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A comparative analysis of the electrophilicity of organic molecules between the computed IPs and EAs and the HOMO and LUMO energies

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Abstract

The electrophilicity index, ω , of a series of substituted ethylenes used in some relevant organic reactions has been evaluated from the ionization potential (IP) and the electron affinity (EA) computed by vertical ionization at the B3LYP/aug-cc-PVTZ level. The corresponding electrophilicity values are well correlated with those obtained from the HOMO and LUMO energies of the neutral molecules. The good linear correlation found between $\omega(I,A)$ and $\omega(H,L)_{LBS}$, and between $\omega(H,L)_{LBS}$ and $\omega(H,L)_{SBS}$ allows to confirm the use of the easily available B3LYP/6-31G* HOMO and LUMO energies to obtain reasonable values of the global electrophilicity index of organic molecules. © 2007 Elsevier B.V. All rights reserved.

1. Introduction

The study of polar processes involving the interaction of electrophiles and nucleophiles may be significantly facilitated if reliable scales of electrophilicity/nucleophilicity are available. The usefulness of such global reactivity scales is of great importance to answer some fundamental questions in organic chemistry such as if a reaction is feasible, whether or not a given reaction will take place and other mechanistic considerations as if the bond formation or bond breaking are stepwise or concerted pathway. An excellent source that illustrates well this concept is the review work recently published by Mayr and Ofial [1]. From long years, Mayr and Patz [2] have devoted to construct reactivity scales through linear free energy relationships. Their model includes the experimental rate constants, and the nucleophilic and the electrophilic parameters [3]. They have had successful not only allowing

to determine whether a certain reaction is likely to take place, but also determining reaction mechanisms and regio- and stereoselectivity [4]. The development of nucleophilicity/electrophilicity theoretical scales based on reactivity indexes, on the other hand, is also desirable as a validation of the experimental scales. The theoretical reactivity scales in addition, could be used to project the global reactivity on particular regions of the molecule. A selectivity model has been recently discussed in electrophile–nucleophile interactions [5,6]. In a recent review, Houk et al. [7] have showed the usefulness of the conceptual density functional theory [8] (DFT) for predicting reactivity and regioselectivity on Diels–Alder and 1,3-dipolar cycloaddition reactions.

One of the forms to model the electrophilicity concept using the electronic structure of molecules have been those based on Parr et al.'s definition of global electrophilicity, ω [9]. The Parr's electrophilicity scales have proved to be applicable for a large number of organic molecules involved in relevant organic reactions such as Diels–Alder reactions [5], 1,3-dipolar cycloadditions [10] or Michael additions [11]. In some cases, for which experimental rate constants were available, a good correlation between

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reactivity and the electrophilicity index was found [10]. The quality of the electrophilicity index to study organic reactions has been widely discussed in Ref. [6]. In all these cases, the ω indexes were computed from the HOMO and LUMO one-electron energies at the ground state of the molecules using the hybrid B3LYP functional together with the standard 6-31G* basis set (SBS). In Parr's Letter [9], the ω values of a series of atoms and small molecules were calculated from the experimental ionization potentials (IP) and electron affinities (EA). Therefore, it would be desirable to have an electrophilicity scale of organic molecules obtained from their experimental IPs and EAs in order to prove those theoretical electrophilicity scales obtained from the HOMO and LUMO energies. However, experimental data of EAs of organic molecules are not frequently available, and in consequence, we need to approach these data through computational methods.

In the present Letter, the electrophilicity index, ω , of a series of 25 substituted ethylenes frequently used in some relevant organic reactions is evaluated from the IP and EA values computed by vertical ionization at the B3LYP/aug-cc-pVTZ level. Therefore, the corresponding electrophilicity values, $\omega(I,A)$, are correlated with those obtained from the HOMO and LUMO energies of the neutral molecules, $\omega(H,L)$. Finally, the dependence of the $\omega(H,L)$ of the basis set is discussed.

2. Computational methods and models

For this study, we have selected a series of 25 ethylene derivatives of increased electrophilicity values. A schematic representation of the structure of these 25 molecules is given in Chart 1. The geometries of these molecules were optimized using the hybrid B3LYP [12,13] functional together with the large aug-cc-pVTZ correlation-consistent basis set (LBS) [14,15]. The energies, $E(M^+)$ and $E(M^-)$, of the ionic states of each molecule M were calculated at the B3LYP/aug-cc-pVTZ level using the optimized geometries of the neutral molecules. The $IP = E(M^+) - E(M)$ and the $EA = E(M) - E(M^-)$ values determined by these DFT energies are the computed vertical ionization potentials and the vertical electron affinities from the bottom of the potential well of the neutral species, respectively [16].

The global electrophilicity index ω , which measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment, has been given the following simple expression [9]:

$$\omega = \frac{\mu^2}{2\eta} \quad (1)$$

in terms of the electronic chemical potential μ and the chemical hardness η . The natural way to approximate the μ and η in DFT is evaluating directly from the IP and EA energies:

$$\mu = -(\text{IP} + \text{EA})/2, \quad (2)$$

$$\eta = \text{IP} - \text{EA}. \quad (3)$$

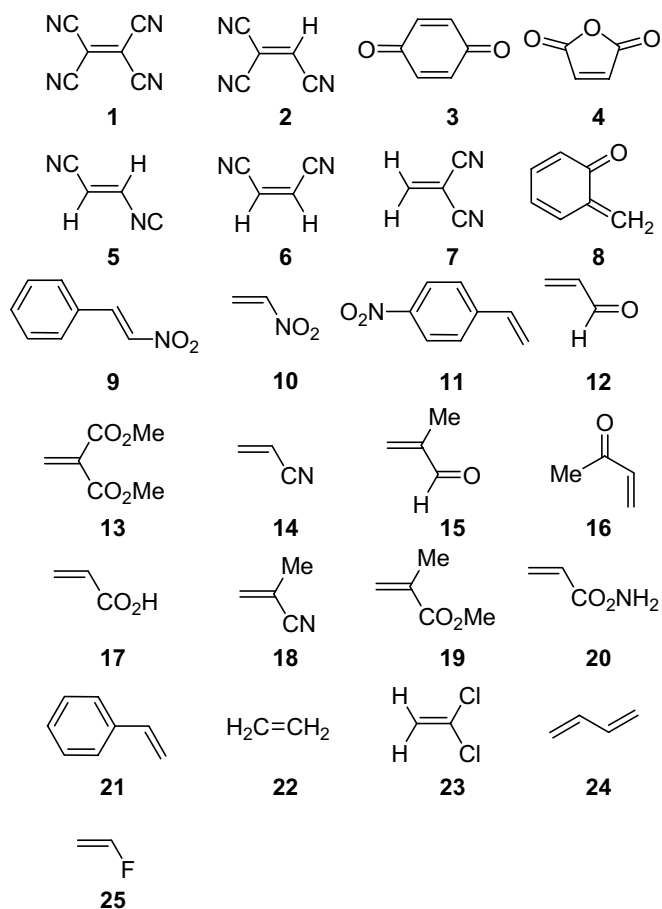


Chart 1.

An alternative DFT approximation, arises from Koopmans's theorem [17]:

$$\mu = (\varepsilon_H + \varepsilon_L)/2, \quad (4)$$

$$\eta = (\varepsilon_L - \varepsilon_H), \quad (5)$$

where ε_H and ε_L correspond to the Kohn–Sham [18] one-electron eigenvalues associated to the frontier molecular orbital HOMO and LUMO, respectively.

The electrophilicity index encompasses both, the propensity of the electrophile to acquire an additional electronic charge driven by μ^2 (the square of electronegativity) and the resistance of the system to exchange electronic charge with the environment described by η , simultaneously. A good electrophile is, in this sense, characterized by a high value of μ and a low value of η .

3. Results and discussion

3.1. DFT evaluation of the ionization potential and electron affinity

The performance on the computation of the IPs and EAs values for atoms and molecules from the DFT has been widely studied in the last decade [16,19,20]. De Proft and Geerlings [20] computed these properties using differ-

ent DFT functionals, which incorporate electron correlation, and different basis sets. They found that the use of the hybrid B3LYP functional together with the large aug-cc-pVTZ basis set (LBS) gave reasonable values of IPs and EAs when they were compared with the G2 thermodynamic and experimental values. Therefore, we have used this methodology to obtain pretty accurate vertical IP and EA values for a series of selected 25 ethylene derivatives, using the GAUSSIAN 03 code [21].

In Table 1, the computed IPs and EAs of the selected 25 molecules are collected. In this table, experimental values of IPs for 15 ethylene derivatives are also shown. The computed IP values range from 8.29 to 11.37 eV. For the subseries of 15 compounds for which the experimental IP values are available, the computed IP values present a mean absolute deviation of 0.13 eV. This value is slightly lower than that obtained for a series of atoms and small molecules at the same level of theory, 0.15 eV [20]. By performing a least-squares fit for this subseries we obtain a good linear correlation relationship between the experimental IPs and those computed at the DFT level

$$\text{IP} = 1.0109\text{IP}_{\text{exp}} - 0.174 \text{ eV} \quad (6)$$

with a $R^2 = 0.97$ (see Fig. 1).

Table 1

Experimental and B3LYP/aug-cc-pVTZ calculated ionization potentials, IP, electronic affinities, EA, chemical potentials, μ , hardnesses, η , and electrophilicity values, $\omega(\text{I,A})$, (IP, EA, μ , η , and $\omega(\text{I,A})$, in eV) for the series of substituted ethylenes

M	IP _{exp} ^a	IP	EA ^b	μ	η	$\omega(\text{I,A})$	η_{cor} ^c	ω_{cor}
1		11.37	3.36	−7.37	8.01	3.39	5.14	5.27
2		11.19	2.39	−6.79	8.80	2.62	5.46	4.22
3	10.04	9.90	1.86	−5.88	8.04	2.15	4.96	3.48
4	10.8	10.92	1.29	−6.11	9.63	1.94	5.82	3.21
5		10.94	1.30	−6.12	9.65	1.94	5.80	3.23
6		10.93	1.21	−6.07	9.72	1.90	5.84	3.16
7	11.38	11.08	1.13	−6.10	9.95	1.87	5.98	3.11
8		8.55	1.19	−4.87	7.37	1.61	4.47	2.65
9		9.07	1.29	−5.18	7.78	1.72	4.69	2.86
10		11.23	0.74	−5.98	10.49	1.71	6.33	2.83
11		8.98	1.21	−5.10	7.76	1.67	4.69	2.77
12	10.103	9.97	−0.02	−4.98	10.00	1.24	5.90	2.10
13		9.79	0.14	−4.97	9.65	1.28	5.65	2.18
14	10.91	10.76	−0.17	−5.30	10.94	1.28	6.42	2.18
15	9.92	9.79	−0.08	−4.85	9.87	1.19	5.83	2.02
16	9.64	9.55	0.00	−4.78	9.55	1.19	5.65	2.02
17	10.6	10.63	−0.26	−5.19	10.89	1.24	6.43	2.09
18	10.34	10.15	−0.09	−5.03	10.24	1.24	6.07	2.09
19	9.7	9.79	−0.28	−4.76	10.06	1.12	5.92	1.91
20		10.01	−0.19	−4.91	10.20	1.18	6.31	1.91
21	8.43	8.29	−0.35	−3.97	8.64	0.91	5.00	1.57
22	10.514	10.59	−0.72	−4.94	11.31	1.08	7.21	1.69
23	9.79	9.80	−0.45	−4.68	10.25	1.07	6.22	1.76
24	9.082	8.90	−0.74	−4.08	9.64	0.86	5.60	1.49
25	10.363	10.53	−0.52	−5.00	11.05	1.13	7.20	1.74

Corrected hardness and electrophilicity values (η_{cor} and ω_{cor} , in eV) are included. See the text for details.

^a From Refs. [16] and [22].

^b Experimental values of EA for **1** and **3** are 2.3 and 1.9 eV, respectively [22].

^c The corrected hardness values are obtained using the Eq. (8).

Only a few experimental EA values for this series of organic molecules are available in the literature, and they are not sufficient for a statistical analysis. De Proft and Geerlings found that the use of the B3LYP functionals together with the Dunning's correlation-consistent aug-cc-pVTZ basis set for a series of atoms and small molecules gave reasonable performance of the EAs calculations [20]. Therefore, we have used this methodology to obtain presumably accurate EA values in order to compute the $\omega(\text{I,A})$ values (see Table 1). Fourteen of the 25 compounds have positive EA values, indicating that the corresponding anions are more stable than the loss of an electron. Note that they correspond to the more electrophilic molecules of this series.

3.2. Evaluation of the electrophilicity indexes from the IPs and EAs, $\omega(\text{I,A})$, and the ε_H and ε_L energies, $\omega(\text{H,L})$

With the IP and EA values calculated in the Section 3.1 and the HOMO and LUMO energies, ε_H and ε_L , obtained using the LBS, we have computed the electrophilicity indexes, $\omega(\text{I,A})$ and $\omega(\text{H,L})_{\text{LBS}}$, respectively. The corresponding values are collected in Tables 1 and 2, respectively. As it is shown in Fig. 2, there is a good linear correlation relationship between the $\omega(\text{I,A})$ and $\omega(\text{H,L})_{\text{LBS}}$

$$\omega(\text{H,L})_{\text{LBS}} = 2.1502\omega(\text{I,A}) - 0.6719 \text{ eV} \quad (7)$$

with a $R^2 = 0.96$. If we exclude the compounds **3** (*p*-benzoquinone), **8** (*o*-methylenbenzoquinone) and **25** (fluoroethylene) of this series, which present the largest deviations, the relationship of the other 22 molecules improves considerably, with a $R^2 = 0.99$.

Eq. (7) shows that the computed $\omega(\text{H,L})_{\text{LBS}}$ values are ca. twice than the $\omega(\text{I,A})$ ones. In order to find the origin of this trend, a comparison of the chemical potential, μ , and the hardness, η , obtained from the IP and EA values,

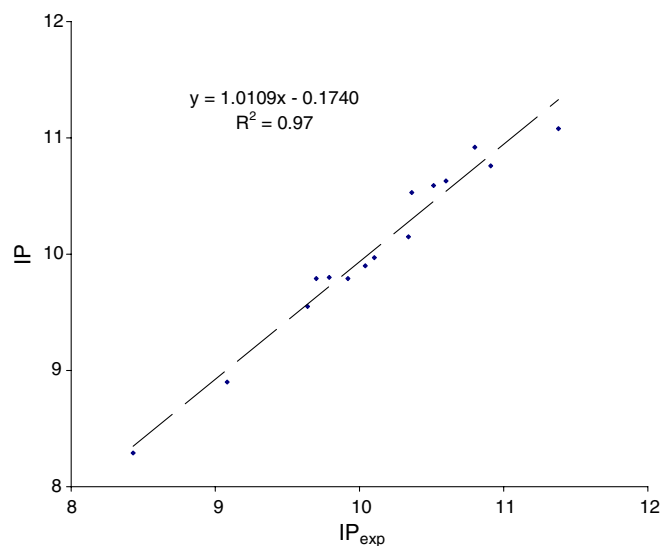


Fig. 1. Plot of the computed B3LYP/aug-cc-pVTZ ones, IP, versus the experimental ionization potential values, IP_{exp} .

Table 2

B3LYP/aug-cc-PVTZ HOMO and LUMO energies (ε_H and ε_L , in a.u.) of the neutral species M, calculated chemical potentials and hardnesses (μ and η , in a.u.), and electrophilicity ($\omega(H,L)_{LBS}$, in eV) values

M	ε_H	ε_L	μ	η	$\omega(H,L)_{LBS}$	$\omega(H,L)_{SBS}^a$
1	-0.3479	-0.1924	-0.2702	0.1554	6.39	5.95
2	-0.3360	-0.1609	-0.2485	0.1751	4.80	4.38
3	-0.2850	-0.1431	-0.2140	0.1420	4.39	3.88
4	-0.3139	-0.1291	-0.2215	0.1848	3.61	3.24
5	-0.3207	-0.1251	-0.2229	0.1956	3.46	3.08
6	-0.3193	-0.1226	-0.2210	0.1967	3.38	3.01
7	-0.3243	-0.1177	-0.2210	0.2066	3.22	2.82
8	-0.2420	-0.1122	-0.1771	0.1299	3.29	2.72
9	-0.2681	-0.1119	-0.1900	0.1562	3.14	2.66
10	-0.3135	-0.1117	-0.2126	0.2019	3.05	2.61
11	-0.2637	-0.1084	-0.1860	0.1553	3.03	2.56
12	-0.2719	-0.0815	-0.1767	0.1904	2.23	1.84
13	-0.2855	-0.0736	-0.1796	0.2119	2.07	1.78
14	-0.3034	-0.0733	-0.1883	0.2300	2.10	1.74
15	-0.2690	-0.0743	-0.1716	0.1947	2.06	1.70
16	-0.2616	-0.0773	-0.1695	0.1844	2.12	1.61
17	-0.2953	-0.0693	-0.1823	0.2260	2.00	1.60
18	-0.2876	-0.0669	-0.1772	0.2207	1.94	1.59
19	-0.2780	-0.0580	-0.1680	0.2200	1.75	1.42
20	-0.2672	-0.0531	-0.1602	0.2141	1.63	1.22
21	-0.2353	-0.0498	-0.1425	0.1855	1.49	1.13
22	-0.2823	-0.0110	-0.1466	0.2712	1.08	1.12
23	-0.2743	-0.0368	-0.1555	0.2375	1.39	1.09
24	-0.2437	-0.0424	-0.1430	0.2013	1.38	1.04
25	-0.2794	-0.0091	-0.1443	0.2703	1.05	0.68

B3LYP/6-31 G* electrophilicity ($\omega(H,L)_{SBS}$, in eV) values.

^a From Refs. [5,6,10,11].

and the ε_H and ε_L energies was performed. This analysis shows that while the mean absolute deviation between the computed μ values is 0.21 eV, the deviation for η is around 4.18 eV.

Very recently, Tozer and De Proft [23] have discussed the computational problems for the hardness values for

molecules presenting negative electron affinities. They proposed a simple equation to compute the hardness from the HOMO and LUMO energies and the IP values [22].

$$\eta = (\varepsilon_L - \varepsilon_H)/2 + I. \quad (8)$$

We recalculated the η values, η_{cor} , using the computed IP values and the HOMO, ε_H , and LUMO, ε_L , energies. With the $\mu(I,A)$ values and the corrected η_{cor} values, we calculated a new scale of corrected electrophilicities (see ω_{cor} in Table 1). A good linear correlation relationship appears between the ω_{cor} and $\omega(H,L)_{LBS}$

$$\omega(H,L)_{LBS} = 1.3983\omega_{cor} - 0.9120 \text{ eV} \quad (9)$$

with a $R^2 = 0.97$ (see Fig. 3). If we exclude again the compounds **3**, **8** and **25** of this series, the relationship of the other 22 molecules improves considerably, with a $R^2 = 0.99$. In addition, the new slope decreases to 1.3734.

3.3. Evaluation of the basis set dependence of the $\omega(H,L)$ electrophilicity index

Finally, an analysis of the electrophilicity power obtained from the HOMO and LUMO energies using the SBS 6-31G* and the LBS aug-cc-PVTZ, was performed in order to evaluate the basis set dependence of the electrophilicity index. In Table 2, the electrophilicity power computed using the SBS for the series of the 25 ethylene derivatives is collected [5,6,10,11]. As it is shown in Fig. 4, there is a very good linear correlation relationship between the electrophilicities obtained using the two selected basis sets.

$$\omega(H,L)_{LBS} = 1.0374\omega(H,L)_{SBS} + 0.2988 \text{ eV} \quad (10)$$

with a $R^2 = 0.99$. Although the absolute electrophilicity values computed from the HOMO and LUMO energies show

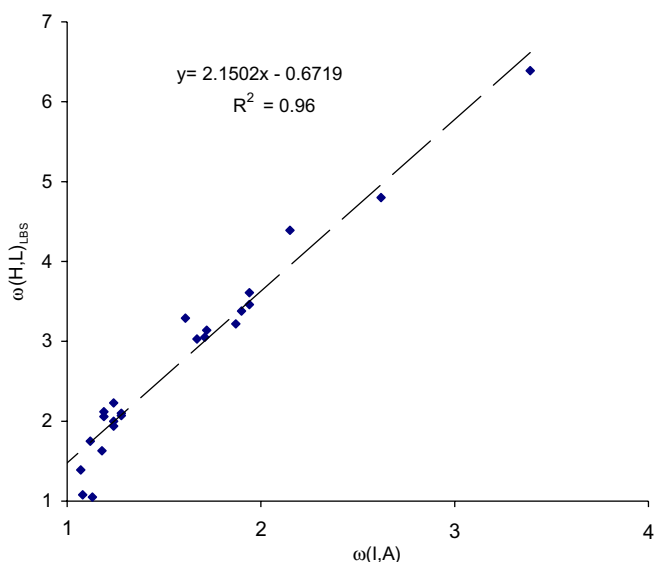


Fig. 2. Plot of $\omega(H,L)_{LBS}$ versus $\omega(I,A)$.

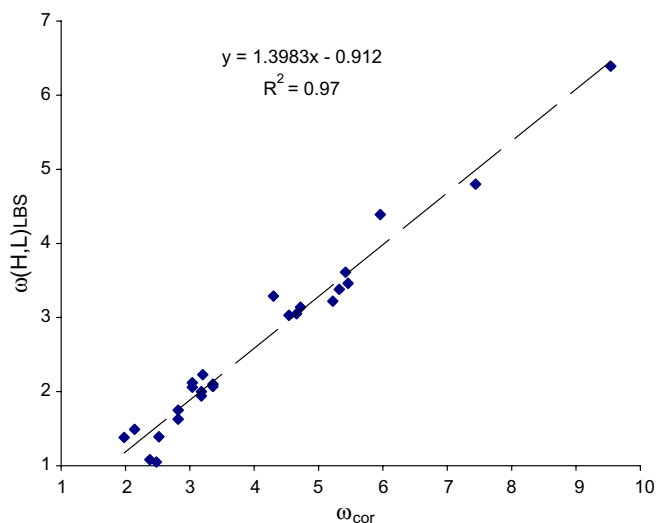


Fig. 3. Plot of the electrophilicity index obtained from the HOMO and LUMO energies, $\omega(H,L)_{LBS}$, versus the corrected electrophilicity values, ω_{cor} .

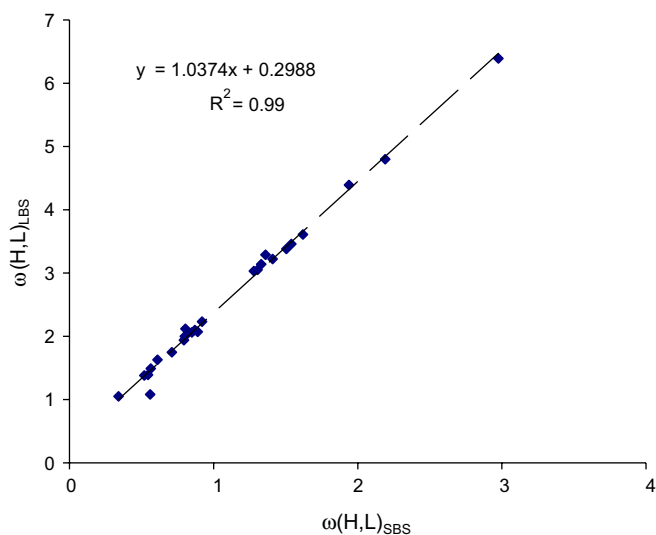


Fig. 4. Plot of $\omega(H,L)_{LBS}$ versus $\omega(H,L)_{SBS}$.

dependence with the basis set, the relative position of a molecule in the electrophilicity scale is not modified. As a consequence, the analyses of reactivity based on the electrophilicity scales are invariant within DFT calculations.

4. Conclusions

The good linear correlation found between the electrophilicity values obtained from the computed IPs and EAs using the LBS and those obtained from the HOMO and LUMO energies with the LBS and SBS, allows us to assert the use of accessible B3LYP/6-31G* HOMO and LUMO energies, ε_H and ε_L , to obtain reasonable values of the global electrophilicity index of organic molecules, and thus to make valuable electrophilicity scales.

It is interesting to note that our main interest in this Letter is to provide a useful tool to estimate accurate values of electrophilicity index through a simple method such as B3LYP/6-31G*. Eq. (10) may be eventually used if the reader needs more accurate numbers for this descriptor.

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