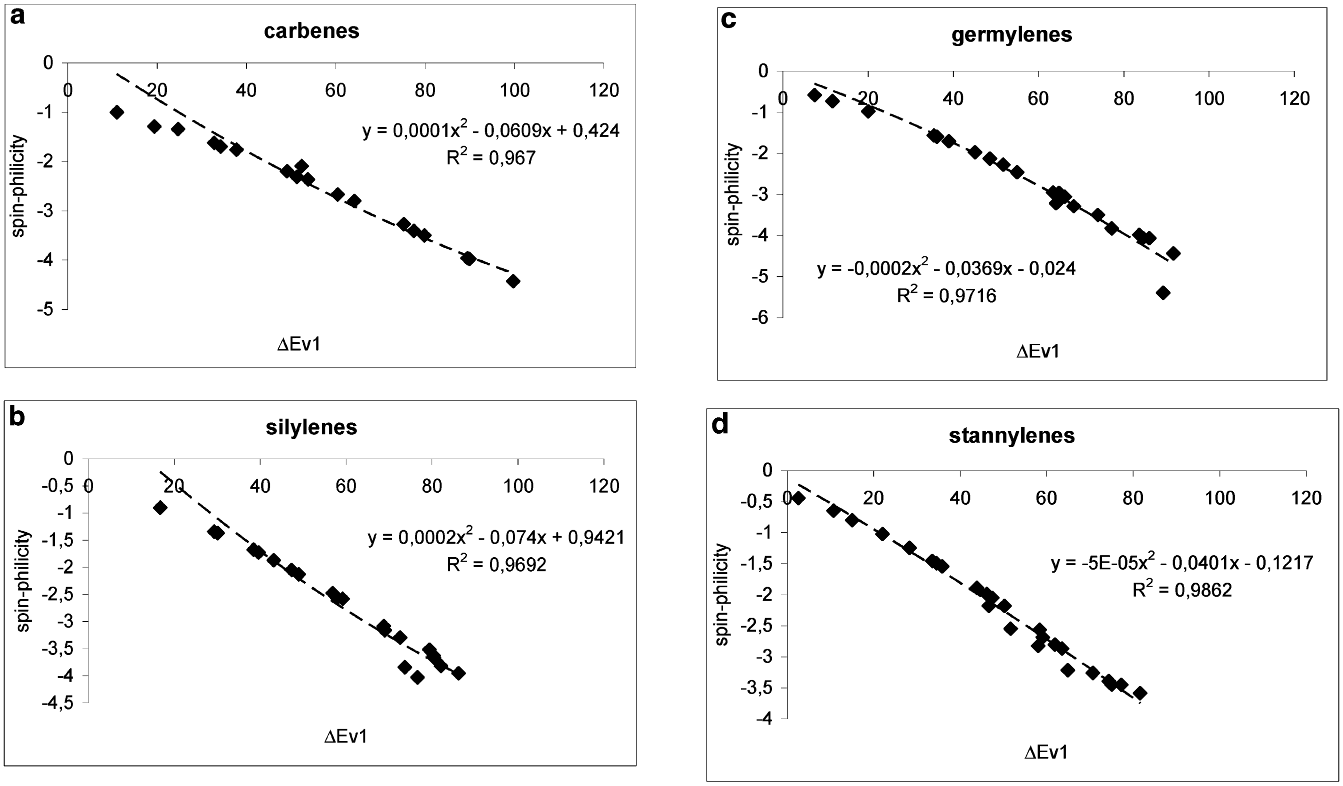


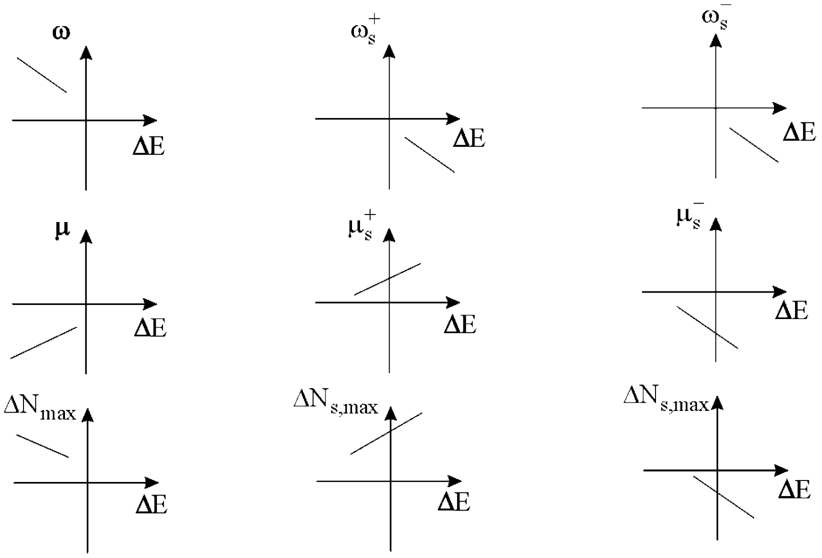
Figure 7. (a, b) Spin-philicities (in eV) plotted against the vertical singlet−triplet gap (in kcal/mol) and the fitted quadratic function for the investigated compounds with singlet ground state. (c, d) Spin-philicities (in eV) plotted against the vertical singlet−triplet gap (in kcal/mol) and the fitted quadratic function for the investigated compounds with singlet ground state.

coefficient of the linear fit is very good ($R^2 = 0.986$ for carbenes, $R^2 = 0.969$ for silylenes, $R^2 = 0.955$ for germylenes, and $R^2 = 0.984$ for stannylenes), one could suggest a quadratic fit based on the behavior of the fitted function near the end points of the range considered. Furthermore, a quadratic dependence of the spin-philicity on the vertical energy is expected on the basis of the formula for spin-philicity (eq 11). From the numerical data presented in Table 1a−d it is obvious that the spin hardness does not change significantly for the different substituents. As a result the spin-philicity is mainly dominated by μ_s^+, calculated in the singlet state, which correlates linearly with the ΔE_v energy difference (eq 6).

The spin-donicity number gives information about the energy changes in the direction of decreasing multiplicity. Since the properties are only computed for ground states, the spin-donicity numbers are only presented in the tables for the compounds with triplet ground state. Most of these molecules belong to the carbenes, therefore the spin-donicity number as a function of the vertical energy is only depicted for the carbenes (Figure 7). (The curve includes those carbenes, as well, whose ground state is singlet, but they are all calculated in the triplet state.) Similarly to the spin-philicity curve, the spin-donicity decreases with the vertical−singlet triplet gap. Note, however, that now the vertical gap is calculated with the triplet state as the reference

CHART 3: Comparison of the Definitions, Defining Equations, Properties of Electrophilicity, Spin-Philicity, and Spin-Donicity Indices As Used in the Present Study

Electrophilicity ω	Spin-philicity ω_s^+	Spin-donicity ω_s^-
$\Delta E = \mu\Delta N + \frac{1}{2}\eta\Delta N^2$	$\Delta E = \mu_s^+\Delta N_s + \frac{1}{2}\eta_{ss}\Delta N_s^2$	$\Delta E = \mu_s^-\Delta N_s + \frac{1}{2}\eta_{ss}\Delta N_s^2$
$\mu < 0 \quad \eta > 0$	$\mu_s^+ > 0 \quad \eta_{ss} < 0$	$\mu_s^- < 0 \quad \eta_{ss} < 0$
$\Delta E_{max} = -\frac{\mu^2}{2\eta} < 0$	$\Delta E_{max} = -\frac{(\mu_s^+)^2}{2\eta_{ss}} > 0$	$\Delta E_{max} = -\frac{(\mu_s^-)^2}{2\eta_{ss}} > 0$
$\omega = \frac{\mu^2}{2\eta} > 0$	$\omega_s^+ = \frac{(\mu_s^+)^2}{2\eta_{ss}} < 0$	$\omega_s^- = \frac{(\mu_s^-)^2}{2\eta_{ss}} < 0$
$\Delta N_{max} = -\frac{\mu}{\eta} > 0$	$\Delta N_{s,max} = -\frac{\mu_s^+}{\eta_{ss}} > 0$	$\Delta N_{s,max} = -\frac{\mu_s^-}{\eta_{ss}} < 0$



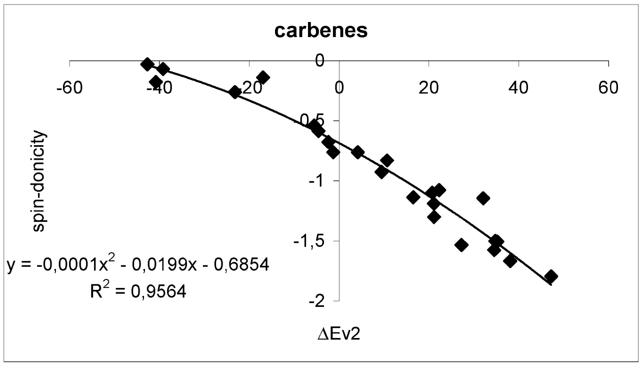


Figure 8. The spin-donicity (in eV) calculated in the triplet state and plotted against the corresponding vertical singlet−triplet gap (in kcal/mol) for the investigated carbenes. The quadratic relationship is shown.

point. A large negative ω_s^- is expected if the vertical gap is large, i.e., much energy is necessary to reach the excited singlet state. The correlation (both of the linear and quadratic fit) for the spin-donicity number curve is much worse than in the case of the spin-philicity powers, which may be explained by the fact that for the majority of the molecules the spin-donicity is calculated in an excited state. If HCNa is excluded from the set, however, a much better correlation is achieved. It is worth noting that the spin-philicity and spin-donicity curves have the same intercept, meaning that they predict the same energy change if the system goes from the triplet state to the singlet state or vice versa if the vertical energy is zero.

It is anticipated that ω_s^+/ω_s^- should be related to the vertical energy, because both of these quantities measure the capability of an agent to accept/donate spins. However, $\Delta E_{v1}/\Delta E_{v2}$ reflects the capability to accept/donate exactly two spins (i.e. the spin of one electron changes), whereas the spin-philicity/spin-donicity index (ω_s^+/ω_s^-) measure the increase of the energy of the ligand due to maximal spin flow between donor and acceptor. The spin change may be either less or more than two. These are values of a similar type as those listed by Parr et al. in the case of the electrophilicity index.[5] They found values slightly less than one for the maximal electron flow. In our case the typical value is around two, which corresponds to the spin change of one electron.

At first sight the energy difference between the corresponding spin states of the molecule may seem to be used for the spin-philicity/spin-donicity index, but the definition ($(\mu_s^\pm)^2/2\eta_{ss}^0$) as in eqs 11 and 12 only pertains the basic quantities governing small changes away from the initial state, the first order $\mu_s^\pm$ and the second-order η_{ss}^0 (as was pointed out by Parr et al. in the case of the electrophilicity index).

In Chart 3 the electrophilicity, spin-philicity, and spin-donicity indices are summarized; the corresponding equations are collected together with the basic quantities. The dependence of these quantities on the energy change of the system is schematically depicted. (ΔE refers to the energy difference between the anion and the neutral molecule ($-$A) in the case of the electrophilicity, and to the energy difference between the singlet and triplet states of the molecule (ΔE_v) in the case of the spin-philicity/spin-donicity indices. ΔE_{max} is the energy change when the ligand acquires ΔN_{max} electrons, and when the spin number change of the molecule is $\Delta N_{S,max}$). All the three indices (ω, ω_s^+, ω_s^-) are based on the same idea: measuring the energy difference in the case of maximal electron/spin flow from the zero potential sea of electrons/spins toward the ligands. All of them decrease if the energy difference between the corresponding states of the molecule increases. As the uptake of electrons from the sea is an energetically favorable process, ΔE is smaller than zero in the case of the electrophilicity index. The spin-philicity and spin-donicity indices refer to an energetically unfavorable process, thus ΔE is larger than zero in those cases. The analysis of ΔN_{max} and $\Delta N_{S,max}$ values shows that in the case of taking up electrons from the sea, the sign of the maximal electron acceptance and the electronic chemical potential is opposite, so ligands with less negative chemical potential will take up fewer electrons from the sea. However, in the case of the spin-philicity and spin-donicity indices $\Delta N_{S,max}$ always has the same sign as the spin potential. As a result molecules with larger ΔE_{v1} (with more stable singlet state) will take up more spins from the "sea of spins" and molecules with larger ΔE_{v2}-(with more stable triplet ground state) will donate more spins to the sea.

4. Conclusion

In the present work spin-related conceptual DFT indices were calculated for a large series of carbenes, silylenes, germylenes, and stannylenes together with the corresponding adiabatic and vertical singlet−triplet energy gaps. It has been shown that the vertical energies correlate linearly with the adiabatic singlet−triplet energy gap. The spin hardness values only slightly change with the different substituents, but increase with the atomic number of the central atom for a given substituent. The spin-philicity and spin-donicity indices are relevant to two neighboring spin states and can describe both ground-state and excited-state properties. It has been shown that both the spin-philicity and spin-donicity indices decrease according to a quadratic function if the energy difference between the corresponding singlet and triplet states increases. The analogy with the electrophilicity index has been discussed in detail and it has been proposed to use $(\mu_s^{\pm})^2/2\eta_{ss}^0$ as the spin-philicity/spin-donicity index similarly to the electrophilicity index. A very good linear correlation has been found between the energy difference estimated on the basis of the sum of the spin potentials and the vertical triplet energy gaps independent of the ground state of the molecule and the atomic number of the central atom. The spin-philicity values can predict the singlet−triplet gaps to a good accuracy, using a quadratic fit, even though a linear correlation already gives quantitative agreement. The maximal spin acceptance and spin release $\Delta N_{S,max}^{\pm}$ values in the case of molecules with large vertical energies may be helpful in the investigation of the spin catalysis phenomenon.

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