# A DFT Study of the Reactivity Indexes of Ionic [4 + 2+] Diels-Alder Cycloaddition to Nitrilium and Immonium Ions

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**Abstract:** The global electrophilicity index, defined within the conceptual density functional theory (DFT), was used to classify the dienes and dienophiles currently used in Diels-Alder reactions on a unique scale of electrophilicity. The index, obtained within the Kohn-Sham scheme, is based on the HOMO and LUMO energies. A systematic study of the global reactivity indexes of the reagents involved in formal [4 + 2+] Diels-Alder cycloaddition reactions of nitrilium and immonium ions with isoprene is presented.

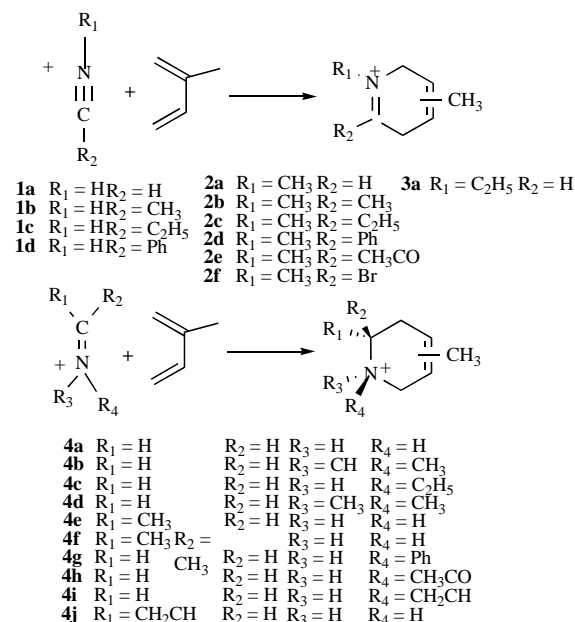**Keywords:** Diels-Alder, reactivity indexes, nitrilium, immonium, electrophilicity, nucleophilicity.

## INTRODUCTION

The conceptual density functional theory (DFT) developed by Parr and Yang [1, 3] is a powerful framework to understand chemical reactivity. It is based on electronic structure descriptors of the isolated reactants from the dawn of theoretical chemistry. However, this formulation as many ordering principles and concepts employed in Chemistry can be traced to early quantum molecular models, such as the Hückel molecular orbital (HMO) theory [4], the valence bond (VB) approximation [5-7], as well the frontier orbital theory (HOMO-LUMO gap) of Fukui [8] can be considered as simple conceptual tools to deal chemical reactivity.

Instead the aforementioned formulation is governed by the analysis of the static descriptors [9] of electronic properties of reactants, the derived quantities provide important clues to board the course of chemical reactions. In a formal framework it has allowed introducing in a many empirical chemical concepts like electronegativity [10], hardness [11], so-called reaction force [12], Fukui function [13], electrophilicity [14], electrofugality and nucleofugality [1, 2, 9, 15-18], nucleophilicity and solution phase ionization potentials, homofugality [19, 20], nucleophilicity [21], among others. In particular, the introduction of concepts like electrophilicity and nucleophilicity to define electron deficient (electrophile) and electron rich (nucleophile) species has gained a continuous interest to construct empirical scales classifying atoms, molecules and charged species [22-29]. The availability of empirical scales of electrophilicity and nucleophilicity, usually based on kinetic parameters, has been very useful to rationalize the chemical reactivity, in terms of selectivity, reaction mechanisms, solvent, substituent effects, etc. [30]. Most of them were early defined by Parr and co-workers and are well described [2]. New developments were recently reviewed [1, 31].

The use of the global electrophilicity index [32], defined within the DFT [2, 11] was reported [29, 33] to classify the

dienes and dienophiles currently used in Diels-Alder (DA) reactions on a unique scale of electrophilicity. A good correlation between the difference in electrophilicity for the diene and dienophile pair, $\Delta\omega$, and the feasibility of the cycloaddition was found [29, 33]. Nitrilium ions ($R-C\equiv N^+-R$) and immonium ions ($RR_1C=N^+R_2R_3$) are important and common ionic species that they might undergo gas-phase Diels-Alder cycloadditions with dienes. In addition, many nitrilium ions occur in the stratosphere and the lower atmosphere [34]. This article therefore describes a systematic study of the reactivity indexes of the formal [4 + 2+] cycloaddition reactions of nitrilium and immonium ions with isoprene (Scheme **1**). These reactions have been studied by means of multiple stage mass spectrometric experiments, performed using a pentaquadrupole instrument. These experiments were complemented by frontier orbital theory using the semiempirical AM1 method [35].



| | | |
|---|---|---|
| **1a** $R_1 = H$ $R_2 = H$ | **2a** $R_1 = CH_3$ $R_2 = H$ | **3a** $R_1 = C_2H_5$ $R_2 = H$ |
| **1b** $R_1 = H$ $R_2 = CH_3$ | **2b** $R_1 = CH_3$ $R_2 = CH_3$ | |
| **1c** $R_1 = H$ $R_2 = C_2H_5$ | **2c** $R_1 = CH_3$ $R_2 = C_2H_5$ | |
| **1d** $R_1 = H$ $R_2 = Ph$ | **2d** $R_1 = CH_3$ $R_2 = Ph$ | |
| | **2e** $R_1 = CH_3$ $R_2 = CH_3CO$ | |
| | **2f** $R_1 = CH_3$ $R_2 = Br$ | |

| | | | |
|---|---|---|---|
| **4a** $R_1 = H$ | $R_2 = H$ | $R_3 = H$ | $R_4 = H$ |
| **4b** $R_1 = H$ | $R_2 = H$ | $R_3 = CH$ | $R_4 = CH_3$ |
| **4c** $R_1 = H$ | $R_2 = H$ | $R_3 = H$ | $R_4 = C_2H_5$ |
| **4d** $R_1 = H$ | $R_2 = H$ | $R_3 = CH_3$ | $R_4 = CH_3$ |
| **4e** $R_1 = CH_3$ | $R_2 = H$ | $R_3 = H$ | $R_4 = H$ |
| **4f** $R_1 = CH_3$ $R_2 =$ | | $R_3 = H$ | $R_4 = H$ |
| **4g** $R_1 = H$ $CH_3$ | $R_2 = H$ | $R_3 = H$ | $R_4 = Ph$ |
| **4h** $R_1 = H$ | $R_2 = H$ | $R_3 = H$ | $R_4 = CH_3CO$ |
| **4i** $R_1 = H$ | $R_2 = H$ | $R_3 = H$ | $R_4 = CH_2CH$ |
| **4j** $R_1 = CH_2CH$ | $R_2 = H$ | $R_3 = H$ | $R_4 = H$ |

**Scheme 1.** [4 + 2+] cycloaddition reactions of nitrilium and immonium ions with isoprene.

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## COMPUTATIONAL DETAILS

The reactivity indexes were estimated according to the equations proposed by Parr *et al.* [2, 11, 32]. The electronic chemical potential ($\mu$) and chemical harness ($\eta$) were evaluated in terms of the one electron energies of frontier molecular orbital HOMO and LUMO using the following equations:

$$\mu \approx \frac{E_{HOMO} + E_{LUMO}}{2}$$

$$\mu \approx E_{LUMO} - E_{HOMO}$$

The global electrophilicity index ($\omega$) which measures the stabilization in energy when the system acquires an additional electronic charge $\Delta N$ from the environment is given by:

$$\omega = \frac{\mu^2}{2\eta}$$

in terms of the electronic chemical potential and the chemical hardness. Moreover, Domingo *et al.* [29, 36]. introduced an empirical (relative) nucleophilicity index, *N*, based on the HOMO energies obtained within the Kohn-Sham scheme [37] and defined as:

$$N = E_{HOMO(Nu)} - E_{HOMO(ref)}$$

The reference value for this nucleophilicity scale is taken by tetracyanoethylene to obtain a scale with only positive values.

Full geometry optimizations were carried out with the Gaussian 03 suite of programs [38]. The calculations were performed within the density functional theory (DFT) [2, 39] using the B3LYP/6-31G* level of theory [40-42]. The geometry optimizations were carried with the Berny analytical gradient optimization method [43-44].

## RESULTS AND DISCUSSION

The electronic chemical potential ($\mu$), the chemical hardness ($\eta$), the global electrophilicity ($\omega$), and the global nucleophilicity (*N*) for isoprene and different nitrilium and immonium ions are shown in Table **1**.

The chemical potential of isoprene ($\mu$ = -0.1362 au) is higher than all the nitrilium and immonium ions, which ranges from -0.3266 au to -0.5058 au, and the model predicts that the net charge transfer for these ionic DA reactions is expected to occur from the isoprene to the electron-deficient ions. Isoprene presents a low electrophilicity value ($\omega$ = 1.24 eV) and could be classified as a moderate electrophile within the electrophilicity scale [33] and the nitrilium and immonium ions are located as strong electrophiles with

**Table 1.** Electronic Chemical Potential, $\mu$, Chemical Hardness, $\eta$, Global Electrophilicity, $\omega$, and Global Nucleophilicity, *N*, for Isoprene and the Nitrilium and Immonium Ions

| | $\mu$ (a.u.) | $\eta$ (a.u.) | $\omega$ (eV) | *N* (eV) |
|---|---|---|---|---|
| **Isoprene** | -0,1362 | 0,2032 | 1,24 | 2,65 |
| **1a** | -0,5058 | 0,4010 | 8,68 | -10,10 |
| **1b** | -0,4401 | 0,3680 | 7,16 | -7,86 |
| **1c** | -0,4023 | 0,3122 | 7,05 | -6,07 |
| **1d** | -0,3428 | 0,1797 | 8,90 | -2,65 |
| **2a** | -0,4380 | 0,3478 | 7,50 | -7,53 |
| **2b** | -0,3960 | 0,3430 | 6,22 | -6,32 |
| **2c** | -0,3776 | 0,3206 | 6,05 | -5,52 |
| **2d** | -0,3266 | 0,1856 | 7,82 | -2,29 |
| **2e** | -0,3909 | 0,2060 | 10,09 | -4,32 |
| **2f** | -0,3864 | 0,2928 | 6,94 | -5,38 |
| **3a** | -0,4028 | 0,2986 | 7,39 | -5,90 |
| **4a** | -0,4863 | 0,3337 | 9,64 | -8,65 |
| **4b** | -0,4366 | 0,2826 | 9,18 | -6,61 |
| **4c** | -0,4114 | 0,2578 | 8,93 | -5,58 |
| **4d** | -0,4096 | 0,2713 | 8,41 | -5,72 |
| **4e** | -0,4374 | 0,2976 | 8,74 | -6,83 |
| **4f** | -0,4113 | 0,2899 | 7,94 | -6,01 |
| **4g** | -0,3465 | 0,1464 | 11,16 | -2,30 |
| **4h** | -0,3465 | 0,1463 | 11,16 | -2,30 |
| **4i** | -0,3851 | 0,1834 | 11,00 | -3,85 |
| **4j** | -0,3910 | 0,2003 | 10,39 | -4,24 |

values bigger that 6.22 eV. Therefore, isoprene acts as a nucleophile in these ionic DA reactions and the nitrilium and immonium ions as electrophiles. Thus the corresponding DA reaction should have an ionic character and, as a result, the nucleophilic addition of isoprene should have an insignificant activation barrier. This behavior is in agreement with the high nucleophilicity of isoprene ($N$ = 2.65 eV) and the negative values for the rest of the ions.

### Nitrilium Ions 1

The group of R-C≡N$^+$-H nitrilium ions has electrophilicity values ranging from 7.05 eV for **1c** to 8.90 eV for the ion **1d**. The $\Delta\omega$ for the reaction between the H-C≡N$^+$-H nitrilium ion and isoprene has a high value of 7.44 eV. Large difference in electrophilicity within the pairs of substrates studied suggests the ionic character of their reaction and, consequently, low activation energy [33]. Experimentally, all the nitrilium ions display reactivity with isoprene and yield product spectra that are dominated by the proton transfer products [35]. When substitution electron-withdrawing groups are increased in the dienophile an increase in the electrophilicity power of the compound is observed. For instance, when a phenyl group is added on the nitrilium ion, ion **1d**, the value of $\Delta\omega$ is increased to 7.66 eV, and decreased to 5.92 and 5.82 eV when the substituent is a methyl or ethyl group respectively.

### Nitrilium Ions 2

The methyl-substituted nitrilium ion (**2a**), H-C≡N$^+$-CH$_3$, has an electrophilicity value of 7.50 eV and a $\Delta\omega$ = 6.26 eV, when the DA reaction takes places with isoprene. According to this model, chemical substitution in the diene with electron-releasing groups make it less electrophilic in global terms. For instance, substitution of the terminal hydrogen atom in ion nitrilium **2a** by a methyl or ethyl group brings the electrophilicity power from 7.50 eV in ion **2a** to 6.22 and 6.05 eV in compounds **2b** and **2c**. However, if the substituent is a phenyl group the electrophilicity value increases until 7.82 eV, ion **2d**, and 10.09 eV when it is substituted by the electron-withdrawing –COCH$_3$ group in compound **2e**. Replacement of the terminal hydrogen by a halogen, bromine in ion **2f,** produces a slight decrease in the electrophilic power of 0.56 eV. In striking contrast to the behavior of ions **1b**, its isomers **2a** react readily with isoprene to give the Diels-Alder cycloadduct [35]. Eberlin *et al.* found that a dramatic change in reactivity was observed when the methyne hydrogen in **2a** was replaced by a methyl (**2b**), ethyl (**2c**), or phenyl (**2d**) group, respectively. These nitrilium ions display a very low overall reactivity and the proton transfer products are therefore dominated [35]. Comparing this result with the electrophilicity power, we can observe than ions **2b** and **2c** have a value lower than **2a**, however the compound **2d** is slightly higher.

### Nitrilium Ion 3

Experimentally, the ion **3a** (H-C≡N$^+$-C$_2$H$_5$) reacts with isoprene to form the corresponding adduct, although the extent to which this reaction occurs and also the overall reactivity of the ion are both smaller than for ion **2a** [35]. In

Table **1** we can compare the reactivity indexes of these ions. The electrophilicity value is 7.50 eV for ion **2a** and 7.39 eV for **2b**, and a value of nucleophilicity of -7.53 eV and -5.90 eV, respectively.

### Immonium Ions 4

A systematic series of several immonium ions (**4a-j**) was investigated for their ability to undergo gas-phase [4+2$^+$] cycloaddition reactions with isoprene by Eberlin *et al.* [35]. The ion **4a** reacts extremely with isoprene to form an abundant DA adduct. Alkyl substitution dramatically decreases the extent to which both the cycloaddition and proton transfer reactions occur. The N-phenyl-substituted (**4g**) and N-acetyl substituted (**4h**) ions favor cycloaddition as the two immonium ions that correspond to the protonated forms of the 2-aza (**4i**) and 1-aza-butadiene (**4j**). The vinyl-substituted ion **4j**, however, is much less reactive with isoprene than ion **4i** [35]. According to the electrophilicity values obtained in Table **1**, the $\Delta\omega$ for the DA reaction between ion **4a** and isoprene has the very high value of 8.40 eV and is expected to have an ionic character. Inclusion of an alkyl group on the ion CH$_2$ = NH$_2$$^+$ decreases the $\Delta\omega$ between 7.94 eV for ion **4b** and 6.70 for ion **4f**. When a hydrogen atom of ion **4a** is substituted by an electron-withdrawing group as phenyl (ion **4g**), brings the $\Delta\omega$ to 9.92 eV, the same value when the substituent is the –COCH$_3$ group (ion **4h**). The two last ions, **4i** and **4j**, are isomers but they have different reactivity indexes, the first ion is more electrophile ($\omega$ = 11.00 eV) than the second ($\omega$ = 10.39 eV) and, as a result, the DA reaction of ion **4i** with isoprene is much reactive than ion **4j**. This prediction is in clear agreement with the experimental results [35].

### CONCLUSIONS

The global electrophilicity index, defined within the DFT becomes a useful quantity to classify the dienes and dienophiles currently used in Diels-Alder reactions on a unique scale of electrophilicity. Reactivity indexes were used to test the electrophilicity trend of ionic [4+2$^+$] Diels-Alder cycloaddition to nitrilium and immonium ions in the gas phase. The electrophilicity order obtained with the reactivity indexes shows good correlations with the experimental results. Substituted ions with electron-withdrawing groups markedly increase the electrophilic reactivity of the compound.

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