Supplementary Material

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

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Estimation of the electrophilic ω 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 ω indices when they are compared with those of the fold conformations (see Table S1). A similarly behavior 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 ω 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, μ, chemical hardness, η, electrophilicity, ω, and nucleophilicity, *N*, indices, of dieniminiums **12**, **16** and **29**, and the estimated electrophilicity ω_{LUMO} index, in eV, of the extended conformations of dieniminiums **12e**, **16e** and **29e**.

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	ε_{HOMO}	ε_{LUMO}	μ	η	ω	*N*	ω_{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 ω indices of the HOMO and LUMO energies, allows establishing a very good polynomic correlation between the electrophilicity ω indices of ten substituted ethylenes given in Figure 1 with the LUMO energies, ε_{LUMO}, of these species, $R^2 = 0.99$ (see Table S2 and Figure S1).

The polynomic equation S1 obtained from this analysis allows establishing an estimated electrophilicity ω_{LUMO} index from the LUMO energies, ε_{LUMO}.

$$\omega_{LUMO} = 0.059 * \varepsilon_{LUMO}^2 - 0.5803 * \varepsilon_{LUMO} + 0.8589 \qquad \text{(S1)}$$

The last column of Table S2 shows the estimated electrophilicity ω_{LUMO} indices for the ten substituted ethylenes. As shows Figure S2, a very good linear correlation between the estimated electrophilicity ω_{LUMO} indices and the electrophilicity ω indices for this series can be found, R^2=0.99.

Table S1. B3LYP/6-31G(d) HOMO and LUMO energies, the electronic chemical potential, μ, chemical hardness, η, electrophilicity, ω, and nucleophilicity, *N*, indices, and the estimated electrophilicity ω_{LUMO} index, in eV, of ten electrophilic ethylenes shown in Figure 1.

ε_{HOMO}	ε_{LUMO}	μ	η	ω	*N*	ω_{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 ω_{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 ω_{LUMO} indices for these dieniminiums, 7.64 (**12e**), 7.91 (**16e**), and 7.30 (**29e**) eV, are found in reasonable agreement with the values computed for the fold conformations of these dieniminiums: 8.36 (**12f**), 9.91 (**16f**) and 10.71 (**29f**) eV.

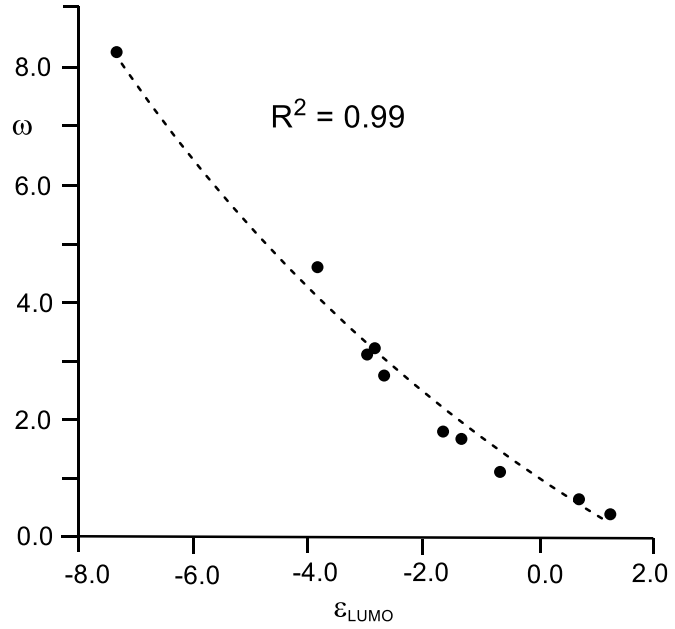

Figure S1. Plot of the electrophilic ω index, in eV, *vs* the LUMO energy, ε_{LUMO} in eV, for the ten electrophilic ethylenes given in Table S1.

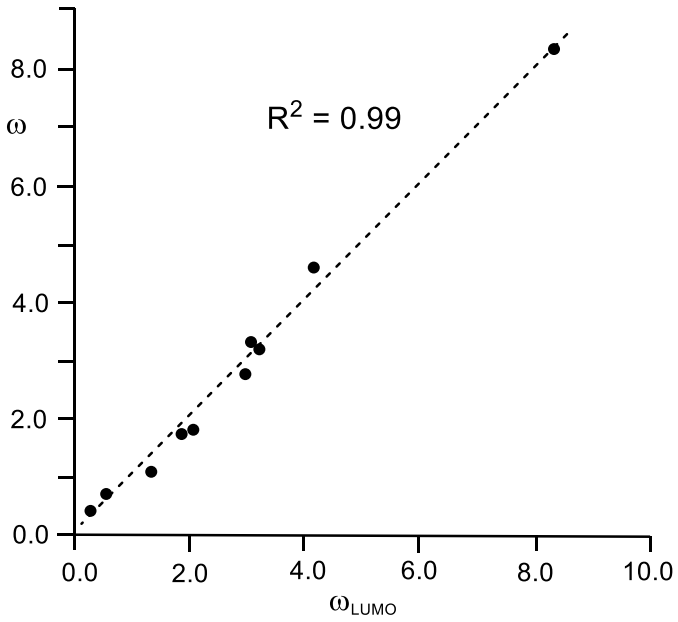

Figure S2. Plot of the electrophilic ω index, in eV, vs electrophilic ω_{LUMO} index, in eV, computed with equation S1 for the ten electrophilic ethylenes given in Table S1.

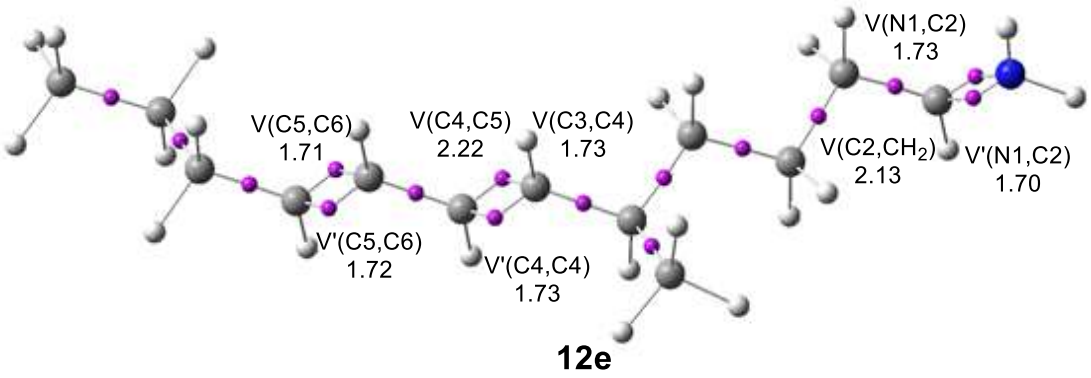

Figure S3. ELF basin attractor positions together with the most relevant valence basin populations, in average number of electrons e, of experimental dieniminium **12e**.

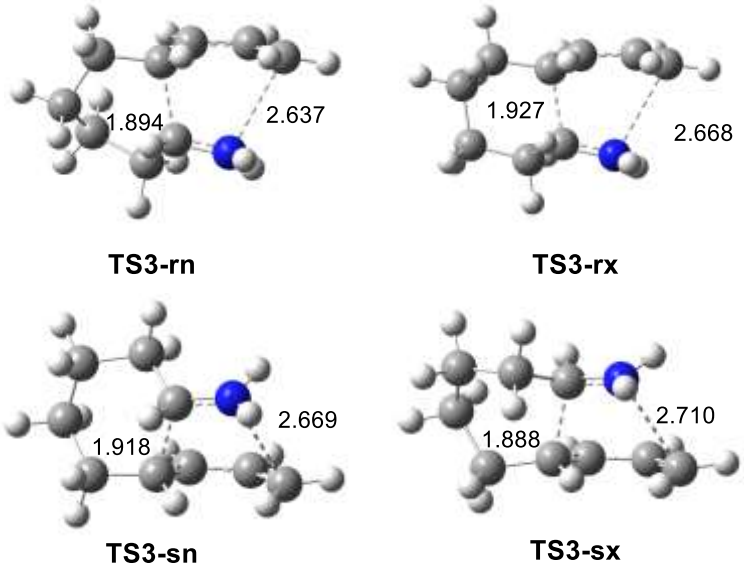

Figure S4. ωB97XD/6-311G(d,p) geometries of the TSs involved in the IIDA reaction of dieniminium **16**. The C–C and C–N distances are given in Angstroms.

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. ωB97XD/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. ωB97XD/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. ωB97XD/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