

Average local ionization potential within the framework of the electron localization function

Eduardo Chamorro^{a,*}, Patricia Pérez^a, Mario Duque-Noreña^a, Pierre Paul Romagnoli^b, Daniel Pons^b & Mauricio González^c

^aDepartamento de Ciencias Químicas, ^bDepartamento de Matemáticas, ^cDepartamento de Física, Facultad de Ciencias Exactas, Universidad Andres Bello. Avenida República 275, 8370146, Santiago, Chile

Email: echamorro@unab.cl

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In this work we explore new insights arising from simple indices intended to measure the average local vertical ionization energy associated to ELF valence population basins. The model has been computationally tested on simple isothiocyanate compounds (R-N=C=S) revealing that the proposed relationships correctly establish both the inductive and electronegativity effects of electronegative groups along the examined series, i.e., methyl- < germyl- < hydrogen- < acetyl- < chlorodifluoroacetyl-, in agreement with the available experimental observations. The proposed energetical descriptors are expected to contribute to the search of relationships between the spatial topology of electronic populations and energetical aspects of the bonding. The present results enhance the possibility of gaining insight into chemical bonding and reactivity within the ELF topological-defined framework of chemical rationalization.

Keywords: Theoretical chemistry, Ionization potential, Electron localization function, Chemical reactivity, Nucleophilicity, Isothiocyanates, Valence basin populations, Lone pairs

For a representation of an N-electron molecular system given in terms of Hartree-Fock or Kohn-Sham molecular orbitals $\psi_i(\mathbf{r})$ with occupation numbers n_i , the Electron Localization Function (ELF)¹, $\eta(\mathbf{r})$, has been identified as a useful relative indicator of electron pair localization characterizing a given electron density distribution $\rho(\mathbf{r}) = \sum_i^N n_i |\psi_i(\mathbf{r})|^2$.^{1,2} Within the realm of density functional theory (DFT), ELF has been rationalized in terms of comparing the positive-definite local Pauli kinetic energy density of the given system $\tau_P(\mathbf{r})$ and that of Thomas Fermi, $\tau_h(\mathbf{r})$, namely,^{2,3}

$$\eta(\mathbf{r}) = [1 + [\tau_P(\mathbf{r}) / \tau_h(\mathbf{r})]^2]^{-1} \quad \dots (1)$$

where $\tau_P(\mathbf{r}) = \sum_i^N |\nabla \psi_i(\mathbf{r})|^2 - \frac{1}{8} |\nabla \rho(\mathbf{r})|^2 / \rho(\mathbf{r})$ and $\tau_h(\mathbf{r}) = \frac{3}{5} (6\pi^2)^{2/3} \rho(\mathbf{r})^{5/3}$. As is well known, the kernel $\tau_P(\mathbf{r}) / \tau_h(\mathbf{r})$ corresponds to the relative local excess of kinetic energy density related to the Pauli principle while $\eta(\mathbf{r})$ becomes valued in the range [0,1]. The highest values of $\eta(\mathbf{r})$ are thereafter associated to the spatial positions \mathbf{r} with more localized electrons (as compared to the arbitrarily chosen uniform electron gas reference).^{2,3} The topological analysis of $\eta(\mathbf{r})$, performed through the

examination of the critical points of its gradient vector field $\nabla \eta(\mathbf{r})$, provides a division of the molecular space into basins of attractors that are (empirically) associated with chemically meaningful concepts such as atomic cores, bonds, lone pairs, atomic shells and other elements of chemical bonding.^{4,5} Both single-determinantal and correlated wavefunctions can be analyzed using extended formulations of the electron localization function.^{6,7} Complete descriptions concerning the language associated with the topological analysis of ELF have been presented elsewhere.^{4,5,8} Here we would like just to mention that valence basins are classified in terms of the so-called synaptic order (i.e., the number of core basins with which they share a boundary), providing a useful way to rationalize multicenter bonds.⁵

Although the formal physical meaning of an ELF basin is still unclear,^{9,10} there exist computational evidence supporting the usefulness of a topological-based population analysis resulting from the integration of the electron density in ELF basins (i.e., electronic basin populations) in order to get a deeper understanding about the nature of chemical bonding. Moreover, the integration of the two-electron density probabilities in the ELF basins

constitutes the basis for the definition of variance-related indices,^{11,12} providing useful tools to rationalize electron delocalization in several molecular systems. However, it should be always cautioned that (formally) the electronic basin population characterizes only the spatial organization of the bonding in terms of the electron pair localization, an aspect that has certainly received a great deal of attention. The search for correlations between such a spatial organization and electronic population analysis based on molecular orbital formalisms,^{9,10,13-17} or even with energetical aspects of the bonding, remains an open problem within this field. Within our ongoing interests in the development and application of reactivity descriptors in a framework based on topological partitions of molecular space,¹⁸⁻²⁶ we herein present results from a computational exploration of a tool devised to approach the average vertical ionization energy characterizing a given electronic basin ELF population. As is well known, ionization potential is a ubiquitous key quantity driven by many global and local DFT-based chemical reactivity descriptors,²⁷⁻³¹ inherently connected to the above general goal in this field. Our aim in this work is to contribute to the association of topological populations with energy-related quantities.

Within the framework of validity/suitability of using orbital energies (e.g., from Hartree-Fock or Kohn-Sham representations)³²⁻³⁴ for describing ionization energies in a molecular system (i.e., $I_i \sim |\varepsilon_i|$), the average per-electron-local ionization energy at spatial point \mathbf{r} , $\bar{I}(\mathbf{r})$, has been introduced by Politzer and co-workers^{35,36} in terms of the single-particle energy density of orbital i , $\varepsilon_i \rho_i(\mathbf{r})$, and the total electron density $\rho(\mathbf{r})$, Eq. (2),

$$\bar{I}(\mathbf{r}) = \sum_i^{occ} \frac{|\varepsilon_i| \rho_i(\mathbf{r})}{\rho(\mathbf{r})} \quad \dots (2)$$

This quantity has emerged as a useful tool for chemical reactivity³⁶⁻⁴⁰ because it can be useful to reveal the most labile or reactive electronic sites (i.e., those with the lowest values of $\bar{I}(\mathbf{r})$) to participate in processes involving interactions with electrophile or radical species.^{35,36} The average local ionization potential has been related to concepts such as local electronic temperatures (i.e., kinetic energy densities), atomic shell structures, electronegativity, local polarizability, hardness, and electrostatic potential.^{38,41-44} In studying reactivity trends, $\bar{I}(\mathbf{r})$ is usually computed on a chosen surface (S) defined to be the 0,001-0,002 au (electrons/bohr³) contour of

$\rho(\mathbf{r})$, i.e., $\bar{I}_S(\mathbf{r})$ ^{36,37}. Although the analysis of local properties on molecular surfaces is appealing,³⁷ it loses a direct connection with typical concepts entering into the analysis/rationalizing of chemistry in terms of bonding and non-bonding regions.^{2,3,8} The topological analysis of ELF provides just such a chemical significant framework. In the present work, we explore a slightly modified approximation based on Eq. (2) within the context of the division of molecular regions in basins of attractors provided by the topological analysis of the electron localization function of Eq. (1). Our aim is to contribute to the field of chemical reactivity by exploring the usefulness of energetical-based indices associated with electronic topological-defined ELF populations characterizing the spatial organization of the bonding as described by the electron localization function.

Theoretical Model

Let us consider a simple approximation to Eq. (2) within a 3D-grid resolution.^{45,46} It follows that a condensed-to-basin average intrinsic vertical ionization potential \bar{Y}_Ω can be approximated simply as,

$$\bar{Y}_\Omega \equiv \sum_i^{occ} \frac{|\varepsilon_i| g_i \bar{N}_{i,\Omega}}{\bar{N}_\Omega} \quad \dots (3)$$

where

$$\bar{N}_{i,\Omega} = \int_\Omega \rho_i(\mathbf{r}) d\mathbf{r}, \text{ and } \bar{N}_\Omega = \int_\Omega \rho(\mathbf{r}) d\mathbf{r} \quad \dots (4)$$

Note that we have introduced a weighting factor, g_i , accounting for the relative probability of occurrence of the contributing $\bar{N}_{i,\Omega}$ population associated with a given energy-state, ε_i , into the topologically-defined basin. The introduction of a weighting factor is justified because whereas basins are determined from the complete (all-electron) density, the core-valence separation is indeed artificial (i.e., ‘core’ electrons and ‘valence’ electrons can delocalize on any region of molecular space).⁴⁷⁻⁴⁹

Thereafter, within a framework representation of HF/KS molecular orbitals (MO) $\psi_i(\mathbf{r})$ expressed in terms of a linear combination of N_b basis functions $\{\chi_\mu(\mathbf{r})\}$, the basin populations can be indeed expressed as a sum of contributions arising from the different occupied electronic states represented by each MO, Eq. (5),^{11,12,46}

$$\bar{N}_\Omega = \sum_i^{occ} \bar{N}_{i,\Omega} = \sum_i^{occ} n_i \sum_\mu^{N_b} \sum_\nu^{N_b} c_\mu^i c_\nu^i S_{\mu\nu,\Omega} \quad \dots (5)$$

where c_μ^i are the eigenvectors of $\psi_i(\mathbf{r})$ and $S_{\mu\nu,\Omega}$ is the overlap matrix elements, i.e.,

$$S_{\mu\nu,\Omega} \equiv \int_\Omega \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) d\mathbf{r} \quad \dots (6)$$

It is clear that several possibilities can be considered to set the relative probabilities g_i in the model Eq. (3). Considering that we are concerned with detachment energies, a simple reasonable first ansatz approximation to deal with such weighting factor is given by Eq. (7),

$$g_i \equiv \frac{e^{-|\varepsilon_i|}}{\sum_i^{occ} e^{-|\varepsilon_i|}} \quad \dots (7)$$

The model proposed in Eq. (3) can be regarded simply as an intrinsic shape factor characterizing the propensity to vertical ionization from a given basin. Under this type of approximation the core molecular orbitals (i.e., those associated to the inner atomic shells) will become 'naturally' quenched within the reactivity analysis. Furthermore, we can even gain a proper measure of the average vertical ionization potential of basins associated exclusively to the valence molecular orbitals, when summation in Eq. (3) excludes all core molecular orbitals without weighting, i.e.,

$$\bar{I}_\Omega \approx \sum_{i \in val}^{occ} \frac{|\varepsilon_i| \bar{N}_{i,\Omega}}{\bar{N}_\Omega} \quad \dots (8)$$

Note that \bar{Y}_Ω can be regarded mostly as an intramolecular descriptor, whereas \bar{I}_Ω is suited to intermolecular analysis. In order to explore the suitability of the proposed models (i.e., Eqs (3) and (8)), we have chosen the recently reported chlorodifluoroacetyl isothiocyanate system⁵⁰, $\text{ClF}_2\text{CC}(\text{O})\text{-N}=\text{C}=\text{S}$ (**1**), and some of its well known simple analogues, namely, $\text{H-N}=\text{C}=\text{S}$ (**2**)⁵¹, $\text{H}_3\text{C-N}=\text{C}=\text{S}$ (**3**)⁵², $\text{H}_3\text{Ge-N}=\text{C}=\text{S}$ (**4**)⁵², $\text{H}_3\text{C-C}(\text{O})\text{-N}=\text{C}=\text{S}$ (**5**)^{53,54} as test examples of a rich bonding pattern (i.e., single, double, and lone pair regions) with significant spectroscopic and electronic properties^{50,53,54} that have found several applications in medicinal/biological, pharmaceutical and industrial chemistry frameworks.⁵⁵⁻⁵⁷

Computational Details

All geometry and energetic characterizations for the isothiocyanates (**1**)-(**5**) were performed at the B3LYP/6-311+G(d) level of theory using the Gaussian 09 series of programs (G09).⁵⁸ The interpretation (and outcomes) of the KS orbital energies as approximate vertical ionization potentials is well known.³²⁻³⁴ Since our interest is the qualitative analysis of reactivity trends, the selected DFT level is sufficiently suitable. Each stationary structure was characterized as a minimum by analytical frequency calculations. In the case of molecular systems (**1**) and (**5**) we have focused only on the gauche-syn configurations which are energetically favored. The average basin ionization potential indicator represented in Eqs (3) and (8) were implemented into the rho_int.f routine of the top_mod 09 package of programs⁴⁶ which enables the ELF topological analysis for molecular densities expressed in terms of gaussian primitive functions, read from G09 WFN formatted files. The topological analysis of ELF has been performed using 3-D grid specifications that guarantee a 0.05 bohr mesh size, as recommended for numerical analysis of topologically-defined valence regions. Visualization was performed using the VMD package.⁵⁹

Results and Discussion

Experimental vertical ionization energies for isothiocyanates (**1**)-(**5**) available in the recent literature from photoelectron spectrum determinations and are summarized here in Table 1. Within a molecular orbital description, these vertical ionization energies have been associated with the ejection of electrons formally located at the highest occupied molecular orbital (HOMO), associated with the sulfur lone-pair electrons. In such frameworks interpretation of the experimental photoelectron spectrum are performed by using comparative results of analogue molecules and/or using high level theoretical determinations as those based on Outer Valence Green's Functions (OVGF) methodologies. The

Table 1—Experimental first vertical ionization potential for isothiocyanates studied in this work

No.	Isothiocyanate	<i>I</i> (eV)	Ref.
1	$\text{ClF}_2\text{C}(\text{O}=\text{C})\text{-C}=\text{N}=\text{S}$	10.43	50
2	$\text{H-C}=\text{N}=\text{S}$	9.94	60
3	$\text{H}_3\text{C-C}=\text{N}=\text{S}$	9.37	60
4	$\text{H}_3\text{Ge-C}=\text{N}=\text{S}$	9.14	60
5	$\text{H}_3\text{C}(\text{O}=\text{C})\text{-C}=\text{N}=\text{S}$	9.75	54

topological partition of the molecular space in basins of attractors yields a division of molecular space in core and valence (both bonding and non-bonding) basins that represents, within a chemical viewpoint, a convenient and unified framework for studying the nature of bonding and reactivity. The topology of the corresponding localization basins (as calculated at the $\text{ELF} = 0.82$ isosurface) for the five isothiocyanates studied here is presented in Fig. 1(a-e), including the numbering of spatial localization of associated ELF attractors (maxima). Naturally, it can be noted that a consistent picture of the $-\text{N}=\text{C}=\text{S}$ valence bonding can be drawn from the ELF analysis, i.e., two monosynaptic basins associated with the sulphur center $V(\text{S})$, one monosynaptic basin associated with the nitrogen center and two disynaptic basins $V(\text{N},\text{C})$ and $V(\text{C},\text{S})$, associated with the allenic-type bonding

between the central carbon center and the nitrogen and sulphur centers, respectively. Chemical substitution does not change the topological pattern at the $-\text{N}=\text{C}=\text{S}$ fragment, except in the case of compound (3) where the monosynaptic valence nitrogen basin merges with the disynaptic basin expected between the metallic and nitrogen centers. In such a case, the merged region localizes to 4.01 electrons. Table 2 reports the average ELF basin (Ω) electron populations \bar{N}_Ω (e), the average vertical ionization potentials \bar{I}_Ω (eV), and the intrinsic shape for ionization \bar{Y}_Ω (eV) for isothiocyanates (1)-(5), respectively. It can be immediately observed that the lowest ionization energy is correctly predicted (in all cases) to be associated with the electron populations corresponding to the monosynaptic basins identified as the sulphur lone-pair region, $V(\text{S})$. Note also from

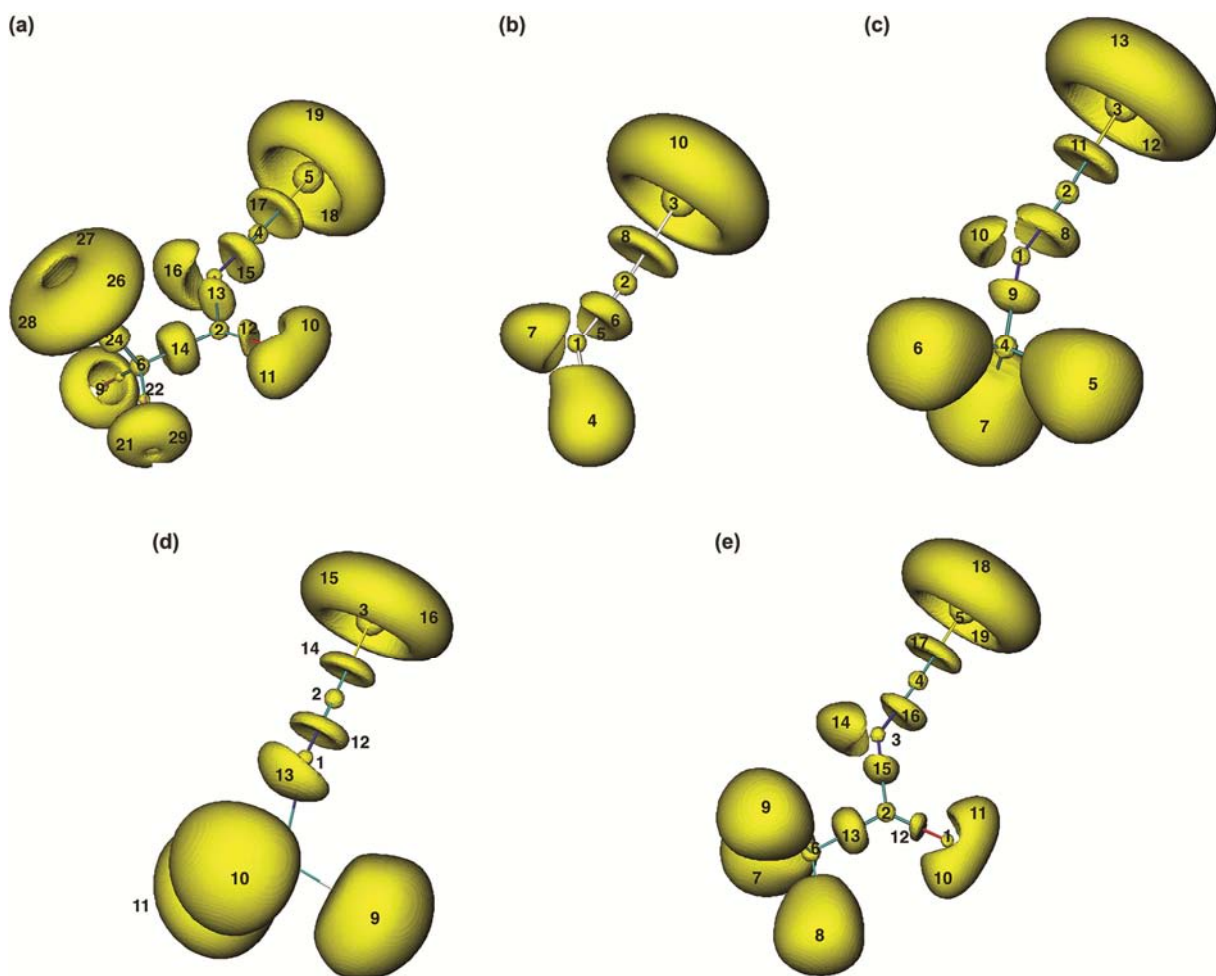


Fig. 1—Electron localization function (ELF) basins topology (as evaluated at the $\text{ELF} = 0.82$ isosurface) for (a) chlorodifluoroacetyl isothiocyanate (1), (b) thiocyanic acid (2), (c) methyl isothiocyanate (3), (d) germyl isothiocyanate (4), and (e) acetyl isothiocyanate (5). [Representations are obtained from the optimized wavefunction at the B3LYP/6-311+G(d) level of theory. Numbering and spatial position of ELF attractors in each basin is indicated as reported in Table 2].

Table 2—Average ELF basin (Ω) electron populations \bar{N}_Ω (e), average vertical ionization potentials \bar{I}_Ω (eV), and intrinsic shape for ionization \bar{Y}_Ω (eV), for isothiocyanates (1)–(5), evaluated at the B3LYP/6-311+G(d) level of theory. [Boldface data correspond to the isothiocyanate fragment -C=N=S; C(X) represents a monosynaptic core basin for atomic center X; V(X,Y) represents a disynaptic valence basin associated to the bonding interatomic region between X and Y centers]

No.	ELF basin (Ω)	\bar{N}_Ω (e)	\bar{I}_Ω (eV)	\bar{Y}_Ω (eV)	No.	ELF basin (Ω)	\bar{N}_Ω (e)	\bar{I}_Ω (eV)	\bar{Y}_Ω (eV)
<i>Chlorodifluoroacetyl isothiocyanate (1)</i>					<i>Germyl isothiocyanate (4)</i>				
1	C(O)	2.12	--	--	1	C(N)	2.11	--	--
2	C(C1)	2.09	--	--	2	C(C)	2.09	--	--
3	C(N)	2.11	--	--	3	C(S)	10.04	--	--
4	C(C2)	2.09	--	--	4	C(Ge)	10.73	--	--
5	C(S)	10.04	--	--	5	C(Ge)	3.82	--	--
6	C(C3)	2.09	--	--	6	C(Ge)	4.09	--	--
7	C(Cl)	10.05	--	--	7	C(Ge)	4.22	--	--
8	C(F1)	2.14	--	--	8	C(Ge)	4.82	--	--
9	C(F2)	2.13	--	--	9	V(H1,Ge)	2.12	10.72	0.81
10	V(O)	2.59	14.96	0.57	10	V(H2,Ge)	2.12	10.71	0.81
11	V(O)	2.59	14.99	0.57	11	V(H3,Ge)	2.13	10.66	0.81
12	V(O,C1)	2.54	19.44	0.62	12	V(N,C)	3.53	16.40	0.98
13	V(C1,N)	2.03	18.47	0.63	13	V(N)	4.01	13.26	0.90
14	V(C1,C3)	2.31	17.52	0.62	14	V(C,S)	2.87	14.41	0.94
15	V(N,C2)	3.05	18.21	0.62	15	V(S)	2.63	10.38	0.78
16	V(N)	2.51	14.35	0.56	16	V(S)	2.65	10.39	0.78
17	V(C2,S)	3.11	15.73	0.59					
18	V(S)	2.49	11.96	0.52	<i>Acetyl isothiocyanate (5)</i>				
19	V(S)	2.51	11.96	0.52	1	C(O)	2.12	--	--
20	V(F2)	3.97	18.74	0.61	2	C(C1)	2.09	--	--
21	V(C3,F1)	2.62	18.69	0.61	3	C(N)	2.11	--	--
22	V(C3,F1)	1.14	22.81	0.65	4	C(C2)	2.09	--	--
23	V(C3,F2)	2.64	18.69	0.61	5	C(S)	10.04	--	--
24	V(C3,Cl)	1.57	17.59	0.61	6	C(C3)	2.09	--	--
25	V(C3,F2)	1.10	22.73	0.65	7	V(H1,C3)	1.96	13.94	0.86
26	V(Cl)	2.15	13.17	0.54	8	V(H2,C3)	2.00	13.81	0.85
27	V(Cl)	2.34	13.17	0.54	9	V(H3,C3)	1.96	13.94	0.86
28	V(Cl)	1.92	13.14	0.54	10	V(O)	2.59	14.17	0.81
29	V(F1)	3.96	18.72	0.61	11	V(O)	2.62	14.14	0.81
					12	V(O,C1)	2.48	18.65	0.89
<i>Thiocyanic acid (2)</i>					13	V(C1,C3)	2.13	15.62	0.88
1	C(N)	2.11	--	--	14	V(N)	2.51	13.62	0.80
2	C(C)	2.09	--	--	15	V(C1,N)	1.93	17.45	0.90
3	C(S)	10.04	--	--	16	V(N,C2)	3.14	17.42	0.89
4	V(H,N)	1.89	16.93	1.79	17	V(C2,S)	3.03	15.11	0.85
5	V(N,C)	1.63	17.01	1.72	18	V(S)	2.54	11.29	0.73
6	V(N,C)	1.63	17.01	1.72	19	V(S)	2.55	11.29	0.73
7	V(N)	2.49	12.99	1.54					
8	V(C,S)	2.93	14.87	1.65					
9	V(S)	2.58	10.92	1.40					
10	V(S)	2.58	10.91	1.40					
<i>Methyl isothiocyanate (3)</i>									
1	C(N)	2.11	--	--					
2	C(C1)	2.09	--	--					
3	C(S)	10.04	--	--					
4	C(C2)	2.09	--	--					
5	V(H1,C2)	2.00	14.30	1.22					
6	V(H2,C2)	2.00	14.30	1.22					
7	V(H3,C2)	2.00	14.30	1.22					
8	V(N,C1)	3.74	16.48	1.22					
9	V(N,C2)	1.81	17.07	1.28					
10	V(N)	1.92	13.40	1.12					
11	V(C1,S)	2.87	14.39	1.18					
12	V(S)	2.65	10.34	0.98					
13	V(S)	2.65	10.34	0.98					

the \bar{I}_Ω values that the predicted ordering for feasibility of ejecting electrons from the isothiocyanate fragment is $V(S) > V(N) > V(S,C) > V(C,N)$ and is in good qualitative agreement with the experimentally available evidence.^{50,53,54,60} Further, as compared to the hydrogen substitution in (3), electron releasing groups (i.e., H_3C- and H_3Ge-) will exhibit an increased $V(S)$ basin population with lower ionization energies. On the other hand, electron withdrawing substituents at the nitrogen center (i.e., systems (1) and (5)), reveal a decreased $V(S)$ population with higher ionization values. The above results emphasize that the model relationships proposed in Eqs (3) and (8) give correct results for the average vertical ionization potential, both the inductive and electronegativity effects of electronegative groups along the series, i.e., methyl- < germyl- < hydrogen- < acetyl- < chlorodifluoroacetyl-, in agreement with the available experimental observations.^{50,53,54,60}

Conclusions

This work focuses on a simple computationally oriented testing of the models given in Eqs (3)-(8) to represent the vertical ionization potential of electron populations associated with the topologically defined localization basins of the electron localization function. Equations (3) and (8) are based on the original ideas introduced by Politzer and co-workers,³⁶ which have proved to be useful within the framework of analyzing several aspects of global (i.e., thermodynamic) and local (i.e., selectivity) reactivity.³⁶ Within such a goal, the condensed-to-basin model approximation introduced in this work can be inherently associated to represent just vertical ionization potentials associated to lone pairs and bonding regions in chemistry. Despite the several approximations behind application of Eq. (3) (within the framework of topological-defined electron localization regions using 3D-grid representations^{45,46}) the above results on isothiocyanates systems (1)-(5) correctly predict the experimental trends.^{50,53,54,60} Reactivity models based on both Eqs (3) and (8) can be regarded as useful tools that contribute to the field of searching suitable correlations between the spatial topology of electronic populations and energetical aspects of the bonding.

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References

- 1 Becke A D & Edgecombe K E, *J Chem Phys*, 92 (1990) 5397.
- 2 Savin A, Becke A D, Flad J, Nesper R, Preuss H & Vonschnering H G, *Angew Chem Int Ed*, 30 (1991) 409.
- 3 Savin A, Nesper R, Wengert S & Fassler T F, *Angew Chem Int Ed*, 36 (1997) 1809.
- 4 Savin A, Silvi B & Colonna F, *Can J Chem*, 74 (1996) 1088.
- 5 Silvi B, *J Mol Struct*, 614 (2002) 3.
- 6 Matito E, Silvi B, Duran M & Sola M, *J Chem Phys*, 125 (2006).
- 7 Feixas F, Matito E, Duran M, Sola M & Silvi B, *J Chem Theory Comput*, 6 (2010) 2736.
- 8 Silvi B & Savin A, *Nature*, 371 (1994) 683.
- 9 Savin A, *J Chem Sci*, 117 (2005) 473.
- 10 Savin A, *J Mol Struct THEOCHEM*, 727 (2005) 127.
- 11 Ponc R & Chaves J, *J Comput Chem*, 26 (2005) 1205.
- 12 Ayers P W, *J Chem Sci*, 117 (2005) 441.
- 13 Chesnut D B, *Chem Phys*, 271 (2001) 9.
- 14 Poater J, Sola M, Duran M & Fradera X, *Theor Chem Acc*, 107 (2002) 362.
- 15 Silvi B, Fourre I & Alikhani M E, *Mon Chem*, 136 (2005) 855.
- 16 Chamorro E, Santos J C, Gomez B, Contreras R & Fuentealba P, *J Phys Chem A*, 106 (2002) 11533.
- 17 Silvi B, *Phys Chem Chem Phys*, 6 (2004) 256.
- 18 Vegas A, Notario R, Chamorro E, Perez P & Liebman J F, *Acta Crystallogr, Sect B: Struct Sci*, 69 (2013) 163.
- 19 Chamorro E, Perez P & Domingo L R, *Chem Phys Lett*, 582 (2013) 141.
- 20 Chamorro E, Duque-Norena M, Notario R & Perez P, *J Phys Chem A*, 117 (2013) 2636.
- 21 Domingo L R, Chamorro E & Perez P, *Org Biomol Chem*, 8 (2010) 5495.
- 22 Tiznado W, Chamorro E, Contreras R & Fuentealba P, *J Phys Chem A*, 109 (2005) 3220.
- 23 Chamorro E, Notario R, Santos J C & Perez P, *Chem Phys Lett*, 443 (2007) 136.
- 24 Chamorro E, Duque M, Cardenas C, Santos C, Tiznado W & Fuentealba P, *J Chem Sci*, 117 (2005) 419.
- 25 Chamorro E, Fuentealba P & Savin A, *J Comput Chem*, 24 (2003) 496.
- 26 Chamorro E, *J Chem Phys*, 118 (2003) 8687.
- 27 Geerlings P, De Proft F & Langenaeker W, *Chem Rev*, 103 (2003) 1793.
- 28 Chattaraj P K, Sarkar U & Roy D R, *Chem Rev*, 106 (2006) 2065.
- 29 Chamorro E, Chattaraj P K & Fuentealba P, *J Phys Chem A*, 107 (2003) 7068.
- 30 Parr R G & Chattaraj P K, *J Am Chem Soc*, 113 (1991) 1854.
- 31 Ayers P W, Anderson J S M & Bartolotti L J, *Int J Quant Chem*, 101 (2005) 520.

- 32 Chong D P, Gritsenko O V & Baerends E J, *J Chem Phys*, 116 (2002) 1760.
- 33 Zhan C G, Nichols J A & Dixon D A, *J Phys Chem A*, 107 (2003) 4184.
- 34 Zhang G & Musgrave C B, *J Phys Chem A*, 111 (2007) 1554.
- 35 Murray J S, Seminario J M, Politzer P & Sjoberg P, *Int J Quant Chem* (1990) 645.
- 36 Politzer P, Murray J S & Bulat F A, *J Mol Model*, 16 (2010) 1731.
- 37 Bulat F A, Toro-Labbe A, Brinck T, Murray J S & Politzer P, *J Mol Model*, 16 (2010) 1679.
- 38 Bulat F A, Levy M & Politzer P, *J Phys Chem A*, 113 (2009) 1384.
- 39 Politzer P, Murray J S & Concha M C, *Int J Quant Chem*, 88 (2002) 19.
- 40 Murray J S, Brinck T, Grice M E & Politzer P, *THEOCHEM*, 88 (1992) 29.
- 41 Politzer P, Shields Z P-I, Bulat F A & Murray J S, *J Chem Theory Comput*, 7 (2011) 377.
- 42 Jin P, Murray J S & Politzer P, *Int J Quant Chem*, 106 (2006) 2347.
- 43 Politzer P, Murray J S & Grice M E, *Collect Czech Chem Commun*, 70 (2005) 550.
- 44 Chattaraj P K, Chamorro E & Fuentealba P, *Chem Phys Lett*, 314 (1999) 114.
- 45 Soler P, Fuster F & Chevreau H, *J Comput Chem*, 25 (2004) 1920.
- 46 Noury S, Krokidis X, Fuster F & Silvi B, *Comput Chem*, 23 (1999) 597.
- 47 Kohout M & Savin A, *Int J Quant Chem*, 60 (1996) 875.
- 48 Kohout M & Savin A, *J Comput Chem*, 18 (1997) 1431.
- 49 Kohout M, Wagner F R & Grin Y, *Theor Chem Acc*, 108 (2002) 150.
- 50 Ramos L A, Ulic S E, Romano R M, Vishnevskiy Y V, Mitzel N W, Beckers H, Willner H, Tong S R, Ge M & Della Vedova C O, *J Phys Chem A*, 117 (2013) 5597.
- 51 Pasinszki T, Kishimoto N & Ohno K, *J Phys Chem A*, 103 (1999) 9195.
- 52 Zheng C, Guirgis G A, Deeb H & Durig J R, *J Mol Struct*, 829 (2007) 88.
- 53 Ramos L A, Ulic S E, Romano R M, Beckers H, Willner H & Della Vedova C O, *J Phys Chem A*, 118 (2014) 697.
- 54 Zeng X-Q, Yao L, Ge M-F & Wang D-X, *J Mol Struct*, 789 (2006) 92.
- 55 Minarini A, Milelli A, Fimognari C, Simoni E, Turrini E & Tumiatti V, *Expert Opin Drug Metab Toxicol*, 10 (2014) 25.
- 56 Gerhauser C, *Top Curr Chem*, 329 (2013) 73.
- 57 Zhang Y S, *Mutat Res-Fundam Mol Mech Mutagen*, 555 (2004) 173.
- 58 Gaussian09; (Gaussian, Inc., Wallingford, CT) 2009.
- 59 Humphrey W, Dalke A & Schulten K, *J Mol Graphics Model*, 14 (1996) 33.
- 60 Craddock S, Ebsworth E A & Murdoch J D, *J Chem Soc Faraday Trans II*, 68 (1972) 86.