Net Electrophilicity

Pratim Kumar Chattaraj,* Arindam Chakraborty, and Santanab Giri

Department of Chemistry & Center for Theoretical Studies, Indian Institute of Technology, Kharagpur 721302, India

Received: April 29, 2009

The concept of net electrophilicity (electroaccepting power relative to electrodonating power) is introduced. It provides expected trends in most cases. A net electrophilicity scale is presented. Various reactivity descriptors for 32 molecules are calculated at the B3LYP/6-311+G(d) level of theory. Profiles of net electrophilicity along the reaction paths of thermoneutral, exothermic, endothermic, and cycloaddition reactions are analyzed. Net electrophilicity often attains its minimum value for a stable state or a favorable reaction.

1. Introduction

Electrophilicity[1−3] is one of the important concepts for rationalizing a wide variety of organic reactions. Its connection with Lewis acidity and oxidizing power expands the domain of its applicability. It contains[4,5] adequate information regarding structure, property, reactivity, dynamics, aromaticity, and toxicity of many-electron systems.

Because molecules contain both electrons and nuclei, an electrophile (also a nucleophile) will face both attractive and repulsive forces during its reaction to any molecule. It is true for an/a atom/group in a molecule as well. We propose in this article that a net electrophilicity (electrophilicity of a system relative to its own nucleophilicity) would be a better descriptor in explaining the electrophilic power of any species. To be precise, the net electrophilicity of a species measures its electron-accepting power relative to its electron-donating power.

Theoretical background of the present work is presented in Section 2, and Section 3 provides the computational details. Results are discussed in Section 4; finally, Section 5 contains some concluding remarks.

2. Theoretical Background

Inspired by the work of Maynard et al.,[6] Parr and coworkers[7] have provided a definition of electrophilicity (ω) as

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \tag{1}$$

where μ is the chemical potential (negative of the electronegativity, χ), a Lagrange multiplier associated with the normalization of density, defined as[8,9]

$$\mu = -\chi = \left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})} \approx -\frac{I + A}{2} \approx \frac{E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}}{2} \tag{2}$$

and η is the hardness given by[10,11]

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})} \approx I - A \approx E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} \tag{3}$$

In the above definitions for an N-electron system with total energy E and external potential $v(\mathbf{r})$, I and A are, respectively, the ionization potential and the electron affinity, whereas E_{HOMO} and E_{LUMO} are the energies of the highest-occupied and lowest-unoccupied molecular orbitals, respectively.

Although the definition of ω provided by Maynard et al.[6] was based on kinetic data, the same definition was obtained by Parr et al.[7] from a thermodynamic consideration, highlighting the power of the same. It measures the energy change associated with the interaction (electron transfer) of a given electrophile with a perfect nucleophile such as a zero-temperature free-electron sea having zero chemical potential. In an important contribution, Gazquez et al.[12] have defined electrodonating (ω^-) and electroaccepting (ω^+) powers as

$$\omega^- = \frac{(\mu^-)^2}{2\eta^-} \tag{4a}$$

$$\omega^+ = \frac{(\mu^+)^2}{2\eta^+} \tag{4b}$$

where $\mu^\pm$ and $\eta^\pm$ are associated directional derivatives (cf. eqs 2 and 3). They have provided[12] two sets of definitions for ω^- and ω^+, viz.

$$\omega^- = \frac{I^2}{2(I - A)} \tag{5a}$$

$$\omega^+ = \frac{A^2}{2(I - A)} \tag{5b}$$

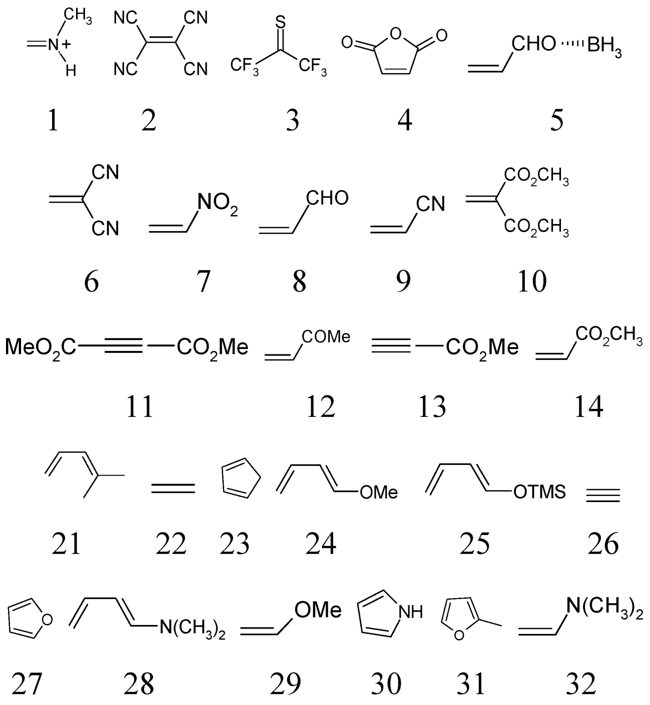
and by using an alternative energy interpolation

---

* Corresponding author. E-mail: pkc@chem.iitkgp.ernet.in.

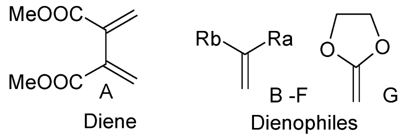
10.1021/jp904674x CCC: $40.75

TABLE 1: Energy of the Highest Occupied Molecular Orbital (E_{HOMO}, au), Lowest Unoccupied Molecular Orbital (E_{LUMO}, au), Electronegativity (χ, electronvolts), Hardness (η, electronvolts), Electrophilicity Index (ω, electronvolts), Chemical Potential for Electron Acceptance (μ^+, electronvolts), Chemical Potential for Electron Donation (μ^-, electronvolts), Electroaccepting Power (ω^+, electronvolts), Electrodonating Power (ω^-, electronvolts), and Net Electrophilicity ($\Delta\omega^\pm$, electronvolts) Values for Some Common Dienes and Dienophiles Involved in Diels−Alder Reactions, viz.



molecules	E_{HOMO} (au)	E_{LUMO} (au)	χ (eV)	η (eV)	ω (eV)	μ^+ (eV) $[\mu^{+(a)}(\mu^{+(b)})]$	μ^- (eV) $[\mu^{-(a)}(\mu^{-(b)})]$	ω^+ (eV) $[\omega^{+(a)}(\omega^{+(b)})]$	ω^- (eV) $[\omega^{-(a)}(\omega^{-(b)})]$	$\Delta\omega^\pm$ (eV) $[\Delta\omega^{\pm(a)}(\Delta\omega^{\pm(b)})]$
1 *N*-methylmethyleneammonium cation	−0.5814	−0.2965	11.945	7.751	9.204	−10.007 (−8.069)	−13.882 (−15.820)	12.920 (4.200)	24.864 (16.140)	37.784 (20.345)
2 tetracyanoethylene	−0.3487	−0.1939	7.382	4.214	6.465	−6.328 (−5.275)	−8.436 (−9.489)	9.503 (3.301)	16.885 (10.680)	26.389 (13.985)
3 hexafluorothioketone	−0.2390	−0.1619	6.190	3.567	5.371	−5.298 (−4.407)	−7.082 (−7.973)	7.870 (2.722)	14.060 (8.912)	21.930 (11.634)
4 maleic anhydride	−0.3160	−0.1316	6.089	5.018	3.694	−4.834 (−3.580)	−7.343 (−8.598)	4.658 (1.277)	10.746 (7.366)	15.404 (8.643)
5 acrolein−BH_3 complex	−0.2794	−0.1255	5.508	4.189	3.622	−4.611 (−3.414)	−6.556 (−7.603)	4.751 (1.391)	10.259 (6.900)	15.010 (8.291)
6 1,1-dicyanoethylene	−0.3243	−0.1179	6.015	5.616	3.221	−4.611 (−3.207)	−7.419 (−8.824)	3.786 (0.916)	9.801 (6.931)	13.587 (7.847)
7 nitroethylene	−0.3148	−0.1140	5.834	5.463	3.116	−4.469 (−3.103)	−7.200 (−8.566)	3.655 (0.881)	9.490 (6.716)	13.145 (7.597)
8 acrolein	−0.2728	−0.0815	4.821	5.206	2.232	−3.520 (−2.218)	−6.123 (−7.424)	2.380 (0.473)	7.201 (5.294)	9.580 (5.766)
9 acrylonitrile	−0.3027	−0.0729	5.110	6.255	2.087	−3.546 (−1.982)	−6.674 (−8.237)	2.010 (0.314)	7.120 (5.424)	9.131 (5.738)
10 dimethyl 2-methylenemalonate	−0.2864	−0.0746	4.911	5.763	2.092	−3.470 (−2.029)	−6.352 (−7.792)	2.090 (0.357)	7.000 (5.268)	9.090 (5.626)
11 dimethyl acetylenedicarboxylate	−0.3055	−0.0699	5.108	6.410	2.035	−3.505 (−1.903)	−6.710 (−8.313)	1.917 (0.282)	7.024 (5.390)	8.941 (5.672)
12 methyl vinyl ketone	−0.2640	−0.0740	4.598	5.170	2.044	−3.305 (−2.013)	−5.890 (−7.183)	2.113 (0.392)	6.711 (4.990)	8.824 (5.382)
13 methyl propiolate	−0.2972	−0.0618	4.884	6.405	1.862	−3.283 (−1.682)	−6.485 (−8.087)	1.683 (0.221)	6.567 (5.105)	8.250 (5.326)
14 methyl acrylate	−0.2893	−0.0623	4.784	6.176	1.853	−3.240 (−1.696)	−6.328 (−7.872)	1.700 (0.233)	6.484 (5.017)	8.184 (5.250)
15 1-acetoxy-1, 3-butadiene	−0.2341	−0.0540	3.920	4.903	1.567	−2.694 (−1.469)	−5.146 (−6.371)	1.481 (0.220)	5.401 (4.140)	6.881 (4.360)
16 1,3-butadiene	−0.2453	−0.0420	3.909	5.533	1.381	−2.526 (−1.142)	−5.292 (−6.675)	1.153 (0.118)	5.062 (4.027)	6.214 (4.145)
17 2-trimethylsilyloxy-1, 3-butadiene	−0.2330	−0.0369	3.672	5.334	1.264	−2.338 (−1.005)	−5.006 (−6.339)	1.025 (0.095)	4.697 (3.766)	5.722 (3.861)
18 2-methyl-1, 3-butadiene	−0.2409	−0.0342	3.742	5.624	1.245	−2.336 (−0.930)	−5.148 (−6.554)	0.970 (0.077)	4.712 (3.819)	5.682 (3.896)
19*N*-methylmethanimine	−0.2632	−0.0254	3.927	6.470	1.192	−2.310 (−0.692)	−5.545 (−7.162)	0.824 (0.037)	4.752 (3.964)	5.576 (4.001)
20 (*E*)-1,3-pentadiene	−0.2333	−0.0338	3.634	5.426	1.217	−2.336 (−0.921)	−4.990 (−6.347)	0.956 (0.078)	4.590 (3.712)	5.546 (3.790)
21 4-methyl-1,3-pentadiene	−0.2279	−0.0289	3.494	5.415	1.127	−2.140 (−0.786)	−4.848 (−6.201)	0.846 (0.057)	4.340 (3.551)	5.186 (3.608)
22 ethylene	−0.2802	−0.0085	3.928	7.394	1.043	−2.079 (−0.231)	−5.777 (−7.625)	0.585 (0.004)	4.513 (3.932)	5.097 (3.935)
23 cyclopentadiene	−0.2251	−0.0276	3.438	5.375	1.100	−2.095 (−0.751)	−4.782 (−6.126)	0.816 (0.052)	4.254 (3.491)	5.071 (3.543)
24 1-methoxy-1,3-butadiene	−0.2165	−0.0285	3.334	5.115	1.086	−2.055 (−0.776)	−4.612 (−5.891)	0.825 (0.059)	4.159 (3.392)	4.984 (3.451)
25 1-trimethylsilyloxy-1,3-butadiene	−0.2136	−0.0240	3.233	5.161	1.013	−1.943 (−0.653)	−4.523 (−5.813)	0.731 (0.041)	3.964 (3.274)	4.696 (3.316)
26 acetylene	−0.3002	0.0145	3.887	8.563	0.882	−1.747 (0.394)	−6.028 (−8.169)	0.356 (0.009)	4.244 (3.896)	4.600 (3.905)
27 furan	−0.2390	−0.0045	3.313	6.380	0.860	−1.718 (−0.123)	−4.908 (−6.503)	0.463 (0.001)	3.776 (3.314)	4.239 (3.316)
28 *N*,*N*-dimethyl-1, 3-butadiene-1-amine	−0.1904	−0.0184	2.840	4.681	0.861	−1.669 (−0.499)	−4.01 (−5.180)	0.595 (0.027)	3.435 (2.866)	4.031 (2.893)
29 methyl vinyl ether	−0.2398	0.0054	3.189	6.674	0.762	−1.520 (0.148)	−4.857 (−6.526)	0.346 (0.002)	3.535 (3.191)	3.882 (3.192)
30 pyrrole	−0.2170	−0.0033	2.997	5.816	0.772	−1.543 (−0.090)	−4.451 (−5.905)	0.410 (7×10^{-4})	3.407 (2.998)	3.817 (2.999)
31 2-methylfuran	−0.2261	0.0024	3.044	6.219	0.745	−1.489 (0.066)	−4.599 (−6.153)	0.357 (3×10^{-4})	3.400 (3.044)	3.757 (3.044)
32 dimethylvinylamine	−0.2017	0.0009	2.732	5.513	0.677	−1.354 (0.025)	−4.110 (−5.488)	0.332 (6×10^{-5})	3.064 (2.732)	3.396 (2.732)

SCHEME 1



Entry	Ra	Rb	Entry	Ra	Rb
B	OMe	OMe	**E**	H	COOMe
C	H	OMe	**F**	CN	CN
D	COOMe	COOMe	**G**	–	–

Reacting pairs:
1. A + B; 2. A + C; 3. A + D; 4. A + E; 5. A + F; 6. A + G

$$\omega^- = \frac{(3I + A)^2}{16(I - A)} \tag{6a}$$

$$\omega^+ = \frac{(I + 3A)^2}{16(I - A)} \tag{6b}$$

It is important to note that a larger ω^+ value corresponds to a better capability of accepting charge, whereas a smaller value of ω^- of a system makes it a better electron donor. To treat ω^+ and ω^- at par, we choose to compare ω^+ with $(-\omega^-)$. Accordingly we propose the following definition of the net electrophilicity

$$\Delta\omega^\pm = \omega^+ - (-\omega^-) = \omega^+ + \omega^- \tag{7}$$

Note that there may be other ways of defining this quantity and keep this idea intact, for example, $(\omega^+ - (1/\omega^-))$.

3. Computational Details

The geometry optimization and subsequent frequency calculations of all the organic compounds are carried out at the B3LYP/6-311+G(d) level of theory with the help of the Gaussian 03 program package.[13] The NIMAG values of all optimized geometries are zero, thereby confirming their existence at the minima of the potential energy surface (PES). The ionization potential (I) and electron affinity (A) are calculated using Koopmans' theorem,[14] viz. I and A are expressed as the negative of the energies of the highest

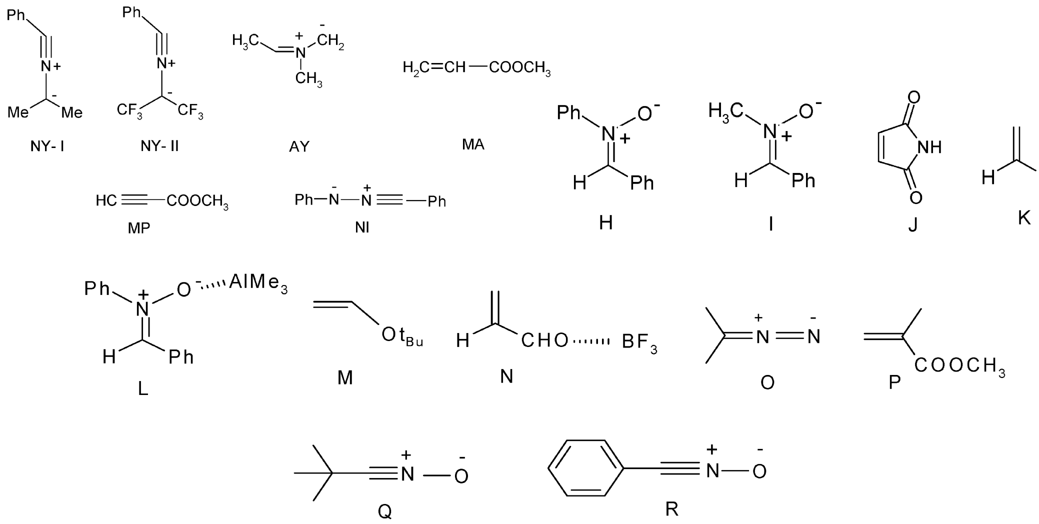
TABLE 2: Energy of the Highest Occupied Molecular Orbital (E_{HOMO}, au), Lowest Unoccupied Molecular Orbital (E_{LUMO}, au), Electronegativity (χ, electronvolts), Hardness (η, electronvolts), Electrophilicity Index (ω, electronvolts), Electrophilicity Difference ($\Delta\omega$, electronvolts), Chemical Potential for Electron Acceptance (μ^+, electronvolts), Chemical Potential for Electron Donation (μ^-, electronvolts), Electroaccepting Power (ω^+, electronvolts), Electrodonating Power (ω^-, electronvolts), Net Electrophilicity ($\Delta\omega^\pm$, electronvolts) and Difference in Net Electrophilicity for the Diene−Dienophile Pair [$\Delta(\Delta\omega)^\pm$, electronvolts]

molecules	E_{HOMO} (au)	E_{LUMO} (au)	χ (eV)	η (eV)	ω (eV)	$\Delta\omega$ (eV)	μ^+ (eV) [$\mu^{+(a)}(\mu^{+(b)})$]	μ^- (eV) [$\mu^{-(a)}(\mu^{-(b)})$]	ω^+ (eV) [$\omega^{+(a)}(\omega^{+(b)})$]	ω^- (eV) [$\omega^{-(a)}(\omega^{-(b)})$]	$\Delta\omega^\pm$ (eV) [$\Delta\omega^{\pm(a)}(\Delta\omega^{\pm(b)})$]	$\Delta(\Delta\omega)^\pm$ (eV) [$\Delta(\Delta\omega)^{\pm(a)}(\Delta(\Delta\omega)^{\pm(b)})$]
A	−0.2747	−0.0664	4.640	5.669	1.899		−3.223 (−1.805)	−6.057 (−7.474)	1.832 (0.288)	6.472 (4.927)	8.304 (5.215)	
B	−0.2254	0.0029	3.027	6.212	0.737	1.162	−1.474 (0.079)	−4.580 (−6.133)	0.350 (5×10^{-04})	3.376 (3.027)	3.726 (3.028)	4.578 (2.187)
C	−0.2398	0.0054	3.189	6.674	0.762	1.137	−1.520 (0.148)	−4.857 (−6.526)	0.346 (0.002)	3.535 (3.191)	3.882 (3.192)	4.422 (2.023)
D	−0.2864	−0.0746	4.911	5.763	2.092	−0.194	−3.470 (−2.029)	−6.352 (−7.792)	2.090 (0.357)	7.000 (5.268)	9.090 (5.626)	−0.786 (−0.411)
E	−0.2893	−0.0623	4.784	6.176	1.853	0.046	−3.240 (−1.696)	−6.328 (−7.872)	1.700 (0.233)	6.484 (5.017)	8.184 (5.250)	0.120 (−0.035)
F	−0.3243	−0.1179	6.015	5.616	3.221	−1.322	−4.611 (−3.207)	−7.419 (−8.824)	3.786 (0.916)	9.801 (6.931)	13.587 (7.847)	−5.283 (−2.632)
G	−0.2195	0.0006	2.994	5.957	0.752	1.147	−1.504 (−0.015)	−4.483 (−5.972)	0.380 (2×10^{-05})	3.373 (2.994)	3.753 (2.994)	4.551 (2.221)

TABLE 3: Energy of the Highest Occupied Molecular Orbital (E_{HOMO}, au), Lowest Unoccupied Molecular Orbital (E_{LUMO}, au), Electronegativity (χ, electronvolts), Hardness (η, electronvolts), Electrophilicity Index (ω, electronvolts), Electrophilicity Difference ($\Delta\omega$, electronvolts), Chemical Potential for Electron Acceptance (μ^+, electronvolts), Chemical Potential for Electron Donation (μ^-, electronvolts), Electroaccepting Power (ω^+, electronvolts), Electrodonating Power (ω^-, electronvolts), Net Electrophilicity ($\Delta\omega^\pm$, electronvolts) and Difference in Net Electrophilicity for the Diene−Dienophile Pair [$\Delta(\Delta\omega)^\pm$, electronvolts]

molecules	$\mathrm{E_{HOMO}}$ (au)	$\mathrm{E_{LUMO}}$ (au)	χ (eV)	η (eV)	ω (eV)	$\Delta\omega$ (eV)	μ^+ (eV) [$\mu^{+(a)}(\mu^{+(b)})$]	μ^- (eV) [$\mu^{-(a)}$ ($\mu^{-(b)}$)]	ω^+ (eV) [$\omega^{+(a)}(\omega^{+(b)})$]	ω^- (eV) [$\omega^{-(a)}(\omega^{-(b)})$]	$\Delta\omega^\pm$ (eV) [$\Delta\omega^{\pm(a)}$ ($\Delta\omega^{\pm(b)}$)]	$\Delta(\Delta\omega)^\pm$ (eV) [$\Delta(\Delta\omega)^{\pm(a)}$ ($\Delta(\Delta\omega)^{\pm(b)}$)]
(a) For Gas Phase												
Cp	−0.2251	−0.0276	3.438	5.375	1.100		−2.095 (−0.751)	−4.782 (−6.126)	0.816 (0.052)	4.254 (3.491)	5.071 (3.543)	
1	−0.2162	−0.1326	4.745	2.275	4.949	−3.849	−4.176 (−3.608)	−5.314 (−5.882)	7.668 (2.861)	12.413 (7.606)	20.081 (10.470)	−15.010 (−6.924)
2	−0.2113	−0.1265	4.596	2.307	4.578	−3.478	−4.019 (−3.442)	−5.173 (−5.750)	7.002 (2.568)	11.598 (7.164)	18.600 (9.732)	−13.529 (−6.189)
3	−0.2153	−0.1263	4.647	2.421	4.461	−3.361	−4.042 (−3.437)	−5.252 (−5.857)	6.749 (2.440)	11.396 (7.087)	18.145 (9.526)	−13.074 (−5.983)
4	−0.2104	−0.1228	4.533	2.385	4.309	−3.209	−3.937 (−3.341)	−5.129 (−5.726)	6.501 (2.341)	11.034 (6.874)	17.535 (9.214)	−12.464 (−5.671)
5	−0.2108	−0.1222	4.531	2.412	4.255	−3.156	−3.928 (−3.325)	−5.134 (−5.737)	6.396 (2.291)	10.927 (6.823)	17.323 (9.114)	−12.253 (−5.571)
6	−0.2075	−0.1207	4.466	2.360	4.224	−3.125	−3.876 (−3.285)	−5.056 (−5.646)	6.364 (2.287)	10.829 (6.752)	17.193 (9.039)	−12.122 (−5.496)
7	−0.2097	−0.1164	4.437	2.539	3.876	−2.776	−3.802 (−3.167)	−5.017 (−5.706)	5.692 (1.975)	10.128 (6.411)	15.820 (8.386)	−10.749 (−4.843)
8	−0.2728	−0.0815	4.821	5.206	2.232	−1.133	−3.520 (−2.218)	−6.123 (−7.424)	2.380 (0.473)	7.201 (5.294)	9.580 (5.766)	−4.509 (−2.223)
9	−0.2699	−0.0746	4.686	5.315	2.066	−0.966	−3.358 (−2.029)	−6.015 (−7.344)	2.121 (0.387)	6.807 (5.074)	8.928 (5.461)	−3.858 (−1.918)
10	−0.2641	−0.0695	4.539	5.295	1.946	−0.846	−3.216 (−1.892)	−5.863 (−7.187)	1.953 (0.338)	6.492 (4.877)	8.445 (5.215)	−3.374 (−1.672)
11	−0.2581	−0.0677	4.432	5.179	1.897	−0.797	−3.138 (−1.843)	−5.727 (−7.022)	1.901 (0.328)	6.334 (4.760)	8.235 (5.088)	−3.164 (−1.545)
12	−0.2607	−0.0689	4.485	5.220	1.926	−0.827	−3.180 (−1.875)	−5.790 (−7.095)	1.937 (0.337)	6.421 (4.821)	8.358 (5.158)	−3.287 (−1.615)
(B) For Solution Phase: (Solvent: Dichloromethane)												
Cp	−0.2266	−0.0287	3.474	5.386	1.120		−2.127 (−0.781)	−4.821 (−6.167)	0.840 (0.057)	4.314 (3.530)	5.154 (3.587)	
1	−0.2280	−0.1258	4.814	2.780	4.168	−3.048	−4.119 (−3.424)	−5.509 (−6.204)	6.103 (2.109)	10.920 (6.923)	17.021 (9.032)	−11.867 (−5.445)
2	−0.2259	−0.1219	4.731	2.829	3.956	−2.836	−4.024 (−3.317)	−5.438 (−6.146)	5.724 (1.944)	10.460 (6.676)	16.179 (8.620)	−11.025 (−5.033)
3	−0.2274	−0.1213	4.745	2.887	3.899	−2.779	−4.023 (−3.301)	−5.467 (−6.188)	5.606 (1.887)	10.350 (6.632)	15.957 (8.520)	−10.802 (−4.933)
4	−0.2253	−0.1167	4.652	2.956	3.661	−2.541	−3.913 (−3.174)	−5.391 (−6.130)	5.180 (1.704)	9.833 (6.356)	15.013 (8.061)	−9.859 (−4.474)
5	−0.2249	−0.1189	4.678	2.883	3.795	−2.675	−3.957 (−3.237)	−5.399 (−6.119)	5.432 (1.817)	10.110 (6.495)	15.542 (8.312)	−10.388 (−4.724)
6	−0.2242	−0.1178	4.653	2.894	3.741	−2.621	−3.930 (−3.206)	−5.377 (−6.100)	5.336 (1.776)	9.989 (6.429)	15.326 (8.205)	−10.171 (−4.618)
7	−0.2243	−0.1117	4.571	3.065	3.409	−2.289	−3.805 (−3.039)	−5.338 (−6.104)	4.723 (1.506)	9.295 (6.077)	14.018 (7.584)	−8.863 (−3.997)
8	−0.2776	−0.0814	4.884	5.337	2.235	−1.115	−3.550 (−2.216)	−6.219 (−7.553)	2.361 (0.460)	7.246 (5.344)	9.607 (5.804)	−4.453 (−2.217)
9	−0.2743	−0.0755	4.758	5.409	2.093	−0.973	−3.406 (−2.053)	−6.110 (−7.463)	2.144 (0.390)	6.902 (5.148)	9.046 (5.537)	−3.892 (−1.950)
10	−0.2713	−0.0713	4.661	5.443	1.995	−0.875	−3.300 (−1.939)	−6.022 (−7.382)	2.000 (0.345)	6.661 (5.006)	8.662 (5.351)	−3.508 (−1.764)
11	−0.2672	−0.0714	4.606	5.328	1.991	−0.871	−3.274 (−1.942)	−5.939 (−7.271)	2.012 (0.354)	6.619 (4.960)	8.631 (5.315)	−3.477 (−1.727)
12	−0.2671	−0.0714	4.604	5.325	1.991	−0.871	−3.273 (−1.942)	−5.936 (−7.267)	2.012 (0.354)	6.616 (4.958)	8.628 (5.312)	−3.474 (−1.725)

SCHEME 3



Reacting pairs: 1. NY-I + MA; 2. NY-II + MA; 3. AY + MP; 4. NI + MP; 5. H + J; 6. I + K; 7. L+M; 9. H + N; 10. O + P; 11. Q + E; 12. R + K

TABLE 4: Energy of the Highest Occupied Molecular Orbital (E_{HOMO}, au), Lowest Unoccupied Molecular Orbital (E_{LUMO}, au), Electronegativity (χ, electronvolts), Hardness (η, electronvolts), Electrophilicity Index (ω, electronvolts), Electrophilicity Difference ($\Delta\omega$, electronvolts), Chemical Potential for Electron Acceptance (μ^+, electronvolts), Chemical Potential for Electron Donation (μ^-, electronvolts), Electroaccepting Power (ω^+, electronvolts), Electrodonating Power (ω^-, electronvolts), Net Electrophilicity ($\Delta\omega^{\pm}$, electronvolts) and Difference in Net Electrophilicity for the Dipole−Dipolarophile Pair [$\Delta(\Delta\omega)^{\pm}$, electronvolts]

molecules	E_{HOMO} (au)	E_{LUMO} (au)	χ (eV)	η (eV)	ω (eV)	$\Delta\omega$ (eV)	μ^+ (eV) [$\mu^{+(a)}(\mu^{+(b)})$]	μ^- (eV) [$\mu^{-(a)}(\mu^{-(b)})$]	ω^+ (eV) [$\omega^{+(a)}(\omega^{+(b)})$]	ω^- (eV) [$\omega^{-(a)}(\omega^{-(b)})$]	$\Delta\omega^{\pm}$ (eV) [$\Delta\omega^{\pm(a)}(\Delta\omega^{\pm(b)})$]	$\Delta(\Delta\omega)^{\pm}$ (eV) [$\Delta(\Delta\omega)^{\pm(a)}$ $(\Delta(\Delta\omega)^{\pm(b)})$]
NY-I	−0.1917	−0.0544	3.348	3.737	1.499	−0.352	−2.414 (−1.479)	−4.282 (−5.217)	1.559 (0.293)	4.907 (3.641)	6.465 (3.933)	−1.713 (−1.314)
NY-II	−0.2460	−0.1007	4.717	3.953	2.814	0.963	−3.728 (−2.740)	−5.705 (−6.693)	3.516 (0.950)	8.233 (5.666)	11.750 (6.616)	3.572 (1.369)
AY	−0.1527	−0.0173	2.313	3.682	0.726	−1.136	−1.392 (−0.472)	−3.233 (−4.154)	0.526 (0.030)	2.839 (2.343)	3.365 (2.373)	−4.884 (−2.952)
NI	−0.1954	−0.0667	3.566	3.503	1.816	−0.046	−2.691 (−1.815)	−4.442 (−5.318)	2.067 (0.470)	5.633 (4.037)	7.701 (4.507)	−0.550 (−0.819)
MA	−0.2893	−0.0623	4.784	6.176	1.853		−3.240 (−1.696)	−6.328 (−7.872)	1.700 (0.233)	6.484 (5.017)	8.184 (5.250)	
MP	−0.2971	−0.0618	4.884	6.404	1.862		−3.283 (−1.682)	−6.485 (−8.086)	1.683 (0.221)	6.567 (5.105)	8.250 (5.325)	
H	−0.2165	−0.0753	3.971	3.843	2.052		−3.010 (−2.050)	−4.932 (−5.892)	2.358 (0.547)	6.329 (4.517)	8.687 (5.064)	
I	−0.2160	−0.0638	3.806	4.141	1.749		−2.771 (−1.736)	−4.841 (−5.876)	1.854 (0.364)	5.660 (4.170)	7.514 (4.533)	
J	−0.2918	−0.1154	5.541	4.799	3.199	−1.147	−4.341 (−3.141)	−6.740 (−7.940)	3.927 (1.028)	9.467 (6.569)	13.390 (7.597)	−4.707 (−2.533)
K	−0.2728	−0.0815	4.821	5.206	2.232	−0.482	−3.520 (−2.218)	−6.123 (−7.424)	2.380 (0.473)	7.201 (5.294)	9.580 (5.766)	−2.066 (−1.231)
L	−0.2193	−0.1055	4.419	3.096	3.153	2.374	−3.645 (−2.871)	−5.193 (−5.967)	4.290 (1.331)	8.709 (5.749)	12.999 (7.080)	9.122 (3.999)
M	−0.2251	−0.0013	3.080	6.090	0.779		−1.558 (−0.035)	−4.603 (−6.125)	0.398 (0.000)	3.479 (3.080)	3.877 (3.080)	
N	−0.3406	−0.1393	6.529	5.478	3.890	−1.839	−5.159 (−3.790)	−7.899 (−9.268)	4.859 (1.311)	11.388 (7.840)	16.246 (9.150)	−7.559 (−4.086)
O	−0.2043	−0.0477	3.428	4.262	1.378	−0.325	−2.362 (−1.297)	−4.493 (−5.559)	1.309 (0.197)	4.737 (3.625)	6.047 (3.822)	−1.527 (−1.107)
P	−0.2793	−0.0555	4.555	6.092	1.703		−3.032 (−1.509)	−6.078 (−7.601)	1.509 (0.187)	6.065 (4.742)	7.574 (4.929)	
Q	−0.2568	−0.0110	3.643	6.691	0.992	−0.861	−1.971 (−0.298)	−5.316 (−6.989)	0.580 (0.007)	4.224 (3.650)	4.804 (3.657)	−3.379 (−1.593)
R	−0.2472	−0.0640	4.235	4.985	1.799	−0.432	−2.989 (−1.743)	−5.481 (−6.728)	1.792 (0.305)	6.027 (4.540)	7.819 (4.844)	−1.761 (−0.920)

occupied and the lowest unoccupied molecular orbitals, respectively. This is an approximation, and an ΔSCF calculation involving energies of the *N*- and ($N \pm 1$)-electron species would have given a more accurate result. The electrophilicity (ω), electronegativity (χ), and hardness (η) are computed using eqs 1, 2, and 3, respectively. The electrodonating (ω^-) and electroaccepting (ω^+) powers are calculated independently from two different approaches using eqs 5a−6b. The net electrophilicity ($\Delta\omega^{\pm}$) has been defined as the net electroaccepting power of a species that is clear from eq 7. The corresponding μ^- and μ^+ values are also computed from two different approaches using the equations $\mu^- = (\partial E/\partial N)_v^- = -I$; $\mu^+ = (\partial E/\partial N)_v^+ = -A$ and $\mu^- = -{}^1/_4(3I + A)$; and $\mu^+ = {}^1/_4(I + 3A)$, respectively.

4. Results and Discussion

Various reactivity descriptors are calculated at the B3LYP/6-311+G(d) level of theory, for 32 molecules, originally considered by Domingo et al.[5a] to construct the electrophilicity scale, and are provided in Table 1. In the last column, $\Delta\omega^{\pm(a)}$ and ($\Delta\omega^{\pm(b)}$) values are obtained by using the definitions eqs 6a and 6b and eqs 5a and 5b, respectively. We prepared the net electrophilicity scale by considering the values decreasing from top to bottom so that a molecule lying above will behave as an electrophile and the one lying below will act as a nucleophile. Stronger electro- (nucleo-) philes appear toward the top (bottom) of the scale. Conversely, weaker electro- (nucleo-) philes appear toward the bottom (top) of the scale. This scale matches in almost all cases (but not all) with that provided by Domingo et al.[5a] $\Delta\omega^{\pm(a)}$ provides a better agreement than $\Delta\omega^{\pm(b)}$, as expected.[12] It is important to note that related local quantities such as a dual descriptor[15a] or a multiphilic descriptor[15b] for an atom-in-molecule or the electrophilicity excess[16] for a functional group in a molecule are known. We also study some selected Diels−Alder reactions (with or without Lewis acid (LA), in gas and solution phases) and 1,3-dipolar cycloadditions taken from Domingo and coworkers.[5b−g] The electrophilicity and net electrophilicity values of different reactions studied (Schemes 1−3) and the other allied density functional theory

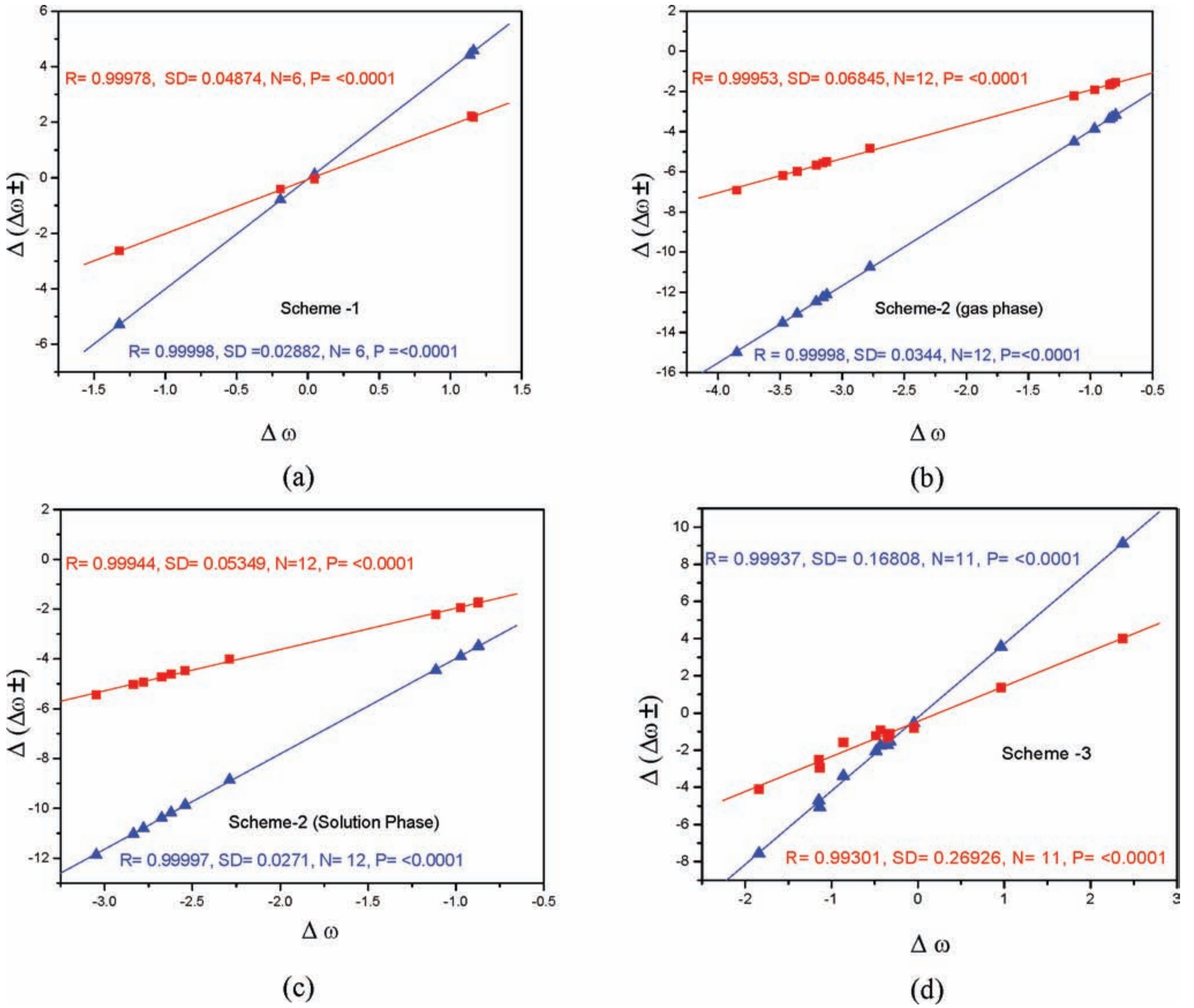
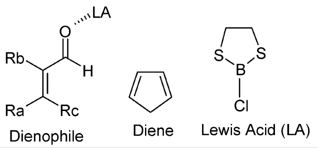


Figure 1. Plots of $\Delta(\Delta\omega)^{\pm}$ versus $\Delta\omega$ (−▲− using eqs 6a and 6b and −■− using eqs 5a and 5b) for different reactions studied in Schemes 1−3.

SCHEME 2



Entry	Ra	Rb	Rc	LA	Entry	Ra	Rb	Rc	LA
1	H	H	H	LA	7	Me	Me	H	LA
2	H	H	Me	LA	8	H	H	H	-
3	H	Me	H	LA	9	H	Me	H	-
4	Me	H	H	LA	10	Me	H	H	-
5	H	Me	Me	LA	11	Me	H	Me	-
6	Me	H	Me	LA	12	H	Me	Me	-

Reacting pairs:
1. Cp + 1-LA; 2. Cp + 2-LA; 3. Cp + 3-LA; 4. Cp + 4-LA; 5. Cp + 5-LA; 6. Cp + 6-LA; 7. Cp + 7-LA; 8. Cp + 8; 9. Cp + 9; 10. Cp + 10; 11. Cp + 11; 12. Cp + 12

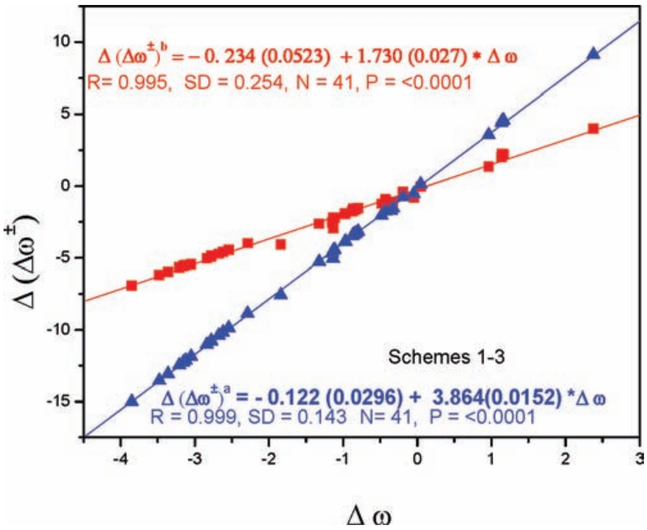
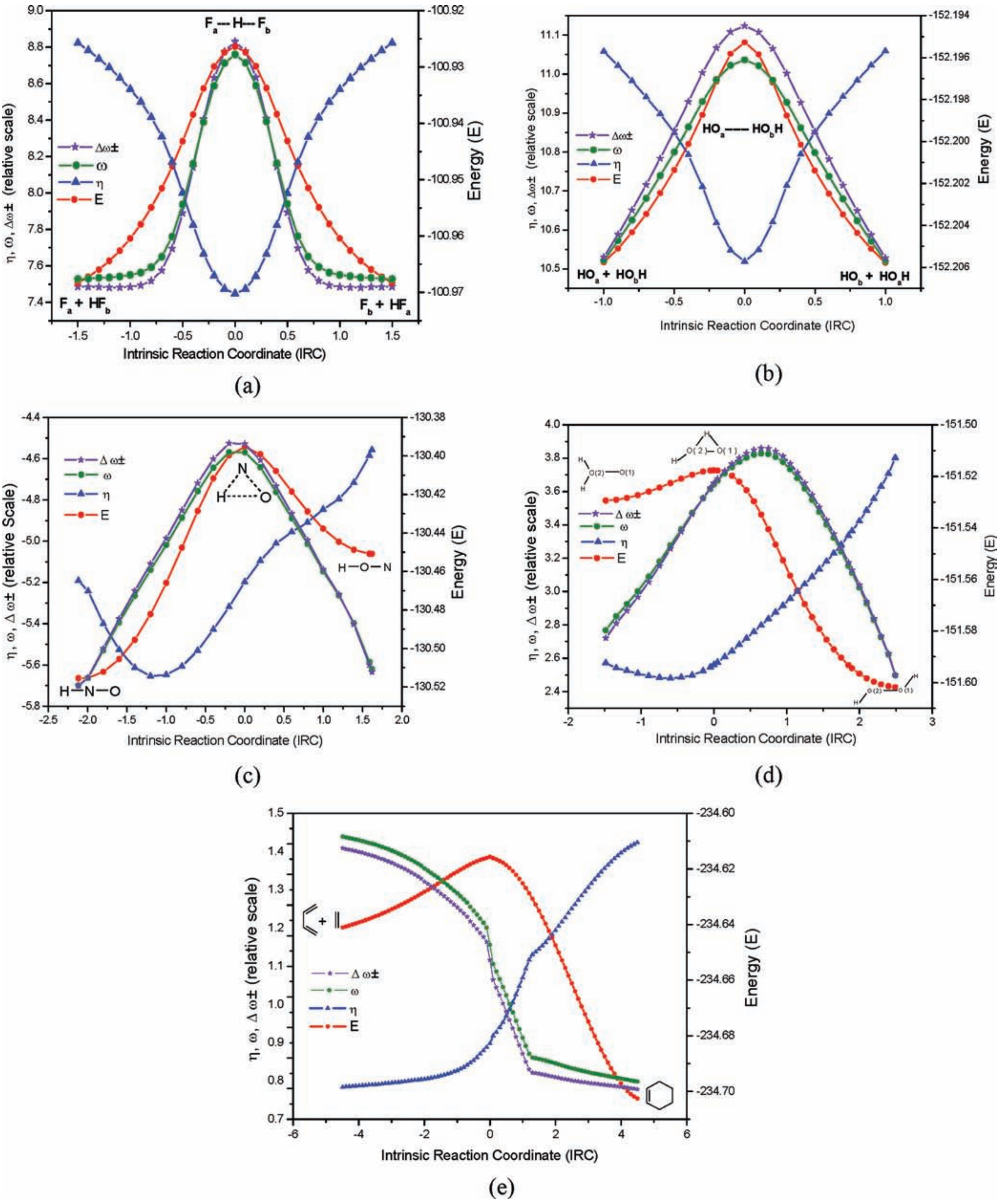


Figure 2. Plot of $\Delta(\Delta\omega^{\pm})$ versus $\Delta\omega$ (−▲− using eqs 6a and 6b and −■− using eqs 5a and 5b) for different reactions studied in Schemes 1−3 (all of the schemes taken together).

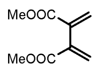
reactivity descriptors of the corresponding reactants are shown elaborately in Tables 2−4, respectively. Tables 2 and 3 present a list of the descriptors associated with the Diels−Alder type reactions, whereas in Table 4, a number of 1,3-dipolar cycloaddition reactions are illustrated. In Table 1, dimethyl 2,3-dimethylenesuccinate (A) is chosen as the diene and is reacted upon with a number of dienophiles (B−F). Similarly, in Table 3, cyclopentadiene (Cp) is reacted with a number of substituted-acrolein derivatives with or



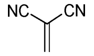
(a) (b) (c) (d) (e)

Figure 3. Profiles of energy (E) and different global reactivity descriptors (η, ω, and $\Delta\omega^{\pm}$) along the paths of the gas-phase thermoneutral (a and b), endothermic (c), exothermic (d), and (4 + 2) cycloaddition (e) reactions.

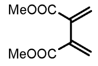
without an LA in gas and solution phases, respectively. Table 4 presents a number of 1,3-dipolar cycloaddition reactions among suitable dipole/dipolarophile pairs. We also present in those tables the value of $\Delta(\Delta\omega^{\pm}) = \Delta\omega^{\pm}$ (diene, dipole) $- \Delta\omega^{\pm}$ (dienophile, dipolarophile) calculated from the two different approaches, as shown by Gazquez et al.[12] It is also well known that the normal electron demand (e.g., a reaction between



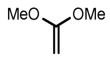
and



) and inverse electron demand reactions[1] (e.g., a reaction between



and



) are characterized by $\Delta(\Delta\omega^{\pm}) < 0$ and $\Delta(\Delta\omega^{\pm}) > 0$, respectively. These facts and features are quite transparent from the $\Delta(\Delta\omega^{\pm})$ values presented in Tables 2−4, and the normal or inverse electron demand nature of the given reactions may be easily recognized. It may be noted that when $\Delta(\Delta\omega^{\pm}) \approx 0$, the reaction type cannot be ascertained unequivocally[1] because in those cases, it is expected that ($E^{\text{diene}}_{\text{LUMO}} - E^{\text{dienophile}}_{\text{HOMO}}$) is comparable to ($E^{\text{dienophile}}_{\text{LUMO}} - E^{\text{diene}}_{\text{HOMO}}$). As shown in terms of $\Delta\omega = \omega(\text{diene, dipole}) - \omega(\text{dienophile, dipolarophile})$ values,[5] viz. the electrophilicity difference between diene/dienophile or dipole/dipolarophile pair, $\Delta(\Delta\omega^{\pm})$ values provide invaluable insight into the nature of these reactions, viz. pericyclic reactions involving small $\Delta(\Delta\omega^{\pm})$ values follow a nonpolar, concerted, frontier-controlled (and hence mainly of soft−soft type) path, whereas a polar, charge-controlled (hard−hard interaction) and stepwise mechanism results for the reactions with larger $\Delta(\Delta\omega^{\pm})$ values. Beautiful correlation is observed for all of these reactions when $\Delta(\Delta\omega^{\pm})$, the difference in net electrophilicity for diene/dienophile or dipole/dipolarophile pair, is plotted against the corresponding $\Delta\omega$ values in Figure 1a−d for Schemes 1, 2 (gas phase and solution phase), and 3, respectively, thereby corroborating the previously reported results.[5] In all of these cases, it may further be noticed that both sets of $\Delta(\Delta\omega^{\pm})$ values computed from the two different approaches[12] show excellent linear corrrelation with the corresponding $\Delta\omega$ values. Figure 2 shows a cumulative plot of $\Delta(\Delta\omega^{\pm})$ versus $\Delta\omega$ involving all reactions of Schemes 1−3 together, which yet again proves the fantastic linearity among the above descriptors, thereby further strengthening the idea of “net electrophilicity”. In Figure 3, we compare the net electrophilicity profile with that of the electrophilicity along the paths of five different reactions, viz. (a,b) thermoneutral: $F_a + HF_b \rightarrow HF_a + F_b$ and $HO_a + HO_bH \rightarrow HO_b + HO_aH$; (c) endothermic: $HNO \rightarrow HON$; (d) exothermic: $H_2OO \rightarrow HOOH$; and (e) (4 + 2) cycloaddition reaction: $CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH_2 \rightarrow C_6H_{10}$. Profiles of these quantities (ω, $\Delta\omega^{\pm}$) mimick each other. A minimum net electrophlicity principle[17,18] seems to be operative in most cases. Further work is in progress.

5. Concluding Remarks

The net electrophilicity of a molecule is defined as its electron-accepting power relative to its electron-donating power. A scale of this quantity is provided. The difference of this quantity for a diene−dienophile/dipole−dipolarophile pair involved in a cycloaddition reaction can provide valuable insight into the reaction such as whether it is of normal (or inverse) electron demand type as well as whether it is polar and stepwise or nonpolar and of concerted nature. The profile of the net electrophilicity mimics that of the electrophilicity along a reaction path.

Acknowledgment. We thank Professor Amit Basak for his valuable suggestions and CSIR, New Delhi and BRNS, Mumbai for financial assistance.

References and Notes

(1) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, 1976.

(2) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry Part A: Structure and Mechanisms*; Springer: New York, 2001.

(3) Carruthers, W.; Coldham, I. *Modern Methods of Organic Synthesis*, Cambridge University Press, 1971.

(4) (a) Chattaraj, P. K.; Sarkar, U.; Roy, D. R. *Chem. Rev.* **2006**, *106*, 2065. (b) Chattaraj, P. K.; Roy, D. R. *Chem. Rev.* **2007**, *107*, PR46. (c) Chattaraj, P. K.; Giri, S. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2009**, *105*, 13.

(5) (a) Domingo, L. R.; Aurell, M. J.; Perez, P.; Contreras, R. *Tetrahedron* **2002**, *58*, 4417. (b) Domingo, L. R. *Eur. J. Org. Chem.* **2004**, 4788. (c) Aurell, M. J.; Domingo, L. R.; Perez, P.; Contreras, R. *Tetrahedron* **2004**, *60*, 11503. (d) Alves, C. N.; Carneiro, A. S.; Andres, J.; Domingo, L. R. *Tetrahedron* **2006**, *62*, 5502. (e) Domingo, L. R.; Aurell, M. J.; Arnó, M.; Saez, J. A. *THEOCHEM* **2007**, *811*, 125. (f) Perez, P.; Domingo, L. R.; Aizman, A.; Contreras, R. Chapter 9. In *Theoretical Aspects of Chemical Reactivity*; Toro-Labbé, A., Ed.; Elsevier: Boston, 2007; pp 139−202. (g) Domingo, L. R.; Chamorro, E.; Perez, P. *J. Phys. Chem. A* **2008**, *112*, 4046.

(6) Maynard, A. T.; Huang, M.; Rice, W. G.; Covell, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95*, 11578.

(7) Parr, R. G.; Szentpály, L. v.; Liu, S. *J. Am. Chem. Soc.* **1999**, *121*, 1922.

(8) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., 1989. (b) Geerlings, P.; De Proft, F.; Langenaeker, W. *Chem. Rev.* **2003**, *103*, 1793. (c) *Chemical Reactivity Theory: A Density Functional View*; Chattaraj, P. K., Ed.; Taylor & Francis/CRC Press: Boca Raton, FL, 2009.

(9) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801.

(10) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

(11) Pearson, R. G. *Chemical Hardness: Applications from Molecules to Solids*; Wiley-VCH: Weinheim, Germany, 1997.

(12) Gazquez, J. L.; Cedillo, A.; Vela, A. *J. Phys. Chem. A* **2007**, *111*, 1966.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi. R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challcombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2004.

(14) Koopmans, T. A. *Physica* **1933**, *1*, 104.

(15) (a) Morell, C.; Grand, A.; Toro-Labbé, A. *J. Phys. Chem. A* **2005**, *109*, 205. (b) Padmanabhan, J.; Parthasarathi, R.; Elango, M.; Subramanian, V.; Krishnamoorthy, B. S.; Gutierrez-Oliva, S.; Toro-Labbé, A.; Roy, D. R.; Chattaraj, P. K. *J. Phys. Chem. A* **2007**, *111*, 9130.

(16) Roy, D. R.; Subramanian, V.; Chattaraj, P. K. *Indian J. Chem., Sect. A* **2006**, *45*, 2369.

(17) Chamorro, E.; Chattaraj, P. K.; Fuentealba, P. *J. Phys. Chem. A* **2003**, *107*, 7068.

(18) Parthasarathi, R.; Elango, M.; Subramanian, V.; Chattaraj, P. K. *Theor. Chem. Acc.* **2005**, *113*, 257.

JP904674X