**Supplementary Material**

**Unveiling the Intramolecular Ionic Diels-Alder Reactions within the Molecular Electron Density Theory**

Luis R. Domingo1\* María José Aurell,1 and Mar Ríos-Gutiérrez1

*1Department of Organic Chemistry, University of Valencia, Dr. Moliner 50, E-46100 Burjassot, Valencia, Spain, E-mail:* *domingo@utopia.uv.es*

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*Estimation of the electrophilic  indices from the LUMO energies.*

As was commented on in Section 3.1.2, the extended conformations of dieniminiums **12** and **16** present anomalous values of the electrophilicity  indices when they are compared with those of the fold conformations (see Table S1). A similarly behaviour is found at the extended conformation of dieniminium **29**, which was used in the synthesis of (±)-lupinine via a IIDA reaction (see reference [16] in the manuscript). As shows Table S1, the extended conformation **29e** presents also a high electrophilicity  value, 17.42 eV, when it is compared with that of the fold conformation **29f**, 10.71 eV.

**Table S1.** HOMO and LUMO energies, the electronic chemical potential, , chemical hardness, electrophilicity, and nucleophilicity, *N*, indices, of dieniminiums**12**, **16** and **29**,and the estimated electrophilicity LUMO index, in eV, of the extended conformations of dieniminiums**12e**, **16e** and **29e**.



|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | HOMO | LUMO |  |  |  | *N* | LUMO |
| **12e** | -7.90 | -6.88 | -7.39 | 1.02 | 26.72 | 1.22 | 7.64 |
| **12f** |  |  | -7.85 | 3.68 | 8.36 | -0.57 |  |
| **16e** | -8.23 | -7.07 | -7.65 | 1.16 | 25.19 | 0.89 | 7.91 |
| **16f** |  |  | -8.23 | 3.76 | 9.01 | -0.99 |  |
| **29e**  | -8.21 | -6.63 | -7.42 | 1.58 | 17.42 | 0.91 | 7.30 |
| **29f** | -8.73 | -6.15 | -7.44 | 2.59 | 10.71 | 0.39 |  |

An analysis of the dependence of the electrophilicity  indices of the HOMO and LUMO energies, allows establishing a very good polynomic correlation between the electrophilicity  indices of ten susbtituted ethylenes given in Figure 1 with the LUMO energies, LUMO, of these species, R2 = 0.99 (see Table S2 and Figure S1).

The polynomic equation S1 obtained from this analysis allows establishing an estimated electrophilicity LUMO index from the LUMO energies, LUMO.

LUMO = 0.059 \* LUMO2 - 0.5803 \*LUMO + 0.8589 (S1)

The last column of Table S2 shows the estimated electrophilicity LUMO indices for the ten substituted ethylenes. As shows Figure S2, a very good linear correlation between the estimated electrophilicity LUMO indices and the electrophilicity  indices for this series can be found, R2=0.99.

**Table S1.** B3LYP/6-31G(d) HOMO and LUMO energies, the electronic chemical potential, , chemical hardness, electrophilicity, and nucleophilicity, *N*, indices, and the estimated electrophilicity LUMO index, in eV, of ten electrophilic ethylenes shown in Figure 1.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| HOMO | LUMO |  |  |  | *N* | LUMO |
| -14.96 | -7.39 | -11.18 | 7.57 | 8.25 | -5.84 | 8.37 |
| -7.88 | -4.03 | -5.96 | 3.85 | 4.61 | 1.24 | 4.16 |
| -6.14 | -2.97 | -4.55 | 3.17 | 3.28 | 2.99 | 3.10 |
| -7.20 | -3.07 | -5.14 | 4.13 | 3.20 | 1.92 | 3.20 |
| -8.47 | -2.82 | -5.64 | 5.65 | 2.82 | 0.65 | 2.97 |
| -7.00 | -1.77 | -4.38 | 5.23 | 1.84 | 2.12 | 2.07 |
| -7.87 | -1.53 | -4.70 | 6.34 | 1.74 | 1.25 | 1.89 |
| -6.03 | -0.83 | -3.43 | 5.20 | 1.13 | 3.09 | 1.38 |
| -7.26 | 0.51 | -3.37 | 7.77 | 0.73 | 1.86 | 0.58 |
| -5.95 | 1.04 | -2.45 | 6.99 | 0.43 | 3.18 | 0.32 |

By using the equation S1, the electrophilicity LUMO indices for the extended conformations of dieniminiums**12**, **16** and **29** can be estimated (see the last columns of Table S1). The estimated electrophilicity LUMO indices for these dieniminiums, 7.64 eV for **12e**, 7.91 eV for **16e**, and 7.30 for **29e**, are found in reasonable agreement with the values computed for the fold conformations of these dieniminiums: 8.36 eV or **12f** and 9.91 eV for **16f** and 10.71 eV for **29f**.



**Figure S1.** Plot of the electrophilic  index, in eV, *vs* the LUMO energy, LUMO in eV, for the ten electrophilic ethylenes given in Table S1.



**Figure S2.** Plot of the electrophilic  index, in eV, vs electrophilic LUMO index, in eV, computed with equation S1 for the ten electrophilic ethylenes given in Table S1.



**Figure S3.** ELF basin attractor positions together with the most relevant valence basin populations, in average number of electrons e, of experimental dieniminium **12e**.



**Figure S4.**B97XD/6-311G(d,p) geometries of the TSs involved in the IIDA reaction of dieniminium **16**. The CC and CN distances are given in Angstroms.

**Table S3.** B3LYP/6-311G(d,p) Total enthalpies (H, in a.u.), entropies (S, in cal·mol-1·K) and Gibbs free energies (G, in a.u.), computed at 165 ºC and 1 atm, of the stationary points involved in the N-DA reaction of butadiene **1** and ethylene **2**, and in the IMDA reaction of (E)-deca-1,3,9-triene **10**.

|  |  |  |  |
| --- | --- | --- | --- |
|  | H | S | G |
| **1**  | -155.943414 | 75.5 | -155.996132 |
| **2** | -78.556580 | 59.5 | -78.598142 |
| **TS-inter**  | -234.458973 | 90.3 | -234.521992 |
| **3**  | -234.545362 | 82.6 | -234.603062 |
|  |  |  |  |
| **10**  | -390.496085 | 132.4 | -390.588538 |
| **TS-intra**  | -390.449161 | 113.0 | -390.528056 |
| **11** | -390.542008 | 108.2 | -390.617586 |

**Table S4.**B97XD/6-311G(d,p) Total energies (E, in a.u.), enthalpies (H, in a.u.), entropies (S, in cal/mol.K) and Gibbs free energies (G, in a.u.), computed at 75 ºC and 1 atm in ethanol, of the stationary points involved in the I-DA reaction of butadiene **1** with ethaniminium **18**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | E | H | S | G |
| **1**  | -155.971411 | -155.878939 | 70.8 | -155.918212 |
| **18**  | -134.402131 | -134.312646 | 65.7 | -134.349095 |
| **MC**  | -290.380710 | -290.196469 | 110.5 | -290.257768 |
| **TS1-n**  | -290.360639 | -290.176819 | 90.4 | -290.226977 |
| **TS1-x**  | -290.359141 | -290.175431 | 91.6 | -290.226255 |
| **22**  | -290.439419 | -290.249367 | 84.8 | -290.296437 |
| **23**  | -290.430824 | -290.240908 | 86.5 | -290.288935 |

**Table S5.**B97XD/6-311G(d,p) Total energies (E, in a.u.) in ethanol of the stationary points involved in the IIDA reactions of dieniminiums **12** and **16**.

|  |  |  |  |
| --- | --- | --- | --- |
| **12e** | -564.374165 | **16e** | -407.118939 |
| **12f** | -564.374636 | **16f** | -407.117322 |
| **TS2-rn** | -564.354065 | **TS3-rn** | -407.090745 |
| **TS2-rx** | -564.360566 | **TS3-rx** | -407.097228 |
| **TS2-sn** | -564.360462 | **TS3-sn** | -407.097319 |
| **TS2-sx** | -564.352466 | **TS3-sx** | -407.090046 |
| **24** | -564.414443 | **26** | -407.162072 |
| **13** | -564.424182 | **17** | -407.167646 |
| **14** | -564.422875 | **27** | -407.166973 |
| **25** | -564.414727 | **28** | -407.157982 |

**Table S6.**B97XD/6-311G(d,p) Total enthalpies (H, in a.u.), entropies (S, in cal/mol.K) and Gibbs free energies (G, in a.u.), computed at 75 ºC and 1 atm in ethanol, of the stationary points involved in the IIDA reaction of dieniminium **12**.

|  |  |  |  |
| --- | --- | --- | --- |
|  | H | S | G |
| **12e** | -563.999312 | 149.5 | -564.082268 |
| **12f** | -564.001063 | 138.4 | -564.077825 |
| **TS2-rn** | -563.980199 | 133.3 | -564.054144 |
| **TS2-rx** | -563.987237 | 135.2 | -564.062250 |
| **TS2-sn** | -563.986749 | 132.9 | -564.060483 |
| **TS2-sx** | -563.978536 | 135.0 | -564.053420 |
| **24** | -564.034738 | 125.7 | -564.104504 |
| **13** | -564.044771 | 126.4 | -564.114922 |
| **14** | -564.043684 | 128.6 | -564.115045 |
| **25** | -564.034904 | 126.7 | -564.105216 |

**Table S7**. ELF valence basin populations and distances of the N1-C6 and C2-C3 forming bonds of the structures of the IRC associated to the IIDA reaction of dieniminium **16**, defining the nine phases of the BET. Distances are given in angstroms, Å, and electron populations in average number of electrons, e.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Structures** | **S0** | **S1** | **S2** | **S3** | **S4** | **S5** | **S6** | **S7** | **S8** | **S9** |
| *Phases* | *I* | *II* | *III* | *IV* | *V* | *VI* | *VII* | *VIII* | *IX* |  |
| d(N1-C6) | 3.145 | 3.077 | 2.866 | 2.863 | 2.849 | 2.840 | 2.822 | 2.115 | 1.997 | 1.522 |
| d(C2-C3) | 2.804 | 2.723 | 2.132 | 2.123 | 2.081 | 2.055 | 2.005 | 1.580 | 1.568 | 1.534 |
| V(N1,C2) | 3.46 | 3.47 | 3.03 | 3.02 | 2.92 | 2.86 | 2.74 | 1.78 | 1.78 | 1.77 |
| V(C3,C4) | 1.56 | 1.55 | 1.49 | 1.49 | 3.11 | 3.09 | 3.06 | 2.35 | 2.26 | 1.73 |
| V'(C3,C4) | 1.73 | 1.75 | 1.66 | 1.65 |  |  |  |  |  |  |
| V(C4,C5) | 2.23 | 2.24 | 2.37 | 2.37 | 2.39 | 2.40 | 2.42 | 3.17 | 1.45 | 1.67 |
| V'(C4,C5) |  |  |  |  |  |  |  |  | 1.81 | 1.78 |
| V(C5,C6) | 1.57 | 3.29 | 3.12 | 3.12 | 3.12 | 2.80 | 2.71 | 2.12 | 2.09 | 2.02 |
| V'(C5,C6) | 1.76 |  |  |  |  |  |  |  |  |  |
| V(N1) |  |  | 0.56 | 0.57 | 0.68 | 0.74 | 0.88 |  |  |  |
| V(C2) |  |  |  | 0.11 | 0.17 | 0.19 |  |  |  |  |
| V(C3) |  |  |  |  |  | 0.32 |  |  |  |  |
| V(C2,C3) |  |  |  |  |  |  | 0.67 | 1.78 | 1.82 | 1.92 |
| V(N1,C6) |   |   |   |   |   |   |   | 1.59 | 1.59 | 1.73 |