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A Quantitative Scale for the Extent of Conjugation of Substituted Olefines

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The olefinic functional group is among the most important chemical building blocks, also playing an important role in organic and bioorganic reactions. The exact description and precise quantification of the degree of the olefinic conjugation in substituted alkenes is not trivial. The present work suggests a novel, yet simple, method toward quantifying the conjugation in a general olefin group (e.g., alkenes) on a linear scale, defined as the "olefinicity scale", achieved using the computed enthalpy of hydrogenation (ΔH_{H2}) of the compound examined. In the present conceptual work, the ΔH_{H2} value for allyl anion is used to define perfect conjugated character (olefinicity = +100%), while ethene represents complete absence of conjugation (olefinicity = 0%). The component ΔH_{H2} values were computed at different levels of theory, providing a near-"method-independent" measure of olefinicity. A total of 67 well-known olefinic compounds were examined to demonstrate the practicality of this protocol. For the compounds examined, a correlation has been made between the computed olefinicity percentage values and their associated proton affinities, as well as their reactivity values in a nucleophilic addition reaction; selected chemical reactions were also studied.

1. Introduction

The olefinic group is among the most important moieties in organic, bioorganic, and industrial chemistry. Substituted olefines, such as enamines, vinyl ethers, and other derivatives are also included in this category.[1] Olefins are also quite common throughout biochemical systems such as proteins, lipids, nucleic acids, and other bioactive compounds including drugs and toxins.[2] Their chemical reactivity may be characterized as being either very stable and resistant chemical systems (e.g., simple olefines), or very active and reactive compounds (enamines, vinyl esters, etc.). There are numerous examples where olefinic derivatives undergo electrophilic or nucleophilic reactions.[1] The large variability in olefin reactivity may be attributed to the potential fine-tuning ability of bond conjugation, facilitated or inhibited by attached substituent groups. The extent of conjugation of a general olefin, as illustrated by its associated resonance structures (**A-I**−**A-V** in Scheme 1), predetermines its specific chemical reactivity. An olefinic bond with stronger conjugation is more resistant to attacks by electrophilic (H^+, $Metal^{n+}$,) and nucleophilic (e.g., HO^-, H_2O, amines, metal hydrides) agents, whereas a weakly conjugated one is correspondingly more reactive. In the latter, the conjugation between the two olefinic C atoms is more extensive, meaning that the contribution of the five most significant resonance structures (**A-I**−**A-V**) are more closely balanced between the neutral and zwitter-ionic resonance structures, than in a strongly conjugated olefinic bond. In the case where there is no significant conjugation, the preferred resonance structure is **A-I**.

2. Methods

2.1. Molecular Computations. All computations were carried out using the Gaussian03 program package.[3] Geometry optimizations and subsequent frequency analyses were carried out on selected olefin-containing systems from which values for the enthalpy of hydrogenation (ΔH_{H2}) were extracted. Different levels of theory were employed, labeled as follows: **A** HF/3−21G, **B** HF/6−31G(d), **C** B3LYP/6−31G(d),[4] **D** B3LYP/6−31G(d,p), **E** B3LYP/6−311++G(2d,2p), **F** MP2(fc)/6−31G(d),[5] **G** CCSD/6−31G(d),[6] and **H** G3MP2B3[7] (Tables 1 and 2). Basis sets were chosen for their reliability in characterizing aromaticity, in agreement with recently established works.[8−16] Analytical vibrational frequencies were computed at the same levels of theory as used for geometry optimization, in order to properly confirm all structures as residing at minima on their potential energy hypersurfaces (PEHSs). Scaling of thermodynamic parameters for method **G** made use of the scaling factor employed for **D**. Thermodynamic parameters (*U*, *H*, *G* and *S*, listed in the Supporting Information, Tables S2−S5) were computed at 298.15 K, using the quantum chemical, rather than conventional, thermodynamic scale.

2.2. The Concept of Olefinicity. A protocol has been developed to quantify the extent of conjugation of the olefinic bond. The parameter, thus obtained, is termed "olefinicity", analogous to "aromaticity",[8−12] "amidicity"[13−15] and "carbonylicity".[16] To measure the reactivity and strength of a general olefinic compound, an *in silico* hydrogenation reaction was carried out (Scheme 2). In computing the ΔH_{H2}, a given stable conformation and configuration of the products was chosen, in

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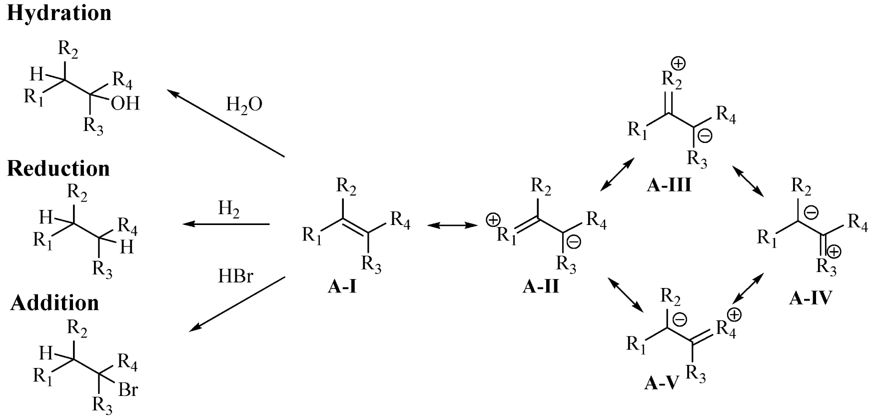
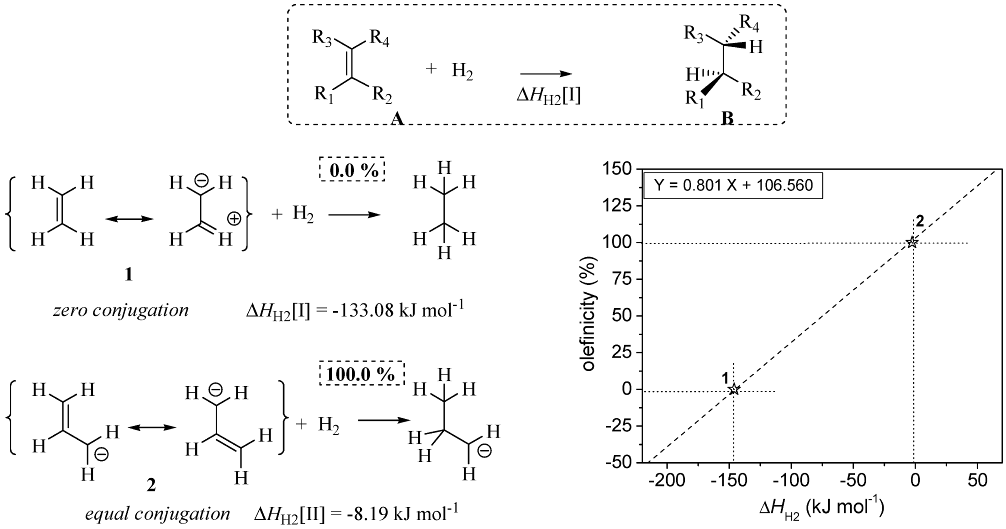
SCHEME 1: Some Selected Typical Reactions of the Olefinic Moiety



SCHEME 2: The Definition of Olefinicitiy Percentage via the Enthalpy of Hydrogenation (ΔH_{H2}) of the Olefinic Group[a]



[a] Values were obtained from the geometry-optimized structures, computed at B3LYP/6-311++G(2d,2p) levels of theory. In structure **B**, the H−C−C−H dihedral angle is in the *anti* orientation. The strait line in the graph ($y = mx + b$) passing through the two reference points (**1** and **2**), corresponding to 0% and 100% olefinicity, has the following parameters: $m = [100\% - 0\%]/[\Delta H_{H2}(100\%) - \Delta H_{H2}(0\%)] = 100/[133.08 - 8.19] = 100/124.89 = 0.801$; $b = [\text{olefinicity}]_0 = m\,\Delta H_{H2}(0\%) = -0.801\,(-133.08) = 106.560$.

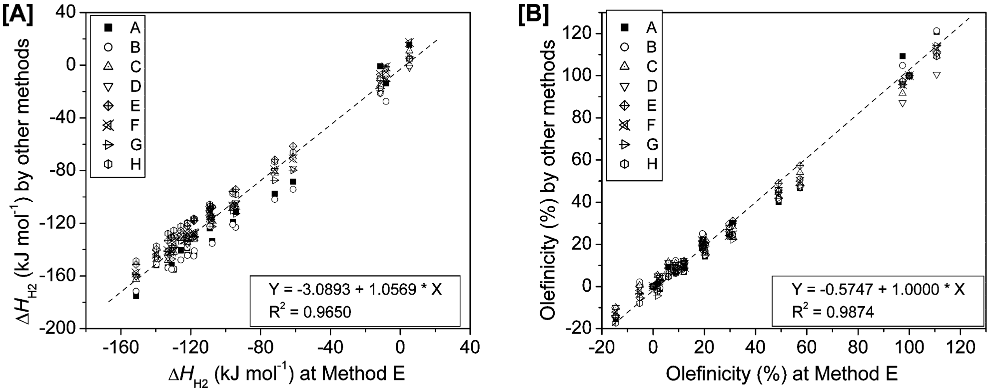


Figure 1. Correlation of ΔH_{H2} (A) in kJ mol^{-1} and olefinicity % (B) values obtained by various methods against the results obtained by B3LYP/6−311++G(2d,2p) (Method **E**) and those obtained by other methods (Methods **A**−**D**, **F**−**H**).

which no significant intermolecular interaction (no new intramolecular H-bond) was identified, which may perturb the system.

The ΔH_{H2}[I] value of ethene (**1**) was taken as being completely devoid of conjugation between the olefinic double bond and the H atom (0% conjugation), and the ΔH_{H2}[II] value (eq 1) of allyl anion (**2**) was defined as a fully or completely conjugated olefinic group (100%). In **1**, delocalization is not possible because of the lack of a lone pair, i.e., double-occupied atomic orbital with the appropriate symmetry. Analogously to the carbonylicity percentage,[16] measuring ΔH_{H2} or determining the enthalpy of formation provides a means to obtain the experimental percentage of olefinicity (eq 2), where parameters *m* and [olefinicity %]$_0$ refer to the slope and the *y*-intercept of the linear equation defined in Scheme 2, which are used later to calculate the olefinicity percentage from ΔH_{H2}. It should

TABLE 1: Computed ΔH_{H2} Values (kJ mol^{-1}) and Olefinicity % for Model Compounds (1−67) Geometry Optimized at the B3LYP/6-311++G(2d,2p) (Method E) Level of Theory

	Method E			Method E	
	ΔH_{H2}[I]	olefinicity		ΔH_{H2}[I]	olefinicity
1	*−133.1*	***0.0***[a]	**16**	−71.9	**49.0**
2	*−8.2*	***100.0***[a]	**17**	−61.4	**57.4**
3	−125.7	**5.9**	**18**	−96.0	**29.7**
4	−107.7	**20.3**	**19**	−139.6	**−5.3**
5	−94.2	**31.1**	**20**	−99.0	**27.3**
6	−117.9	**12.1**	**21**	−111.5	**17.3**
7	−108.6	**19.6**	**22**	−124.2	**7.1**
8	−129.7	**2.7**	**23**	−109.6	**18.8**
9	−118.2	**11.9**	**24**	−121.8	**9.0**
10	−122.0	**8.9**	**25**	−109.4	**18.9**
11	−122.1	**8.8**	**26**	−130.9	**1.7**
12	−109.0	**19.2**	**27**	−101.4	**25.4**
13	−11.5	**97.4**	**28**	−109.2	**19.1**
14	5.2	**110.7**	**29**	−89.7	**34.7**
15	−151.3	**−14.6**			
35	−204.3[b]	**−151.0**	**30**	−154.2[c]	**−57.3**
36	−107.2[b]	**3.9**	**31**	−115.8[c]	**3.4**
37	−90.1[b]	**38.4**	**32**	−106.4[c]	**18.0**
38	−98.3[b]	**29.5**	**33**	−109.5[c]	**13.6**
39	−87.6[b]	**32.4**	**34**	−101.4[c]	**27.0**
40	42.6	**147.4**	**41**	−275.5	**−126.2**
42	−94.3	**31.1**	**51**	−86.2	**37.5**
43	−109.5	**18.9**	**52**	−152.1	**−15.3**
44	−91.8	**33.0**	**53**	−143.4	**−8.3**
45	−112.8	**16.2**	**54**	−99.8	**26.7**
46	−131.8	**5.1**	**55**	−64.1	**55.2**
47	−121.3	**9.4**	**56**	−53.1	**64.0**
48	−102.6	**24.4**	**57**	−113.1	**16.0**
49	−121.5	**9.3**	**58**	−104.9	**22.5**
50	−75.1	**46.4**			
59	−106.7	**21.1**	**64**	−98.2[e]	**27.9**[e]
60	−107.0	**20.9**	**65**	−94.1[e]	**31.2**[e]
61	−105.1	**22.4**	**66**	−107.7[e]	**20.3**[e]
62	−98.3	**27.9**	**67**	−15.2[e]	**94.4**[e]
63	−95.6	**30.0**			

[a] By definition. [b] Modified by ring strain $\Delta\Delta H_{H2}$(RS1), see Scheme 4. [c] Modified by ring strain $\Delta\Delta H_{H2}$(RS2), see Scheme 5. [d] Supposing that $\Delta\Delta H_{H2}(RS) = 0$ kJ mol^{-1}. [e] At B3LYP/6−31++G(d,p).

perhaps be emphasized that, in the choice of these standards (compounds **1** and **2**), care was taken to pick structural similarities and simplicities, since both **1** and **2** correspond to nonstrained and sterically nonhindered structures.

$$\Delta H_{H2}[I] = H_B - H_A - H_{H2} \tag{1}$$

$$[\text{olefinicity }\%] = m\Delta H_{H2}[I] + [\text{olefinicity }\%]_0 \tag{2}$$

Clearly, [olefinicity %] is not the result of a mathematical fit to a set of points, but it is a linear transformation of the ΔH_{H2}[I] scale. Such transformations of scales are, in fact, used in chemistry. The p*K*a and pH scales represent logarithmic transformation of the exponential scale. As a result, we have, for example, in the pH scale, numbers from 0 to 14. Subsequently, for concentrated strong acidic and strong bases solutions, the pH scale was extended. For H_0 values the numbers are smaller than 0 (negative) and for the H_- values they are larger than 14. In the present case, the 0% and 100% olefinicity are just as arbitrary as pH = 0 and pH = 14 measuring hydrogen ion concentration, yet these reference points are useful in the practical sense.

In order to evaluate the quantitative olefinicity scale (eq 2), a wide variety of olefin compounds (**3−67**) were investigated and discussed (Scheme 3, Tables 1 and 2 and Figure 2), in addition to and comparison with the two reference compounds (**1** and **2**). The resonance energy (RE, ΔH_{RE}) of the olefinic bond for compound **X**, together with steric effect and potential ring-strain energy, is the basic characteristic of conjugation.

From the olefinicity percentage, one may define the resonance energy by the following equations (eq 3a−3e), analogously to that for amidicity[13−15] and carbonylicity.[16]

$$[\text{olefinicity }\%](\mathbf{X}) = m\Delta H_{H2}[I](\mathbf{X}) + [\text{olefinicity }\%]_0 \tag{3a}$$

$$[\text{olefinicity }\%](\mathbf{1}) = m\Delta H_{H2}[I](\mathbf{1}) + [\text{olefinicity }\%]_0 \tag{3b}$$

$$[\text{olefinicity }\%](\mathbf{X})\text{-}[\text{olefinicity }\%](\mathbf{1}) = m[\Delta H_{H2}[I](\mathbf{X}) - m\Delta H_{H2}[I](\mathbf{1})] \tag{3c}$$

Since [olefinicity %](**1**) ≡ 0, and $\Delta H_{RE}(\mathbf{X}) \equiv \Delta H_{H2}[I](\mathbf{X}) - \Delta H_{H2}[I](\mathbf{1})$,

$$[\text{olefinicity }\%](\mathbf{X}) = m\Delta H_{RE}(\mathbf{X}) \tag{3d}$$

or

$$\Delta H_{RE}(\mathbf{X}) = [\text{olefinicity }\%](\mathbf{X})/m \tag{3e}$$

The resonance enthalpy (ΔH_{RE}) is an indicator of the overall enhancing of a reaction. Instead of studying the Gibbs free energy, the enthalpy was used to measure this enhancing quantity, in order to study the effects of the enthalpy and entropy change of a reaction independently.

In order to obtain accurate olefinicity values for cyclic structures (**30−34** and **35−39**), one should consider the change of ring strain (RS) in the hydrogenation reaction process. For compounds **30−34**, we applied the same procedure as used previously in the determinations of amidicity[13−15] and carbonylicity.[16] For this reason, reference reactions were considered for each endocyclic alkene, where the same cycloalkene was hydrogenated to the appropriate cycloalkane ($\Delta H_{H2}[II] \equiv \Delta H_{H2}[I]$, Scheme 4). These values were compared with the corresponding ΔH_{H2} of *cis*-2-butene changing to *gauche*-butane (ΔH_{H2}[III]; eq 4), thereby obtaining, for the estimated ring strain (RS), the $\Delta\Delta H_{H2}$(RS1) values for each reaction. One may correct the ΔH_{H2}[I] values of compounds **30−34** with the calculated $\Delta\Delta H_{H2}$(RS1), yielding $\Delta H_{H2}{*}[I]$ values (eq 4 and 5, Table S1). The final step is to convert the $\Delta H_{H2}{*}[I]$ to olefinicity %, using eq 2. Ring strain energy contribution is taken to be zero in the case of open chain compounds.

$$\Delta\Delta H_{H2}(RS1) = \Delta H_{H2}[II] - \Delta H_{H2}[III] \tag{4}$$

$$\Delta H_{H2}{*}[I] = \Delta H_{H2}[I] + \Delta\Delta H_{H2}(RS1) \tag{5}$$

To correct for strain in exocyclic alkenes (**35−39**), where strain may come from stretched valency of the olefinic carbon atom in the ring(C=C<, Scheme 5), homodesmotic reactions with ethane were used, as described in Scheme 5 and Eq. 6 and 7.

$$\Delta\Delta H_{H2}(RS2) = \Delta H_{H2}[IV] - \Delta H_{H2}[V] \tag{6}$$

$$\Delta H_{H2}{*}[I] = \Delta H_{H2}[I] + \Delta\Delta H_{H2}(RS2) \tag{7}$$

Olefin strain has also been studied by Schleyer et al.[17]

TABLE 2: Parameters for the Linear Scale of Olefinicity Percentage, Calculated from Theoretical ΔH_{H2} Values (kJ mol^{-1}) Obtained for 1 and 2, According to Eq 2

	method	ΔH_{H2}(1) 100%	ΔH_{H2}(2) 0%	*m*	[olefinicity %]$_0$
A	HF/3−21G(d)	−13.9	−153.5	0.72	109.9
B	HF/6−31G(d)	−27.5	−154.0	0.79	121.7
C	B3LYP/6−31G(d)	−2.7	−148.2	0.69	101.9
D	B3LYP/6−31G(d,p)	−2.6	−146.0	0.70	101.9
E	B3LYP/6−311++G(2d,2p)	−8.2	−133.1	0.80	106.6
F	MP2(fc)/6−31G(d)	−1.2	−140.8	0.72	100.8
G	CCSD/6−31G(d)	−12.2	−141.5	0.77	109.4
H	G3MP2B3	−6.8	−127.8	0.82	105.6
	average	−9.4	−143.1	0.75	107.2
	S.Dev.	8.6	9.3	0.05	6.8

TABLE 3: Computed Olefinicity Values in % and ΔH_{PA} and ΔH_{React} values in kJ mol^{-1} for the Compounds Examined (1−24, 26, 27, 42−49), Obtained at the B3LYP/6-311++G(2d,2p) Level of Theory

	olefinicity	ΔH_{PA}	ΔH_{NU}		olefinicity	ΔH_{PA}	ΔH_{NU}
1	0.0	−677.9	−72.3	**18**	29.7	−1432.4	[a]
2	100.0	−1614.8	[a]	**19**	−5.3	−204.2	[a]
3	5.9	−701.7	−125.9	**20**	27.3	−890.2	−160.6
4	20.3	−815.5	−150.2	**21**	17.3	−899.1	[a]
5	31.1	−916.9	−170.3	**22**	7.1	−655.1	−133.8
6	12.1	−760.2	−96.3	**23**	18.8	−688.2	−149.6
7	19.6	−718.7	[a]	**24**	9.0	−699.4	−131.8
8	2.7	−720.4	[a]	**26**	1.7	−673.3	[a]
9	11.9	−818.5	[a]	**27**	25.4	−900.0	−125.8
10	8.9	−795.4	−138.7	**42**	31.1	−991.2	−152.6
11	8.8	−709.2	−139.3	**43**	18.9	−904.1	[a]
12	19.2	−719.4	[a]	**44**	33.0	−999.4	[a]
13	97.4	−1598.3	[a]	**45**	16.2	−888.9	−128.1
14	110.7	−1657.6	[a]	**46**	5.1	−920.3	−95.4
15	−14.6	−122.1	[a]	**47**	9.4	−802.3	[a]
16	49.0	−1462.1	[a]	**48**	24.4	−874.2	−167.1
17	57.4	−1410.0	[a]	**49**	9.3	−812.7	[a]

[a] The tetrahedral intermediate is not a minimum.

2.3. Method Independence. The method dependence of this protocol was examined by calculating the ΔH_{H2} values at the B3LYP/6−311++G(2d,2p) level of theory (**E**) and subsequently converting it to olefinicity percentages for 20 selected olefinic compounds (**1**−**19** and **26**) with varied substituents (Scheme 3 and Table 1).

Results for level **E** were then compared to those obtained at different levels (Tables 2 and S1), with correlation between their ΔH_{H2} values being relatively small, but a noticeable method dependence ($R^2 = 0.9650$; Figure 1A) emerged. However, after converting all ΔH_{H2} values to olefinicity percentages, one finds a fairly good fit ($R^2 = 0.9874$; Figure 1B) and thus considerable reduction of method dependency. Additionally, all MIN−MAX and standard deviation (S.Dev.) values of the olefinicity percentages are significantly smaller than the corresponding ΔH_{H2} values (Table 2, Figure 1). The calculated average values of ΔH_{H2} and olefinicity are very close (Table 2) to those obtained by Methods **E** and **F** [B3LYP/6−311++G(2d,2p), MP2(fc)/6−31G(d)]. On the other hand, the calculated olefinicity percentages for a compound are in the same range, irrespective of the theoretical method applied, thus, the percentage olefinicity scale is virtually method independent. This methodology may therefore be considered as a quasi-rigorous method-independent technique, just as in the cases of aromaticity,[9] amidicity,[13] carbonylicity.[16] It is also emphasized that there is no limitation in the theoretical method to be employed, meaning that one may use as high or as low a level of computational theory as desired. The results discussed in this paper is based on Method **E**.

3. Results

3.1. Computed Data. The very different types of 67 model compounds (**1**−**67**) were classified into five groups, each representing different considerations (Scheme 3). Compounds **1**, **3**−**29** (Group 1), were used to study the inductive effects of 28 functional groups from the periodic system including simple neutral groups as well as those with and without net charge. From a theoretical point of view, **7** and **12** represent an interesting class of molecules, where an empty p orbital may interact with the olefin group, withdrawing electron density from the double bond.

The role of ring strain (Group 2) was also studied for three- to seven-membered ring sizes, using model compounds, such as small endocyclic **30**−**34** and exocyclic **35**−**39** double bonds. In Group 3, two endocyclic alkenes, benzene (**40**) and cylobutadiene (**41**), were chosen to account and calibrate for aromatic stabilization and antiaromatic destabilization, respectively. In compound **40**, one may suppose that the aromaticity and olefinicity promote one another, meaning stronger conjugation results in higher aromaticity. In contrast, the aromaticity and olefinicity are in competition in compound **41**; here stronger conjugation results in stronger antiaromaticity, destabilizing the system.

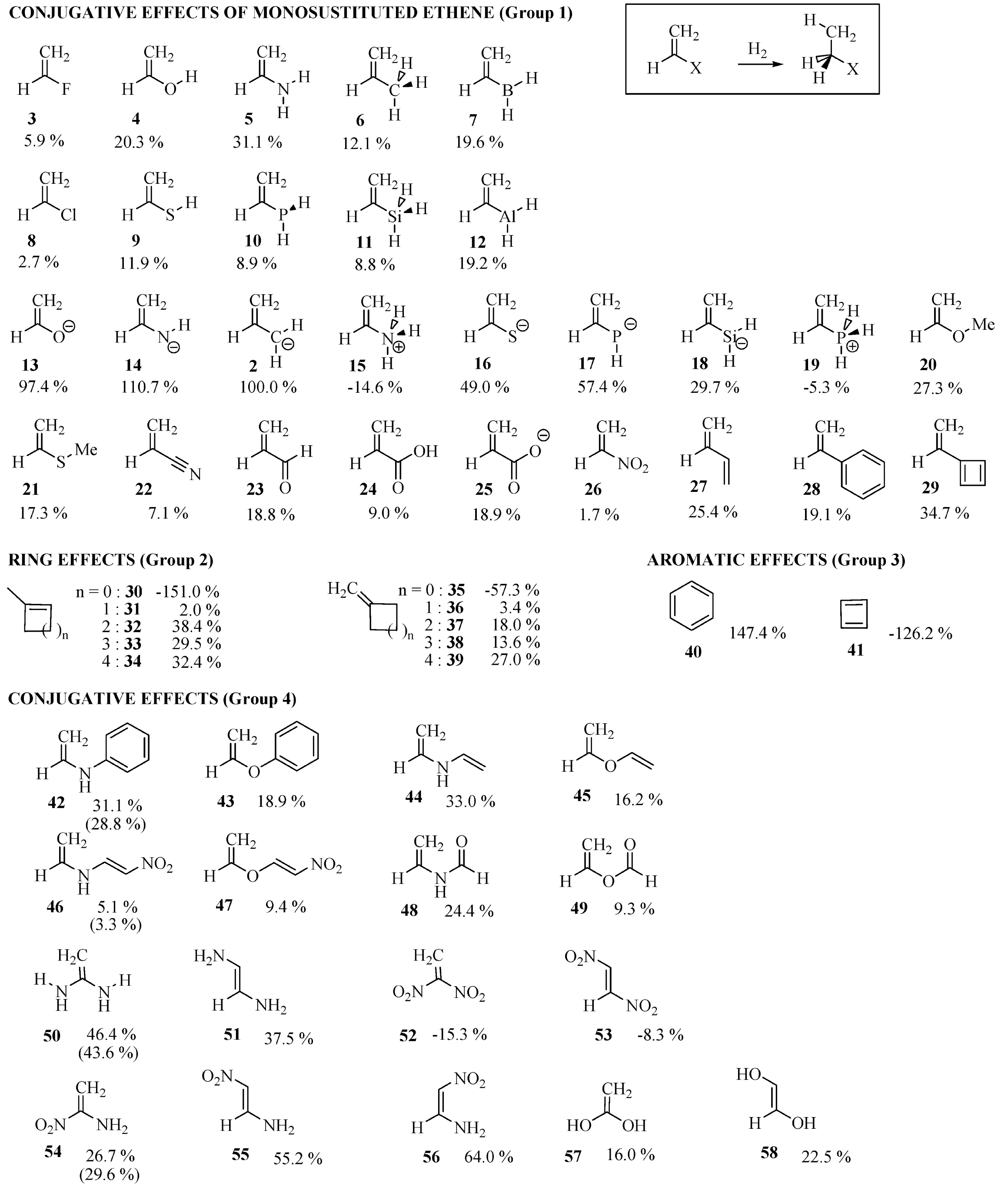
The conjugated olefinic compounds **42**−**58** (Group 4) were also considered, wherein C=C double bond conjugation is in competition with another conjugation type, changing the olefinicity values of the compounds. This selection of simple model compounds covers a wide variety of olefin types. Group 5 helps quantify the inductive and steric effects of sequential Me and *t*-Bu substituent additions (**1**, **6**, **59**−**67**), which is a quite fashionable topic in organic chemistry.[18−21]

4. Discussion

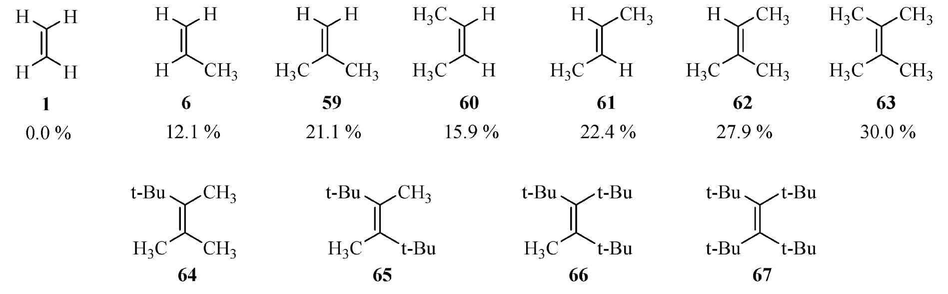
4.1. Structural Features. For Group1, addressing the conjugative effect of simple X substituents, results reproduce general chemical expectations (Figure 2A), wherein three different classes can be recognized (Scheme 6). Olefins bound to electron donating groups [EDGs; e.g., X = OH (**4**), NH_2 (**5**)] exhibit higher olefinicity percentages than those bound to non- or weakly conjugative groups [X = CH_3 (**6**), SiH_3 (**11**)]. Strong electron withdrawing groups (EWGs) show larger olefinicity values than is expected from their corresponding carbonylicity values [EWG; e.g., X = CN (**22**), CHO (**23**), NO_2 (**26**)]. The stronger relative conjugative effect of EWGs to the olefin group,

SCHEME 3: (A) Summary of Olefinicity Values for Selected Model Compounds (1−58), Measuring the Extent of Conjugation of Substituted Olefinic Bonds.[a] (B) Summary of Olefinicity Values for Selected Model Compounds (1, 6, 59−67), Measuring the Extent of Conjugation of the C=C Double Bond[b]

(A) CONJUGATIVE EFFECTS OF MONOSUSTITUTED ETHENE (Group 1)



(B) STERIC EFFECTS (Group 5)



[a] The numerical values under the structures represent the olefinicity % values at B3LYP/6-311++G(2d,2p) level of theory. [b] The numerical values under the structures represent the olefinicity % values at B3LYP/6-311++G(2d,2p) level of theory. The values, indicated by * are calculated by B3LYP/6-31++G(d,p).

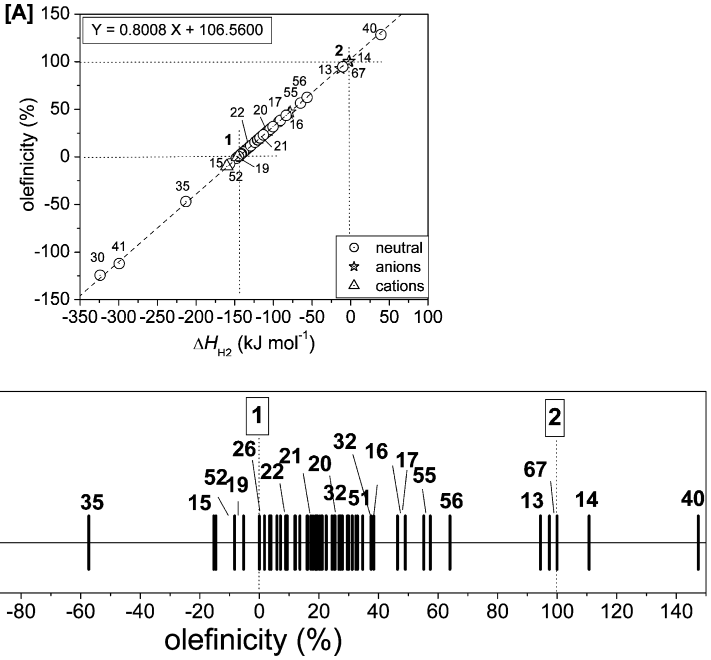
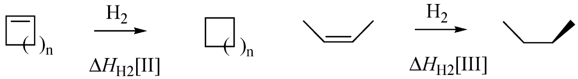


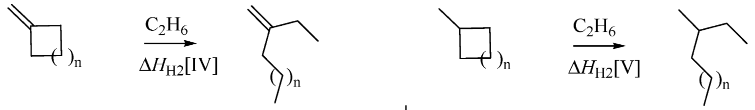
Figure 2. (A) The theoretical olefinicity scale. Percentage value of olefinicity based on the ΔH_{H2} value of a given compound computed at the B3LYP/6−311++G(2d,2p) level of theory (Table 1 and Scheme 3 detail compound identities). (B) Theoretical olefinicity values for compounds **1**−**67**, shown as a bar-diagram, in a style that is reminiscent to a spectrum.

SCHEME 4: Estimation of Ring Strain (RS) for Endocyclic Olefinic Compounds (30−34) via Correction by Reference Reactions at B3LYP/6-311++G(2d,2p) Levels of Theory



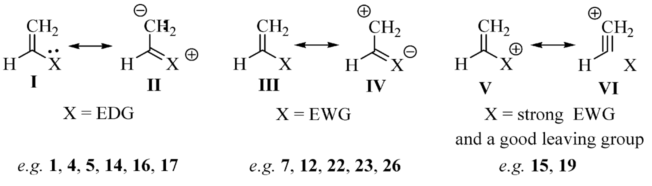
ΔH_{H2}[II]	ΔH_{H2}[III]	ΔH_{H2}[II] - ΔH_{H2}[III]
n = 0 : -224.41 kJ mol^{-1}	-106.99 kJ mol^{-1}	n = 0 : -117.42 kJ mol^{-1}
1 : -128.42 kJ mol^{-1}		1 : -21.43 kJ mol^{-1}
2 : -102.10 kJ mol^{-1}		2 : 4.89 kJ mol^{-1}
3 : -104.92 kJ mol^{-1}		3 : 2.06 kJ mol^{-1}
4 : -112.00 kJ mol^{-1}		4 : -5.01 kJ mol^{-1}

SCHEME 5: The Estimation of Ring Strain (RS) of Exocyclic Olefinic Compounds (35−39) via Correction by Reference Reaction at the B3LYP/6-311++G(2d,2p) Level of Theory



	ΔH_{H2}[IV]	ΔH_{H2}[V]	ΔH_{H2}[IV]-ΔH_{H2}[V]
35	n = 0 : -133.86 kJ mol^{-1}	n = 0 : -83.72 kJ mol^{-1}	n = 0 : -48.14 kJ mol^{-1}
36	1 : -90.10 kJ mol^{-1}	1 : -77.88 kJ mol^{-1}	1 : -12.03 kJ mol^{-1}
37	2 : -8.74 kJ mol^{-1}	2 : -5.32 kJ mol^{-1}	2 : -3.11 kJ mol^{-1}
38	3 : 9.61 kJ mol^{-1}	3 : 16.27 kJ mol^{-1}	3 : -6.90 kJ mol^{-1}
39	4 : -14.15 kJ mol^{-1}	4 : -15.35 kJ mol^{-1}	4 : 1.95 kJ mol^{-1}

SCHEME 6



compared to the effect with the carbonyl group can be attributed to the shift in balance between resonance structures (Scheme 6).

Deprotonated molecules (**2**, **13**, **14**, **16**−**18**) show very high olefinicity values, in sharp contrast to protonated ones (**15**, **19**). The cations promote strong electron-withdrawing effects, exhibiting extremely low olefinicity values (Figure 2). Positively charged X substituents behave as good leaving groups, and may be described by the two resonance structures **V** and **VI**, wherein the C═C bond distance is shorter in **VI** than in **V**, similar to anticonjugation, characterized by negative olefinicity values. In comparing the olefinicity and corresponding carbonylicity values, one may conclude that the former are significantly lower for EDGs (the extent of the conjugation is less significant), than for the corresponding carbonyl compounds. However, compounds functionalized with EWGs (e.g. **7**, **12**, **22**, **24**, **26**) show larger conjugation with the ethene moiety than with the carbonyl group in their carbonyl analogues with the same X functional groups (Figure 3). This effect can be attributed to the fact that the CH_2 group more readily accommodates positive than

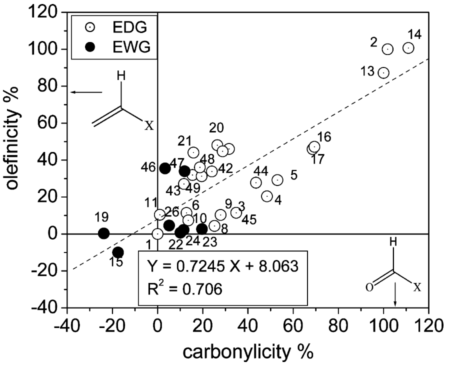


Figure 3. Correlation between carbonylicity and olefinicity values for carbonyl and olefinic compounds with the same X functional group, calculated at the B3LYP/6-31G(d,p) level of theory.

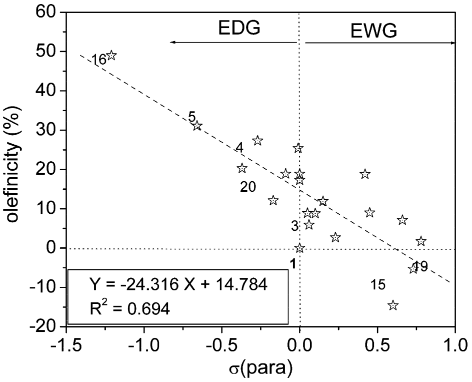


Figure 4. Correlation between Hammet $\sigma_{(para)}$ parameter and the olefinicity values calculated for selected model compounds at the B3LYP6−311++G(2d,2p) level of theory. The X = O$^-$ case (**13**) is omitted from the fitting.

negative charges, in direct contrast to the C═O group, which prefers negative (conjugating with EDG) over positive charges (conjugating with EWG).

Compounds **27**, **28** and **29** show how aromatic or antiaromatic moieties modify the olefin bond behavior when conjugated to an "external" double bond. The original olefinicity value of the butadiene moiety (**27**, 24.8%) is decreased when the conjugative double bond is aromatic in nature (**28**, 19.4%), as the ring prefers retention of its respective aromaticity over conjugation with the double bond. In contrast, the olefinicity increases when the ring is antiaromatic (**29**, 32.4%), due to conjugation between the endocyclic and the exocyclic double bonds helping to decrease the degree of antiaromaticity, wherein this increased conjugation is advantageous (to olefinicity).

Although these olefinic compounds are not aromatic, their olefinicity values provide a measure of the electron-donating and withdrawing effect of a substituent (X), in the same manner than a Hammett σ-value does. This merits an attempt to correlate olefinicity values obtained with their experimental Hammet $\sigma_{(para)}$ parameters,[22] as successfully applied in the case of P-containing compounds;[10] the results thereof are presented in Figure 4, with noticeable scattering ($R^2 = 0.648$). The *second group* was used to study the effect of ring-size on the computed olefinicity percentages for systems with an endo- (**30**−**34**) or exocyclic (**35**−**39**) double bond (Figure 5A). With the exception of the three- and four-membered rings (**30-35** and **31**−**36**), all cases showed endocyclic alkenes to have larger olefinicity values than their exocyclic isomers, but, in the case of the four-membered rings, the values are almost equal (**31**−**36**). The two curves in Figure 5A predict the product of a hypothetical exo → endo or endo → exo transformation for different ring sizes. The former is preferred in the cases of five-, six-, and seven-membered rings, while for the three-membered ring the opposite direction is predicted.

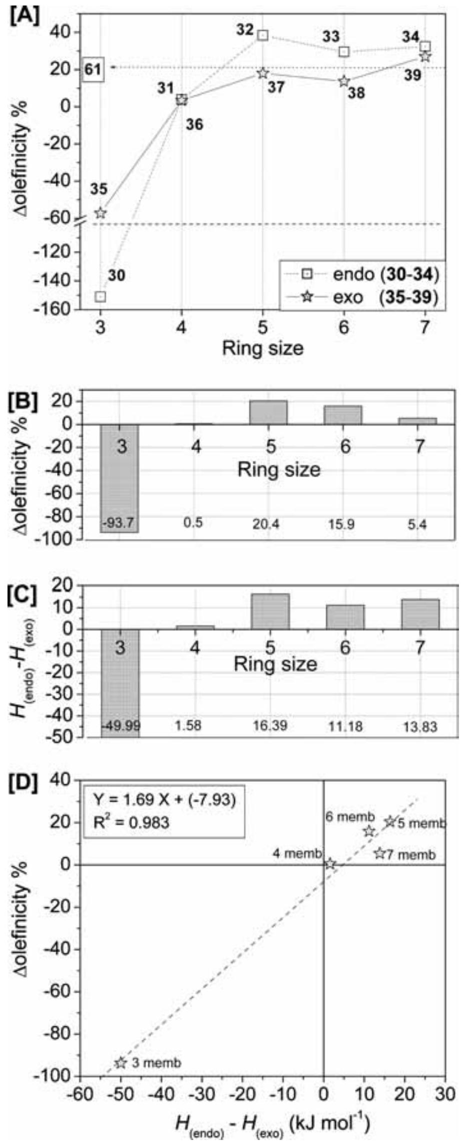


Figure 5. (A) Correlation between the ring size and the olefinicity % for compounds **30**−**39**. (B) Difference in olefinicity between endo- and exocyclic olefinic compounds. (C) Difference in enthalpy between endo- and exocyclic olefinic compounds. (D) Correlation between the difference of olefinicity values and the enthalpy of endo- and exocyclic olefinic compounds. All of the data are calculated at the B3LYP/6-311++G(2d,2p) level of theory.

This is in agreement with the calculated enthalpies of **30**−**39**, namely, olefinic compounds having larger olefinicity values have lower internal enthalpies, as illustrated in Figure 5B,C. Excellent correlation is obtained in correlating $\Delta_{\text{olefinicity}}$ and $H_{(\text{endo})} - H_{(\text{exo})}$ values (Figure 5D), indicating that the main enhancement of these hypothetical exo → endo and endo → exo transformations is to increase the olefinicity value. This is in agreement with experimental findings, where similar transformations can be observed for analogue compounds.

One aromatic and one antiaromatic compound comprised the *third group* (**40**, **41**). A very large olefinicity value (128.5%) was obtained for benzene (**40**), attributed to its extensive aromatic character[8] and conjugation, subsequently eliminated as a consequence of the hydrogenation reaction. The inverse

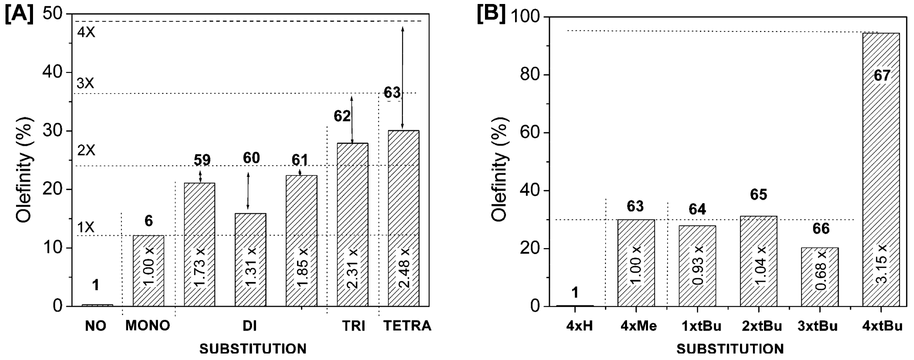


Figure 6. (A) Olefinicity values of compounds **1**, **6**, and **59**−**63**. (B) Olefinicity values of compounds **1** and **63**−**67**. The numbers in the shaded boxes (e.g., 3.15 ×) show the multiplicity of the olefinicity with respect to the reference compounds chosen: **6** for panel A, and **63** for panel B.

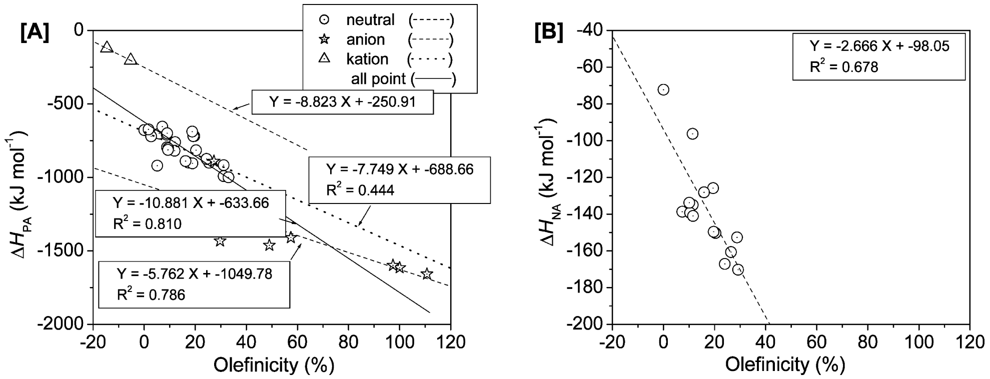
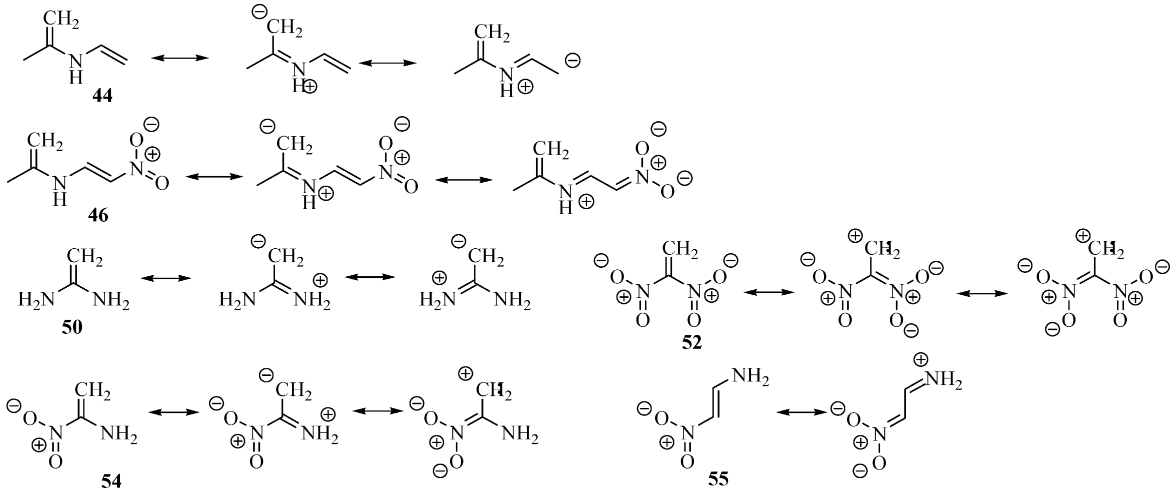


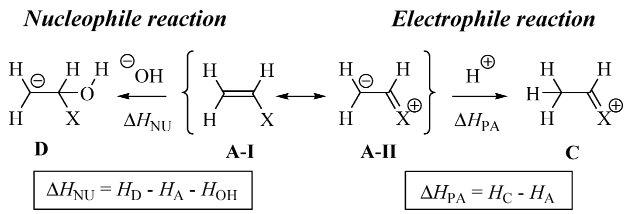
Figure 7. (A) Correlation between calculated olefinicity percentage and the PA of each olefinic-type compound (ΔH_{PA}), ranked by their charges for compounds **1**−**24**, **26**, **27**, **28**, and **42**−**49**. (B) Correlation between calculated olefinicity percentage and the reactivity of olefines (ΔH_{NU}) in a nucleophilic addition reaction for selected neutral compounds (**1**−**24**, **26**, **27**, **28**, **42**−**49**).

SCHEME 7: Selected Representative Resonance Structures of 44, 46, 50, 52, 54, and 55 (Group 4 Model Compounds)



was found for cyclobutadiene (**41**), with the low olefinicity value (−112.0%) originating from the antiaromatic character.[8]

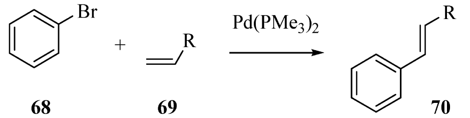
SCHEME 8



In the *fourth group* (**42**−**58**), an additional set of mono- and disubstituted olefins with different degrees of conjugation were considered (Scheme 7), wherein the olefinic and another functional group are competing for the lone pair of the N and O atoms. As expected, the less conjugated R groups [phenyl and vinyl (**42**, **43** and **44**, **45**)] do not greatly disturb the extent of conjugation, as indicated by similar olefinicity values for **4** and **5**. Somewhat stronger competition was attributed to nitrovinyl groups (**46** and **47**), again found between the olefinic moiety and the lone pair of the N or O atom of the unsaturated R-group, resulting in lowered olefinicity percentage. Vinylformylamide (**48**) and vinylformylester (**49**) are usually more unstable than their vinylamine and vinylalcohol counterparts, as a result of the competing carbonyl group, exhibiting lower olefinicity values compared to the amine (**5**) and alcohol (**4**). Compounds **50**−**58** are functionalized by electron-donating and/or electron-withdrawing groups attached to solely C1 or else to

SCHEME 9

R-I



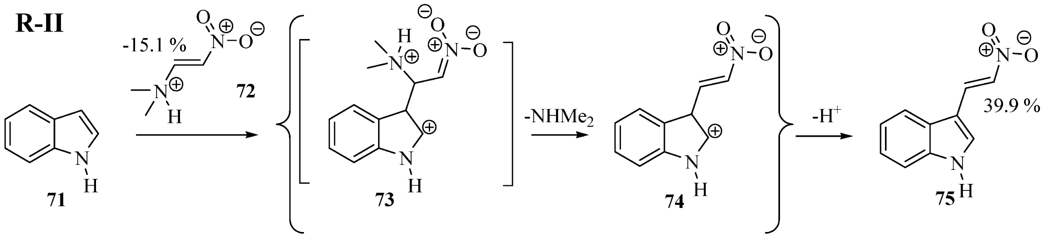
68 **69** **70**

R = H, COOMe, NO_2, OMe

	Olefinicity		ΔOlefinicity
	69	70	
H	0.0	19.1	+19.1
COOMe	11.3	32.7	+21.4
NO_2	1.7	27.3	+25.6
OMe	27.3	34.7	+7.4

SCHEME 10

R-II



Δolefinicity = 39.9 - (-15.1) = 55.0 kJ mol^{-1}
ΔH(RE) = 68.8 kJ mol^{-1}

both C1 and C2 atoms. In **50** and **57**, two electron-donating groups (NH_2 and OH) are attached to the same C1 atom and therefore conjugate their electron pairs in the same direction, increasing their olefinicity values (to 43.6 and 22.9%, respectively) relative to their monoderivatized analogues (29.2% and 20.4%, for **5** and **4**, respectively) as specified in Scheme 3A. Alternative 1,2 substitution of ethene with the same functional groups shows lower olefinicity for **51** (38.4%) relative to **50** (1,1 disubstituted). The inverse is observed for **52** and **53**, where the two electron-withdrawing NO_2 groups decrease the olefinicity values (−7.5% and 0.6%), relative to **26** (5.1%). In the case of **54**, the electron-donating (NH_2) and withdrawing groups (NO_2) compensate one another (29.6%). The "push−pull" systems, such as **55** and **56**, increase the olefinicity values (56.6% and 62.5%,) as a result of the strong conjugation between the NH_2 and NO_2 moieties, wherein the intramolecular H-bond increases the push−pull effect, raising the olefinicity for **56**.

The *fifth group* (**1**, **6**, **60**−**67**) was used to characterize the effect of substitutions bulky group sterics (e.g., *t*-Bu). As Figure 6A shows, the second substitution nearly doubles olefinicity values (175%−189% increase), irrespective of Me-group positions, indicative of negligible steric effects. The third and fourth Me substitutions do not significantly increase olefinicity values because of steric hindrance. Increased *t*-Bu substitution only enhanced olefinicity in the case of **67**, where no double bond exists as a result of the perpendicular arrangement of the two *t*-Bu moieties (Figure 6B). In this particular case, there is no possibility for strong conjugation with **67** preferring complete delocalization.[18−21]

3.4. Correlation between Olefinicity and Computed Reactivity toward Electrophilic and Nucleophilic Reactivity. Olefinic compounds are able to participate in both electrophilic- and nucleophilic-type addition reactions (Scheme 8).[23] The former is initiated through attack by a cation (e.g., H^+), where intermediate **C** may be related to the **A-II** resonance structure. The nucleophilic reaction starts with the addition of an anion to the double bond (e.g., OH^-), where intermediate **D** is reminiscent of the **A-I** resonance structure.

Protonation of the olefinic functionality initiates electrophilic additions at the carbon atom of lowest order. Thus, in agreement with Markownikov's rule,[23] the CH_2 moiety was protonated (**1**−**24**, **26**, **27**, **42**−**49**) to measure the associated proton affinities (PAs) and subsequently may be compared to previously calculated olefinicity values (Figure 7). A relatively good PA−olefinicity correlation was observed considering the large diversity of X functionalities. A stronger conjugation (larger olefinicity) should therefore exhibit greater affinity to protonation, and thus increased reactivity in electrophilic reactions (Figure 7A), while protonation of a weakly conjugative olefin is less advantageous. However, PA is dependent on other parameters such as the relative steric hindrance and identity of the EWG attached to CH_2; thus it is expected that the fit is not significant ($R^2 = 0.810$). As the original geometry of compound **25** changes, it was omitted from the fitting. The PA−olefinicity correlation improves upon separation of these compounds into three groups (neutral, anionic, and cationic), resulting in three nearly parallel lines with smaller slopes.

The correlation between olefinicity percentage and intrinsic reactivity to nucelophiles (neglecting the steric hindrance, solvent and other secondary effects) was characterized using the gas-phase attack of olefinic compounds **1**−**27**, and **42**−**49** by OH^- ion, as previously applied to amides and carbonyl compounds.[16] Reactivity was quantified by the ΔH_{NU} value, as defined in Scheme 8; olefinicity is only able to measure the intrinsic reactivity of alkenes (Figure 7B). When X is a good leaving group, the adduct is not an intermediate, thus these cases (**2**, **7**−**9**, **12**−**19**, **21**, **26**, **43**, **44**, **47**, and **49**), where the adducts were not a minimum, were not involved in the fitting. The olefinicity−nucleophillic reactivity (ΔH_{NU}) correlation is not good ($R^2 = 0.676$, Figure 7B), yet a trend emerges, wherein an olefinic compound of low olefinicity is more active in an addition reaction than one with high olefinicity. However, characterizing the bases of the reactivity requires more complex considerations, where not only the strength of the olefinic bond, but also steric hindrance around the olefinic group (among other variables), may influence the ΔH_{NU} values.

4.3. Olefinicity for Selected Reactions. In many organic reactions, the olefin group is significantly affected, through increasing or decreasing its olefinicity values and thereby providing an enhancing or inhibiting force for reaction, respectively. Here we introduce the $\Delta_{olefinicity}$ value (analogous to $\Delta_{aromaticity}$,[9] $\Delta_{amidicity}$[13] and $\Delta_{carbonilicity}$[16]), which represents the difference between the olefinicity values of the reactant and product materials (eq 8).

$$\Delta_{\text{olefinicity}} = \sum \text{}_{\text{olefinicity(products)}} - \sum \text{}_{\text{olefinicity(reactants)}} \qquad (8)$$

As $\Delta_{\text{olefinicity}}$ refers to the change in the resonance energy of the olefinic unit, the sign of $\Delta_{\text{olefinicity}}$ can therefore be used as an indicator of this phenomenon's contribution to the overall enhancing, with the latter being composed of other effects (e.g., change in amidity, carbonylicity, aromaticity, entropy, etc.). In reactions where only the olefinic portion of a system is affected, the sign of the $\Delta_{\text{olefinicity}}$ may indicate whether a reaction is thermodynamically favorable. However, this in itself is not enough to predict that the reaction will, in fact, proceed, as kinetic and steric forces also mediate reactions, regardless of whether it is thermodynamically favorable.

Two well-known and important organic chemical reactions are were also considered wherein the $\Delta_{\text{olefinicity}}$ is the most important driving force with respect to other forces. Recently, coupling reactions, catalyzed by Pd(0), show marked improvement, furnishing many sophisticated cross-coupled compounds, where synthesis was previously very challenging. In the first reaction, known as a Heck-type coupling (Scheme 9),[24−27] a halogenated aromatic compound (e.g., bromo benzene, **68**) is coupled to a substituted olefin, typically having an EWG; other examples are also described. Four such olefins were characterized, including COOMe (**69a**), NO_2 (**69b**), H (**69c**), and OMe (**69d**), toward characterizing the reaction as driven by $\Delta_{\text{olefinicity}}$. As observed experimentally, the most effective coupling is for R = EWG (NO_2 or COOMe), while for R = EDG (OMe) yields are very low.[24−27]

A very clever and effective process was developed to introduce a nitrovinyl functional group at the 3-position of indole, with high yield and "atom economy" (**R-II** in Scheme 10).[28] In this reaction, we studied only the conversion of reactant to product, toward understanding the driving force of the overall process, assuming that the aromaticity of the benzene ring in indole is roughly constant in **71** and **75**. Dimethylaminonitroethylene is protonated by a strong acid (e.g., trifluoroacetic acid (TFA)), generating **72**, with olefinicity decreasing to −15.1%, due to the disruption of conjugation between NO_2 and Me_2N. To increase its olefinicity value, **72** reacts with indole (**71**), while the Me_2NH eliminates from the molecule, generating the cationic **73**; the principal driving force of this step is the leaving of Me_2NH. During the final favorable deprotonation step, furnishing the product (**75**), olefinicity is raised (39.9%), which together with amine elimination provides the driving force for this reaction. The overall resonance enthalpy released for the process is 68.8 kJ mol^{-1}.

5. Conclusion

A new linear scale, olefinicity, has been defined to measure the strength of the conjugation of a substituted olefin. The scale is based on the relative enthalpy values of hydrogenation reactions (ΔH_{H2}), arbitrarily choosing allyl anion (**2**) as +100% and ethylene (**1**) as 0%. A representative set of 67 general olefinic compounds were included herein, with conclusion that the ΔH_{H2} value may be a good measure of olefinicity. Olefinicity percentage was computed at eight different levels of theory, from which it has been concluded that this methodology is quasi-method independent. Alternatively, olefinicity percentage may also be determined using experimental enthalpies of hydrogenation. A comparison has been made between the novel olefinicity percentage values of the compounds examined and their calculated PAs, as well as their reactivity to OH^- ions, with a linear relationship observed for both cases.

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Supporting Information Available: Tables S1−S5 contain the computed energies (E), zero-point energies (E_{ZPE}), internal energies (U), and enthalpies (H) in hartree at various levels of theories for compounds **1**−**75**. This material is available free of charge via the Internet at http://pubs.acs.org.

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