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Ab Initio SCF and DFT Studies on Solvent Effects on Intramolecular Rearrangement Reactions

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Two intramolecular rearrangement reactions *trans*-$N_2H_2 \rightarrow$ *cis*-N_2H_2 and $F_2S_2 \rightarrow$ FSSF have been studied in both gas and solution phases using the ab initio SCF method at the Hartree−Fock level as well as using density functional theory with B3LYP exchange-correlation functionals with 6-311G** and 6-311++G** basis sets. Polarizability calculations have been performed using Sadlej's basis set also. Maximum hardness and minimum polarizability principles have been found to be valid in almost all cases. For the former reaction, the maximum molecular valency principle is obeyed. Reactions become more favorable, thermodynamically and kinetically, in the presence of the solvent. Variation of electrophilicity along the internal reaction coordinate is analyzed in terms of the profiles of the global electrophilicity index as well as condensed electrophilic Fukui functions at different atomic sites. It is found that electrophilicity decreases in the solution phase.

1. Introduction

Intramolecular rearrangement reactions are present in a vast majority of organic reactions that involve changes at functional groups while the molecular skeletons of the reactants remain unchanged.[1] Usually, these reactions proceed through a cyclic transition state (TS) containing four, five, or six atoms. These reactions have been shown to be important in gaining insights into the popular chemical concepts associated with reactivity and selectivity. Although chemical reactivity is characterized by global reactivity parameters like electronegativity[2,3] (χ), hardness[4−7] (η), polarizability[8,9] (α), molecular valency[10,11] (V_M), etc., the selectivity is usually understood in terms of local functions like the Fukui function[12] ($f(r)$) and local softness[13] ($s(r)$) or their condensed-to-atom variants.[14,15] Electronegativity[16] (χ) and hardness[17] (η) have been defined within density functional theory[18] (DFT) as follows:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{\nu(r)} \tag{1}$$

and

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu(r)} \tag{2}$$

where μ and $\nu(r)$ are the chemical and the external potentials of an N-electron system with total energy E.

According to the electronegativity equalization principle,[19] "all the constituent atoms in a molecule have the same electronegativity value which is roughly equal to the geometric mean of the electronegativities of the isolated atoms." The hard−soft acids−bases (HSAB) principle[4−6,17,20] states that, "among the potential partners of same electronegativity, hard likes hard and soft likes soft", and the statement of the maximum hardness principle[21,22] (MHP) is, "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible." On the basis of an inverse relationship[23] between α and η, a minimum polarizability principle[24,25] (MPP) has been proposed as, "the natural direction of evolution of any system is toward a state of minimum polarizability." It has also been found[10,11,26] that the molecular valency often becomes maximum for the most stable configuration conformation. These electronic structure principles help in understanding the reactivity pattern associated with any physicochemical process.

The most important local descriptor of site selectivity is the Fukui function,[12] which is defined as follows:

$$f(r) = \left(\frac{\delta \mu}{\delta \nu(r)}\right)_N = \left(\frac{\partial \rho(r)}{\partial N}\right)_{\nu(r)} \tag{3}$$

Three types of Fukui functions can be defined[12] on the basis of the discontinuity of the $\rho(r)$ vs N curve,[27] viz.

$$f^+(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^+_{\nu(r)} = [\rho_{N+1}(r) - \rho_N(r)] \simeq \rho_{\mathrm{LUMO}}(r) \tag{4}$$

for nucleophilic attack

$$f^-(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^-_{\nu(r)} = [\rho_N(r) - \rho_{N-1}(r)] \simeq \rho_{\mathrm{HOMO}}(r) \tag{5}$$

for electrophilic attack

$$f^\circ(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^\circ_{\nu(r)} = \frac{1}{2}[f^+(r) + f^-(r)] = \frac{1}{2}[\rho_{\mathrm{LUMO}}(r) + \rho_{\mathrm{HOMO}}(r)] \tag{6}$$

for radical attack.

It is possible to condense $f(r)$ to a specific atom in a molecule by taking the respective electron population. Three different local softness $s(r)$ can also be defined[13,28] using the relation

$$s(r) = f(r)S \tag{7}$$

where $f(r)$ can be taken from eqs 4−6 and the global softness[29]

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TABLE 1: Computed Frequencies at the Stationary Points along the IRC for the Intramolecular Conversion of N_2H_2 and F_2S_2[a]

HF/6-311G** $\epsilon = 1.0$						
	BU	AU	AG	AG	AG	BU
t-N_2H_2	1462.0592	1474.1115	1741.1232	1895.4072	3556.0421	3591.0630
	A′	A″	A′	A′	A′	A′
TS	1754.5837 *i*	791.8715	1669.8337	1886.4194	3297.0322	4121.3919
	A″	A′	A′	A′	A′	A′
c-N_2H_2	1408.0324	1494.0996	1699.3821	1891.7399	3455.0920	3528.3690
HF/6-311++G** $\epsilon = 1.0$						
	BU	AU	AG	AG	AG	BU
t-N_2H_2	1457.2553	1465.2795	1734.9799	1881.6253	3565.7299	3601.2602
	A′	A″	A′	A′	A′	A′
TS	1739.5208 *i*	767.5658	1660.1917	1871.4887	3314.6946	4122.6989
	A″	A′	A′	A′	A′	A′
c-N_2H_2	1359.6754	1489.5971	1692.3113	1882.1014	3463.4060	3532.9798
B3LYP/6-311G** $\epsilon = 1.0$						
	AU	BU	AG	AG	AG	BU
t-N_2H_2	1356.1185	1360.5972	1608.0639	1654.1063	3218.8366	3248.6521
	A′	A″	A′	A′	A′	A′
TS	1608.2753 *i*	697.5265	1524.7083	1693.7829	2771.7068	3905.5771
	A″	A′	A′	A′	A′	A′
c-N_2H_2	1280.8038	1343.2434	1552.1370	1663.6634	3056.8630	3162.0374
B3LYP/6-311++G** $\epsilon = 1.0$						
	AU	BU	AG	AG	AG	BU
t-N_2H_2	1346.7141	1355.2744	1594.2533	1647.0873	3233.9888	3266.5587
	A′	A′	A′	A′	A′	A′
TS	1445.2883 *i*	775.4442	1511.5311	1691.4550	2926.9921	3854.1506
	A″	A′	A′	A′	A′	A′
c-N_2H_2	1271.2973	1341.1728	1542.8268	1656.3416	3073.0734	3169.7275
HF/6-311G** $\epsilon = 1.0$						
	A	A	A	A	A	A
F_2S_2	295.7075	371.8227	461.4415	715.2972	801.8829	832.5680
	A	A	A	A	A	A
TS	555.8837 *i*	179.9070	351.4232	395.2914	795.8474	877.6747
	A	A	A	A	A	A
FSSF	184.3117	293.2211	348.8175	569.3182	799.2924	824.8564
HF/6-311++G** $\epsilon = 1.0$						
	A	A	A	A	A	A
F_2S_2	290.9587	380.6641	459.6727	715.5544	794.4600	826.6096
	A	A	A	A	A	A
TS	523.4909 *i*	180.0368	350.6538	388.6991	794.4424	873.0159
	A	A	A	A	A	A
FSSF	182.6462	292.9133	348.3070	570.2207	796.2444	823.2692
B3LYP/6-311G** $\epsilon = 1.0$						
	A	A	A	A	A	A
F_2S_2	242.2870	297.1974	363.7258	590.8282	635.2083	719.8575
	A	A	A	A	A	A
TS	452.0122 *i*	147.1130	288.5802	356.1892	662.3273	726.8914
	A	A	A	A	A	A
FSSF	180.0686	272.2436	297.4197	517.9876	614.0682	643.9727
B3LYP/6-311++G** $\epsilon = 1.0$						
	A	A	A	A	A	A
F_2S_2	241.1224	293.5432	358.5190	575.6219	627.3023	717.7761
	A	A	A	A	A	A
TS	438.0688 *i*	142.3575	289.7168	361.7948	657.7996	725.0464
	A	A	A	A	A	A
FSSF	173.1405	270.9562	295.0883	570.8126	608.0159	641.1090

[a] Values are given in cm^{-1}.

S is the inverse of hardness:

$$S = 1/(2\eta) \tag{8}$$

Recently, Parr et al.[30] have introduced an electrophilicity index ω defined as

$$\omega = \mu^2/(2\eta) \tag{9}$$

According to the definition of ω, this index measures the propensity of a species to "soak up" electrons.[30]

The solvent plays an important role in most of the reactions occurred in the solution phase, however very little work has been done to better understand the specific effect of the solvent in these reactions vis-à-vis the variations in different global and local reactivity descriptors. For this purpose, in the present work, we study two intramolecular rearrangement reactions: *trans*-N_2H_2 → *cis*-N_2H_2 (reaction I) and F_2S_2 → FSSF (reaction II) in a vacuum as well as in aqueous solution in terms of the profiles of μ, η, α, ω, condensed form of $f(r)$, etc. Atomic and

TABLE 2: Global Molecular Properties at the Three Stationary Points along the IRC for the Intramolecular Conversion of N_2H_2 and F_2S_2

	energy [au]	dipole moment [D]	α_{Pople} [au]	α_{Sadlej} [au]	μ [kcal/mol]	η [kcal/mol]	ω [kcal/mol]	V_M
HF/6-311G** $\epsilon = 1.0$								
t-N_2H_2	−110.027 833	0.0000	13.413	17.606	−80.355 729	169.399 327	19.058 64	1.899 37
TS	−109.937 346	2.2149	13.301	19.402	−54.448 999	146.598 769	10.111 59	1.711 83
c-N_2H_2	−110.016 764	3.1624	13.772	17.865	−83.066 570	169.305 201	20.377 56	1.853 73
HF/6-311G** $\epsilon = 78.5$								
t-N_2H_2	−110.033 148	0.0000	16.080	21.468	−77.039 341	169.546 792	17.502 72	1.939 05
TS	−109.945 451	2.5957	15.928	23.856	−51.286 351	146.975 275	8.948 07	1.720 60
c-N_2H_2	−110.026 944	3.6843	16.246	21.654	−78.401 037	169.684 844	18.112 17	1.932 04
HF/6-311++G** $\epsilon = 1.0$								
t-N_2H_2	−110.032 331	0.0000	15.579	17.606	−110.58 9137	143.269 010	42.681 80	1.947 79
TS	−109.943 607	2.2176	16.033	19.402	−90.3143 05	116.123 104	35.120 80	1.462 13
c-N_2H_2	−110.020 262	3.2711	15.870	17.865	−116.277 510	139.613 788	48.420 93	1.600 55
HF/6-311++G** $\epsilon = 78.5$								
t-N_2H_2	−110.037 578	0.0000	18.695	21.468	−105.468 659	143.676 888	38.710 60	2.011 28
TS	−109.951 670	2.6250	19.236	23.856	−84.1866 75	117.136 526	30.252 72	1.175 49
c-N_2H_2	−110.030 625	3.8365	18.804	21.654	−108.386 578	141.800 646	41.423 12	2.042 24
B3LYP/6-311G** $\epsilon = 1.0$								
t-N_2H_2	−110.672 857	0.0000	13.912	19.291	−94.308 403	58.490 160	76.030 52	1.724 94
TS	−110.591 730	2.0816	14.118	22.180	−71.504 708	38.767 537	65.943 36	1.633 73
c-N_2H_2	−110.663 452	2.9519	14.590	19.893	−97.091 407	58.901 179	80.021 67	1.625 21
B3LYP/6-311G** $\epsilon = 78.5$								
t-N_2H_2	−110.677 596	0.0000	16.614	23.515	−90.938 677	58.778 815	70.347 14	1.780 35
TS	−110.598 575	2.4426	16.890	27.431	−68.251 071	39.053 054	59.639 49	1.665 00
c-N_2H_2	−110.672 252	3.4805	17.081	24.090	−92.124 670	59.249 447	71.620 54	1.740 80
B3LYP/6-311++G** $\epsilon = 1.0$								
t-N_2H_2	−110.679 668	0.0000	16.341	19.291	−103.699 082	57.595 629	93.353 44	1.492 37
TS	−110.606 384	1.7216	17.388	22.180	−83.973 321	38.579 063	91.390 49	0.017 90
c-N_2H_2	−110.669 006	3.1095	16.869	19.893	−105.15 4904	57.645 830	95.909 40	1.180 20
B3LYP/6-311++G** $\epsilon = 78.5$								
t-N_2H_2	−110.684 326	0.0000	19.467	23.515	−98.311 913	57.812 119	83.591 75	1.591 27
TS	−110.612 775	2.0630	20.703	27.431	−77.754 702	38.886 541	77.736 33	0.425 47
c-N_2H_2	−110.678 069	3.6992	19.763	24.090	−98.396 627	57.934 482	83.559 01	1.422 74
HF/6-311G** $\epsilon = 1.0$								
F_2S_2	−993.900 367	1.8405	30.803	42.422	−108.637 024	140.308 181	42.057 43	0.561 71
TS	−993.797 709	5.4038	36.967	45.507	−150.097 561	111.981 729	100.593 54	0.580 66
FSSF	−993.914 570	2.1202	30.113	41.131	−105.781 788	160.909 807	34.770 37	0.392 58
HF/6-311G** $\epsilon = 78.5$								
F_2S_2	−993.905 316	2.3182	37.787	54.913	−98.088 339	142.931 233	33.657 17	0.567 59
TS	−993.819 258	6.8099	45.457	59.501	−139.407 683	113.478 375	85.630 86	0.590 74
FSSF	−993.919 933	2.5358	36.734	53.046	−95.559 416	162.353 113	28.122 66	0.365 70
HF/6-311++G** $\epsilon = 1.0$								
F_2S_2	−993.910 840	1.6388	35.797	42.422	−112.201363	138.111 845	45.575 91	−0.440 77
TS	−993.814 923	5.6742	41.194	45.507	−156.193961	111.125 158	109.770 61	−0.378 26
FSSF	−993.928 948	1.9966	34.899	41.131	−115.194 654	154.904 398	42.832 25	−0.369 84
HF/6-311++G** $\epsilon = 78.5$								
F_2S_2	−993.915 243	2.3038	45.131	54.913	−101.605 613	141.208 678	36.554 77	−0.358 48
TS	−993.836 786	7.1499	51.985	59.501	−144.431 016	113.814 100	91.642 06	−0.186 44
FSSF	−993.934 008	2.4447	43.490	53.046	−107.971 848	153.316 761	38.019 07	−0.435 13
B3LYP/6-311G** $\epsilon = 1.0$								
F_2S_2	−996.112 862	1.7729	34.885	47.242	−130.992 581	59.040 633	145.315 65	0.572 64
TS	−996.043 840	3.9867	38.279	50.508	−146.012 377	30.836 549	345.687 42	0.534 12
FSSF	−996.115 395	2.1556	34.752	46.651	−124.594 970	68.851 977	112.733 92	0.494 87
B3LYP/6-311G** $\epsilon = 78.5$								
F_2S_2	−996.116 940	2.1414	44.275	62.364	−121.833 862	59.665 020	124.390 22	0.567 25
TS	−996.056 231	5.0684	49.523	67.696	−137.333715	32.279 855	292.141 17	0.539 90
FSSF	−996.120 416	2.6163	43.879	61.380	−115.878 656	69.172 015	97.061 38	0.482 45
B3LYP/6-311++G** $\epsilon = 1.0$								
F_2S_2	−996.127 309	1.9396	40.616	47.242	−135.134 242	58.350 356	156.479 45	−0.402 24
TS	−996.065 235	4.4250	44.782	50.508	−154.694 177	31.147 174	384.148 64	−0.282 84
FSSF	−996.134 491	2.2138	40.549	46.651	−131.714 234	68.020 507	127.525 07	−0.103 29
B3LYP/6-311++G** $\epsilon = 78.5$								
F_2S_2	−996.131 333	2.5246	52.401	62.364	−125.771 578	59.235 166	133.522 80	−0.374 26
TS	−996.078 879	5.7936	58.456	67.696	−145.579 386	33.403 124	317.236 16	−0.142 33
FSSF	−996.139 445	2.7359	52.014	61.380	−122.382 946	68.409 572	109.469 95	−0.042 21

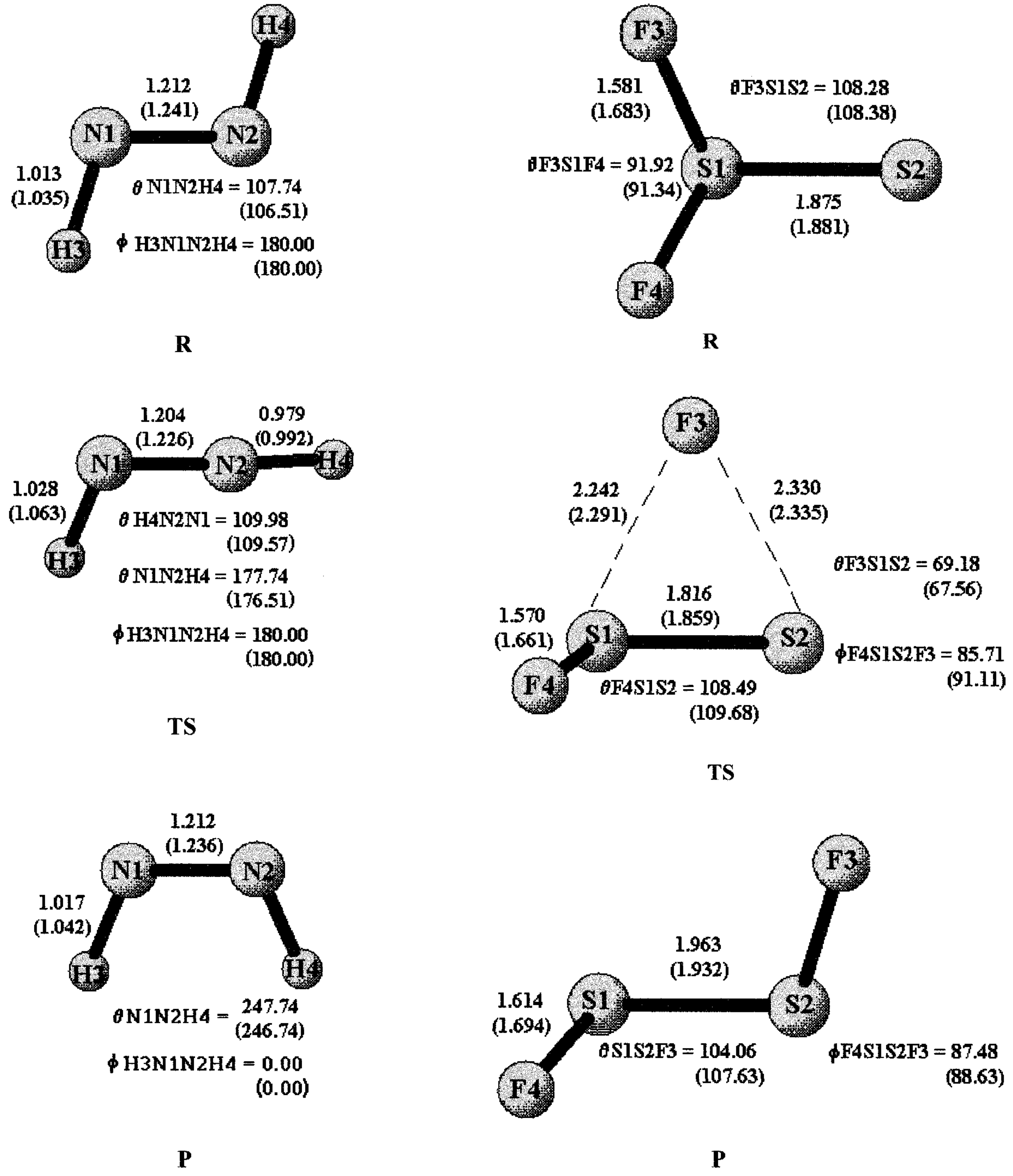

Figure 1. Optimized geometries for the reactants, TS, and products involved in (a) reaction I, HF/6-311G** calculations, values in brackets are from DFT calculations and (b) reaction II, HF/6-311++G** calculations, values in brackets are from DFT calculations. Bond lengths are given in angstroms and angles in degrees.

molecular valencies are calculated in the stationary points. The effect of inclusion of diffuse functions has also been studied. Both Hartree−Fock (HF) and DFT calculations have been performed. The theoretical background of the present work is given in section 2, whereas section 3 deals with the details of computation. Section 4 presents the results and discussion, and section 5 contains some concluding remarks.

2. Theoretical Background

A finite difference approximation to μ (eq 1) and η (eq 2) leads to[31]

$$\mu = -\left(\frac{I + A}{2}\right) \tag{10}$$

and

$$\eta = \left(\frac{I - A}{2}\right) \tag{11}$$

where I is the first ionization potential and A is the electron affinity. Further use of Koopmans' theorem gives[31]

$$\mu = \frac{\epsilon_{\mathrm{HOMO}} + \epsilon_{\mathrm{LUMO}}}{2} \tag{12}$$

and

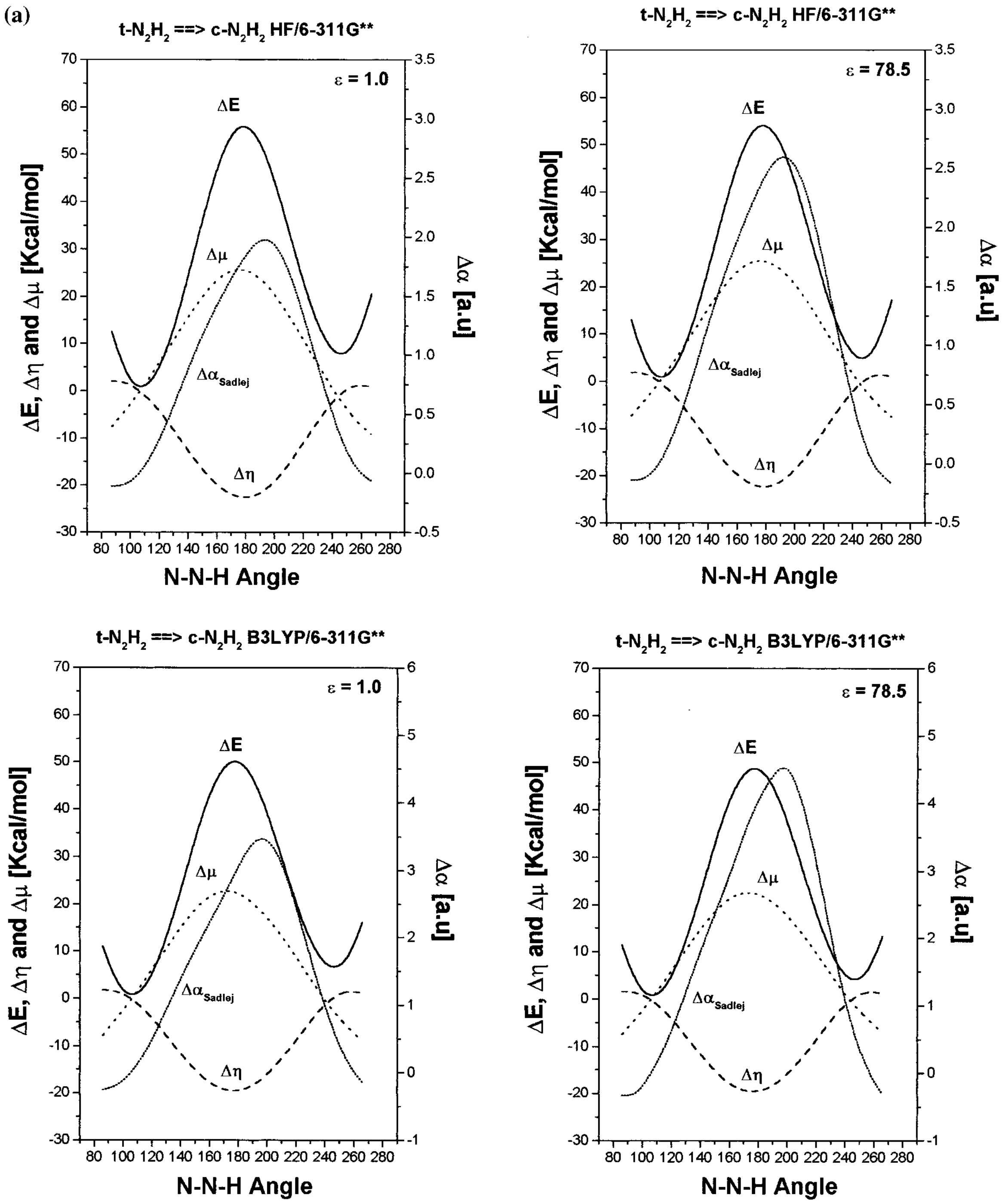

Figure 2. (a) Profiles of energy, chemical potential, hardness, and polarizability in vacuum and solvent for reaction I.

$$\eta = \frac{\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}}{2} \tag{13}$$

where $\epsilon_{\mathrm{HOMO(LUMO)}}$ is the energy of the highest occupied (lowest unoccupied) molecular orbital.

Condensed Fukui functions in atom A in a molecule are calculated as

$$f_{\mathrm{A}}^{+}(r) = [q_{N+1}^{\mathrm{A}}(r) - q_{N}^{\mathrm{A}}(r)] \tag{14}$$

and

$$f_{\mathrm{A}}^{-}(r) = [q_{N}^{\mathrm{A}}(r) - q_{N-1}^{\mathrm{A}}(r)] \tag{15}$$

where q_{M}^{A} is the Mulliken population at the atomic site A in a molecule containing M electrons. The geometries of ($N + 1$)- and ($N - 1$)-electron systems are taken to be the same as that of the N-electron system.[3]

Atomic valencies V_{A} are calculated by adding all of the off-diagonal elements (for a given atomic site) of the bond order matrix (Mulliken population), and the molecular valency is obtained as[26]

$$V_{\mathrm{M}} = \frac{1}{2}\sum_{\mathrm{A}} V_{\mathrm{A}} \tag{16}$$

For the two reactions studied here, the reactants and products are chosen in such a way that a reactant goes to the respective product via the corresponding TS when the value of the

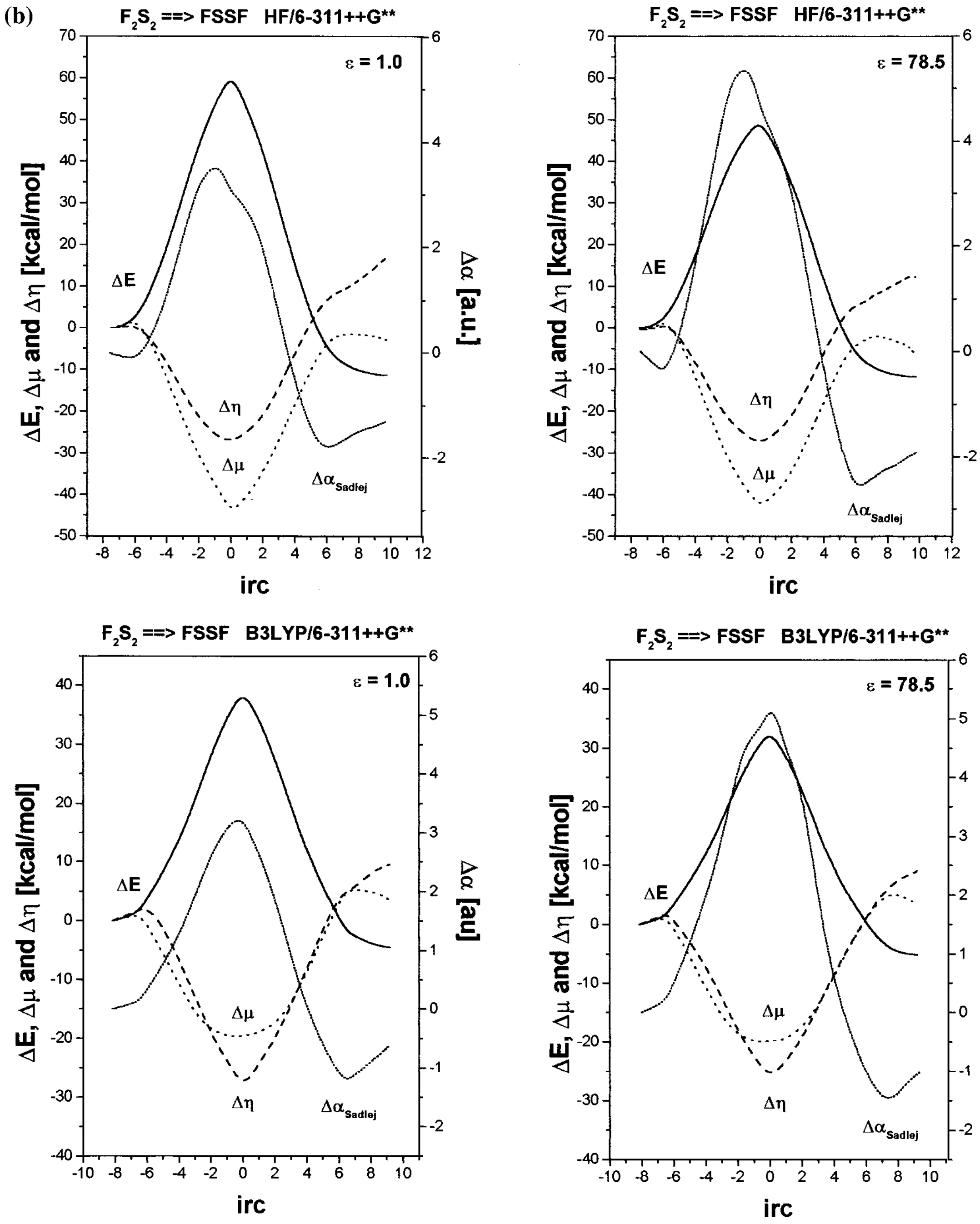

Figure 2. (b) Profiles of energy, chemical potential, hardness, and polarizability in vacuum and solvent for reaction II. See the text for details.

associated reaction coordinate increases. For this definition, reaction I is endothermic and reaction II is exothermic.

3. Computational Details

Geometry optimization and frequency calculation for various species associated with the intramolecular rearrangement reaction I have been performed at the HF/6-311G** and DFT/6-311G** levels of theory, whereas for reaction II, it has been performed at the HF/6-311++G** as well as DFT/6-311++G** levels. To see the effect of including the diffuse functions the reactant, the TS and the product for the former reaction have been studied also with 6-311++G** basis set and for the latter with 6-311G** basis set as well. The exchange-correlation functionals in all DFT calculations have been taken to be B3LYP.[32,33]

Various profiles are generated along the internal reaction coordinate (IRC), which is just the N1−N2−H4 angle for the first reaction that goes from $\theta = 107.74°$ at the trans conformation to $\theta = 247.74°$ at the cis one passing through the TS at $\theta = 177.74°$, as is shown in Figure 1a. In the $F_2S_2 \rightarrow$ FSSF reaction, a fluorine atom migrates from one sulfur to another following a more complex IRC with a F3−S1−S2 angle $\theta = 69.18°$ at the TS structure (see Figure 1b). The μ and η values are calculated using eqs 12 and 13, respectively, and $f_A^{\pm}$ and V_M are obtained by using respectively eqs 14−16. The polarizability is calculated using both Pople's as well as Sadlej's[34] basis set. All of the calculations have been accomplished using the Gaussian 94 package.[35]

The solvent is taken to be water ($\epsilon = 78.5$) and has been modeled as SCI-PCM.[36] The self-consistent reaction field

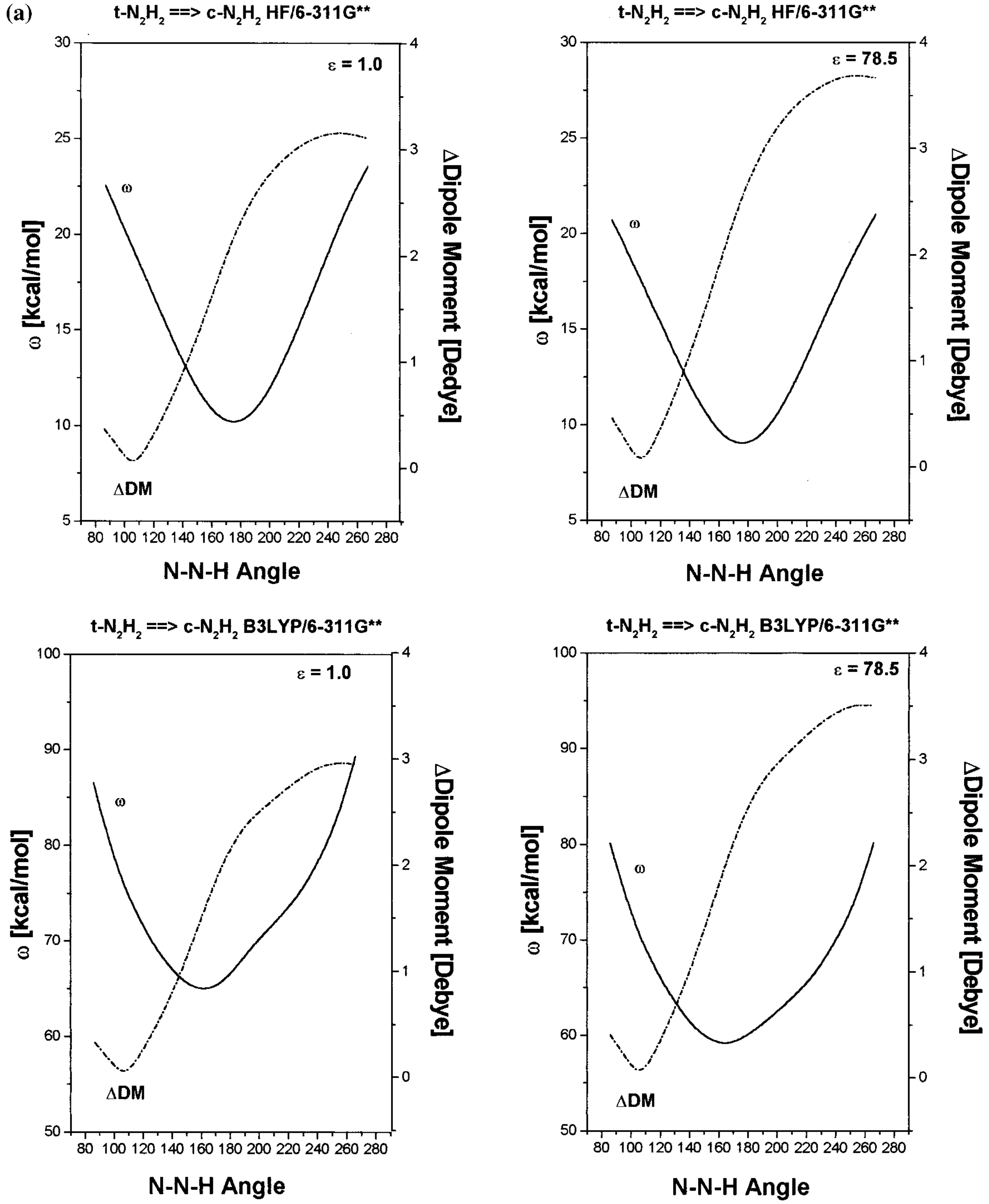

Figure 3. (a) Profile of the electrophilicity index and dipole moment in vacuum and solvent for reaction I.

(SCRF) models of solvation represent the solvent as a continuum of uniform dielectric constant ϵ, and the solute is placed into a cavity within the solvent. In the SCI-PCM model, the cavity, defined as an isosurface, and the electron density are necessarily coupled in the SCF procedure.[36]

4. Results and Discussion

Optimized structures of the reactant (R), the TS, and the product (P) of the reactions I and II along with the geometrical parameters are depicted in Figure 1a,b, respectively. The quantities within the brackets are from the DFT calculations. Table 1 presents all six vibrational frequencies of R, TS, and P for both of the reactions. All of the frequencies for R and P confirm that they correspond to minimum energy equilibrium structures, whereas one imaginary frequency each for the TSs of both reactions confirm that they are true TSs.

Energy (au), chemical potential (kcal/mol), hardness (kcal/mol), dipole moment (D), polarizability (au, with Pople and Sadlej basis sets), electrophilicity index (kcal/mol), and molecular valency values for R, TS, and P for both of the reactions in gas and solution phases calculated at HF(B3LYP)/6-311G** and HF(B3LYP)/6-311++G** levels are presented in Table 2. In reaction I, R is more stable than P, whereas P is more stable than R in reaction II. The TSs have been found to be softer and more polarizable in all cases, indicating the validity of MHP and MPP. The α values for reaction I obtained with Pople's basis set do not always show the proper behavior. However, for reaction II, both Pople's and Sadlej's bases provide

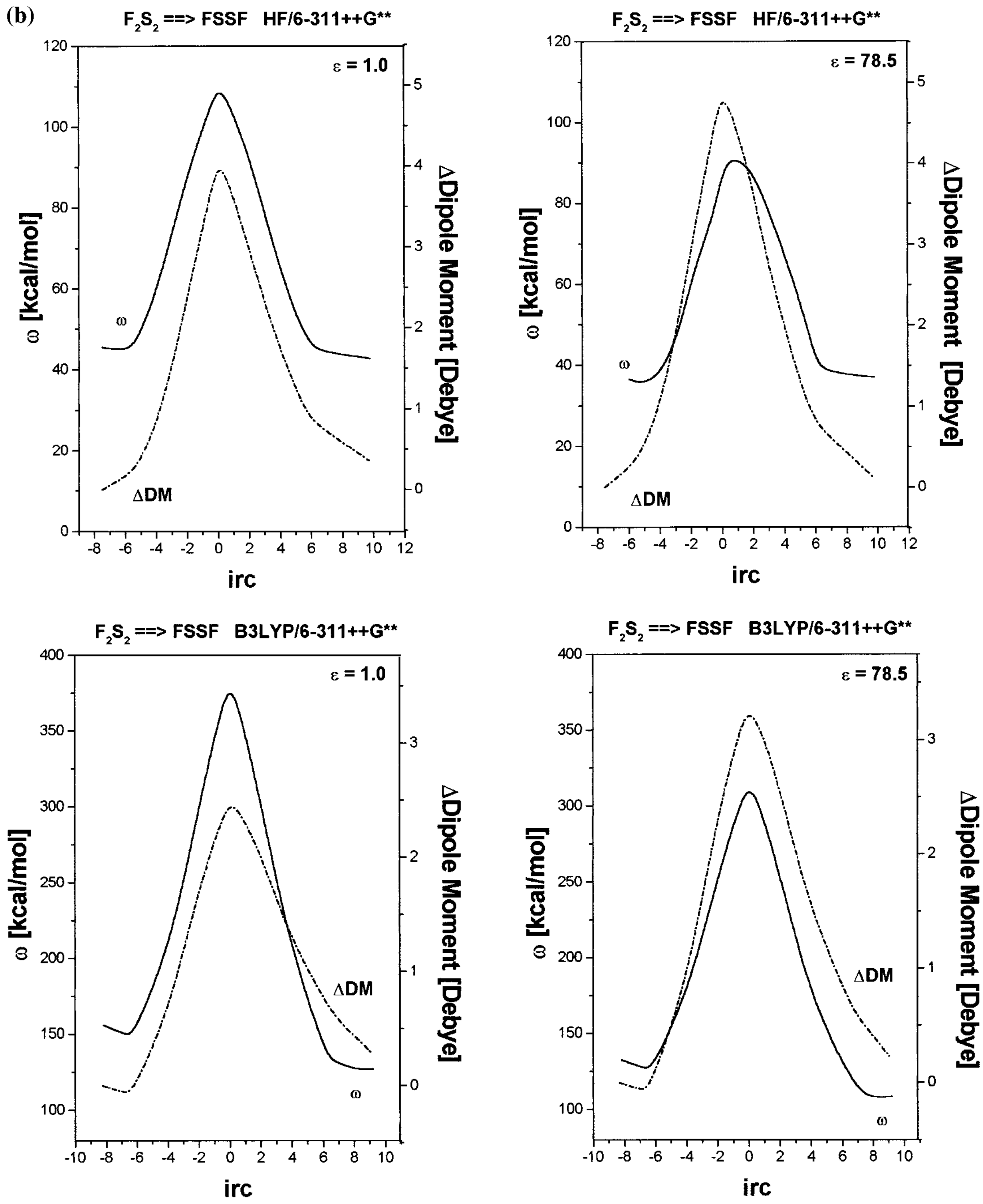

Figure 3. (b) Profiles of the electrophilicity index and dipole moment in vacuum and solvent for reaction II. See the text for details.

identical trends. In reaction I, the dipole moment of the TS is between those of R and P, whereas in reaction II, the TS is more polar than those of both R and P. Water being a polar solvent will have more dramatic effects on all quantities for the species with larger dipole moment. Because R is more stable than P in reaction I, one would expect $\eta_R > \eta_P$ and $\alpha_R < \alpha_P$. Although $\alpha_R < \alpha_P$ is always found to be valid, the $\eta_R > \eta_P$ condition is found to be valid only for HF/6-311G** calculations without solvent. The condition $\eta_R > \eta_P$ is satisfied in both the presence and absence of the solvent when diffuse functions are included at the HF level of calculation. There is no change in the trend for the DFT calculation even when diffuse functions are added.

For reaction II, which is of Hammond type,[1] P is more stable than R, and as expected from MHP and MPP, $\eta_P > \eta_R$ and $\alpha_P < \alpha_R$ in all of the cases. Molecular valency is minimum for the TS and maximum for the most stable species in most cases of reaction I, but it becomes negative for reaction II when calculated using diffuse functions and shows uncharacteristic trends otherwise. Even though in both reactions the TS is softer than those of both R and P, for reaction I, the TS is less electronegative and less electrophilic than those of both R and P, whereas for reaction II, the TS is more electronegative and more electrophilic than those of both R and P. This result justifies the definition of the electrophilicity index given by Parr et al.[30] because a more electronegative system is supposed to be more electrophilic as well.

Profiles of Global Reactivity Indices along a Reaction Path. In Figure 2, we present the profiles of ΔE, $\Delta\mu$, $\Delta\eta$, and $\Delta\alpha$ along the IRC. The quantities are calculated relative to the corresponding reactant value, viz., for a property Q, $\Delta Q(\mathrm{IRC}) = Q(\mathrm{IRC}) - Q(\mathrm{reactant})$. All of these quantities attain their

TABLE 3: Reaction and Activation Global Properties for the Intramolecular Conversion of N_2H_2 and F_2S_2[a]

	HF/6-311G**		HF/6-311++G**		B3LYP/6-311G**		B3LYP/6-311++G**	
	$\epsilon = 1.0$	$\epsilon = 78.5$	$\epsilon = 1.0$	$\epsilon = 78.5$	$\epsilon = 1.0$	$\epsilon = 78.5$	$\epsilon = 1.0$	$\epsilon = 78.5$
$t\text{-}N_2H_2 \Rightarrow c\text{-}N_2H_2$								
ΔE°	6.9459	3.8928	7.5737	4.3630	5.9013	3.3533	6.6901	3.9268
$\Delta E^{\neq}$	56.7807	55.0303	55.6752	53.9077	50.9075	49.5858	45.9859	44.8992
$\Delta\mu^\circ$	−2.7108	−1.3617	−5.6884	−2.9179	−2.7830	−1.1860	−1.4558	−0.0847
$\Delta\mu^\ddagger$	25.9067	25.7530	20.2748	21.2820	22.8037	22.6876	19.7258	20.5572
$\Delta\eta^\circ$	−0.0941	0.1381	−3.6552	−1.8762	0.4110	0.4706	0.0502	0.1224
$\Delta\eta^\ddagger$	−22.8006	−22.5715	−27.1459	−26.5404	−19.7226	−19.7258	−19.0166	−18.9256
$\Delta\alpha^\circ_{\text{Pople}}$	0.3592	0.1663	0.2901	0.1096	0.6781	0.4674	0.5285	0.2952
$\Delta\alpha^\ddagger_{\text{Pople}}$	−0.1121	−0.1514	0.4531	0.5410	0.2065	0.2766	1.0467	1.2354
$\Delta\alpha^\circ_{\text{Sadlej}}$	0.2582	0.1854	0.2582	0.1854	0.6013	0.5745	0.6013	0.5745
$\Delta\alpha^\ddagger_{\text{Sadlej}}$	1.7961	2.3879	1.7961	2.3879	2.8881	3.9162	2.8881	3.9162
$F_2S_2 \Rightarrow FSSF$								
ΔE°	−8.9127	−9.1725	−11.3632	−11.7755	−1.5895	−2.1813	−4.5069	−5.0905
$\Delta E^{\neq}$	64.4204	54.0035	60.1903	49.2337	43.3130	38.0964	38.9529	32.9162
$\Delta\mu^\circ$	2.8552	2.5289	−2.9933	−6.3662	6.3976	5.9552	3.4200	3.3886
$\Delta\mu^\ddagger$	−41.4605	−41.3193	−43.9926	−42.8254	−15.0198	−15.4999	−19.5599	−19.8078
$\Delta\eta^\circ$	20.6016	19.4219	16.7926	12.1081	9.8113	9.5070	9.6702	9.1744
$\Delta\eta^\ddagger$	−28.3265	−29.4529	−26.9867	−27.3946	−28.2041	−27.3852	−27.2032	−25.8320
$\Delta\alpha^\circ_{\text{Pople}}$	−0.6901	−1.0533	−0.8982	−1.6411	−0.1333	−0.3961	−0.0674	−0.3871
$\Delta\alpha^\ddagger_{\text{Pople}}$	6.1643	7.6705	5.3973	6.8540	3.3942	5.2484	4.1661	6.0550
$\Delta\alpha^\circ_{\text{Sadlej}}$	−1.2913	−1.8671	−1.2913	−1.8671	−0.5912	−0.9841	−0.5912	−0.9841
$\Delta\alpha^\ddagger_{\text{Sadlej}}$	3.0852	4.5880	3.0852	4.5880	3.2664	5.3321	3.2664	5.3321

[a] Variations in energy, chemical potential, and hardness are given in kcal/mol. Variations in polarizability are given in au.

TABLE 4: Condensed To Atom Fukui Functions and Atomic Valency at the Stationary Points along the IRC for the Intramolecular Conversion of N_2H_2 and F_2S_2

	f^+_{N1}	f^+_{N2}	f^+_{H3}	f^+_{H4}	f^-_{N1}	f^-_{N2}	f^-_{H3}	f^-_{H4}	V_{N1}	V_{N2}	V_{H3}	V_{H4}
HF/6-311G** $\epsilon = 1.0$												
$t\text{-}N_2H_2$	0.356 23	0.356 23	0.143 77	0.143 77	0.324 73	0.324 73	0.175 27	0.175 27	1.343 34	1.343 34	0.556 03	0.556 03
TS	0.344 00	0.376 85	0.161 55	0.117 59	0.230 55	0.519 14	0.163 09	0.087 22	1.153 10	1.079 55	0.432 63	0.758 38
$c\text{-}N_2H_2$	0.355 14	0.355 38	0.144 72	0.144 76	0.309 25	0.300 76	0.196 03	0.193 96	1.366 08	1.367 86	0.487 19	0.486 34
HF/6-311G** $\epsilon = 78.5$												
$t\text{-}N_2H_2$	0.363 18	0.363 18	0.136 82	0.13682	0.292 09	0.292 09	0.207 91	0.207 91	1.354 75	1.354 75	0.584 30	0.584 30
TS	0.354 86	0.374 88	0.147 26	0.123 00	0.178 70	0.493 79	0.182 77	0.144 74	1.18902	1.048 32	0.472 26	0.731 59
$c\text{-}N_2H_2$	0.359 15	0.359 09	0.140 82	0.140 94	0.266 66	0.256 08	0.241 48	0.235 78	1.368 87	1.370 96	0.562 53	0.561 72
B3LYP/6-311G** $\epsilon = 1.0$												
$t\text{-}N_2H_2$	0.348 64	0.348 64	0.151 36	0.151 36	0.333 80	0.333 80	0.166 20	0.166 20	1.228 61	1.228 61	0.496 33	0.496 33
TS	0.321 81	0.340 22	0.194 00	0.143 97	0.285 21	0.416 70	0.186 39	0.111 70	1.112 15	1.129 73	0.296 70	0.728 87
$c\text{-}N_2H_2$	0.341 70	0.341 73	0.158 35	0.158 22	0.313 05	0.314 51	0.186 14	0.186 31	1.250 70	1.248 90	0.375 05	0.375 75
B3LYP/6-311G** $\epsilon = 78.5$												
$t\text{-}N_2H_2$	0.359 82	0.359 82	0.140 18	0.140 18	0.303 81	0.303 81	0.196 19	0.196 19	1.251 48	1.251 48	0.528 87	0.528 87
TS	0.340 24	0.357 21	0.164 00	0.138 55	0.234 12	0.383 66	0.216 77	0.165 45	1.157 01	1.116 96	0.33966	0.716 37
$c\text{-}N_2H_2$	0.352 13	0.351 96	0.148 03	0.147 89	0.271 84	0.274 05	0.226 23	0.227 89	1.275 74	1.273 67	0.465 74	0.466 44
	f^+_{S1}	f^+_{S2}	f^+_{F3}	f^+_{F4}	f^-_{S1}	f^-_{S2}	f^-_{F3}	f^-_{F4}	V_{S1}	V_{S2}	V_{F3}	V_{F4}
HF/6-311++G** $\epsilon = 1.0$												
F_2S_2	0.566 89	0.408 70	0.012 13	0.012 23	0.223 23	0.653 82	0.061 45	0.061 50	−0.354 61	0.288 39	−0.407 36	−0.407 96
TS	0.564 21	0.969 31	−0.608 12	0.074 61	0.126 99	0.213 05	0.608 43	0.051 53	−0.102 12	0.20653	−0.406 41	−0.454 52
FSSF	0.594 39	0.594 11	−0.094 21	−0.094 29	0.220 47	0.602 51	0.094 99	0.082 03	−0.001 70	0.063 19	−0.400 57	−0.400 59
HF/6-311++G** $\epsilon = 78.5$												
F_2S_2	0.591 50	0.369 49	0.019 46	0.019 55	0.190 12	0.712 47	0.048 59	0.048 82	−0.300 18	0.246 15	−0.331 22	−0.331 70
TS	0.382 37	0.996 38	−0.451 39	0.072 65	0.118 02	0.162 91	0.685 64	0.033 43	0.091 72	0.343 83	−0.388 85	−0.418 74
FSSF	0.573 73	0.573 29	−0.073 47	−0.073 56	0.128 51	0.714 60	0.089 32	0.067 58	−0.020 64	−0.020 61	−0.414 49	−0.414 52
B3LYP/6-311++G** $\epsilon = 1.0$												
F_2S_2	0.517 98	0.404 67	0.038 41	0.038 95	0.247 50	0.544 57	0.103 13	0.104 44	−0.270 09	0.308 00	−0.421 13	−0.421 27
TS	0.317 67	0.461 17	0.137 40	0.083 76	0.226 41	0.312 31	0.354 08	0.099 60	0.015 27	0.227 36	−0.403 50	−0.404 81
FSSF	0.516 41	0.471 51	0.013 20	0.003 42	0.353 86	0.354 35	0.146 03	0.145 76	0.253 27	0.253 17	−0.356 56	−0.356 45
B3LYP/6-311++G** $\epsilon = 78.5$												
F_2S_2	0.492 58	0.414 62	0.046 36	0.046 43	0.240 76	0.608 84	0.074 91	0.075 50	−0.274 36	0.310 87	−0.392 18	−0.392 86
TS	0.327 20	0.470 43	0.123 08	0.079 28	0.258 66	0.309 94	0.359 21	0.072 19	0.136 64	0.327 94	−0.376 07	−0.373 17
FSSF	0.486 60	0.486 74	0.013 50	0.013 16	0.325 09	0.418 30	0.135 64	0.120 97	0.275 00	0.346 31	−0.352 77	−0.352 97

extremal potential (maximum or minimum) values around the IRC of the TS except for the $\Delta\alpha$ profile of reaction I, which is slightly asymmetric and shifted toward the right. Because the $\Delta\alpha_{\text{Pople}}$ profile does not reproduce the expected trend in reaction I, in Figure 2, we present only the $\Delta\alpha_{\text{Sadlej}}$ profiles. It is heartening to note that the $\Delta\alpha$ profile generally mimicks the ΔE profile, whereas the $\Delta\eta$ profile mirrors them as a clear signature of MHP and MPP in the context of intramolecular

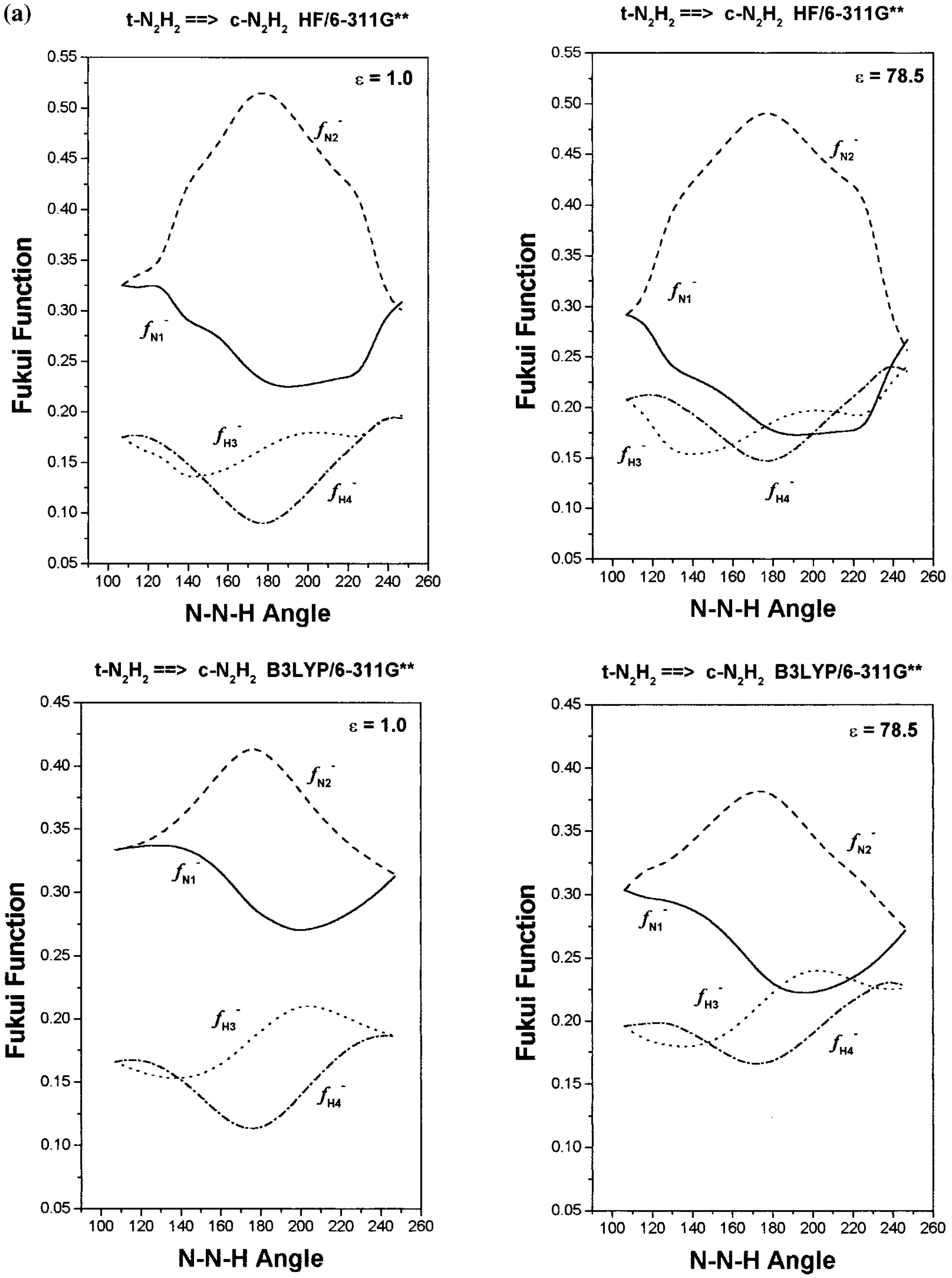

Figure 4. (a) Profiles of the nucleophilic Fukui function at site k$_1f_k^-$ in vacuum and solvent for reaction I.

rearrangement reactions. The profile of $\Delta\mu$ is a mirror image of the $\Delta\eta$ profile for reaction I, and it is like the $\Delta\eta$ profile for reaction II. The most discernible change in the presence of a solvent is shown by the $\Delta\alpha$ profile in all cases. It may be noted that all quantities do not exhibit clear-cut extrema in all of the cases of reactants and products, which may be due to the approximations (cf. eqs 12 and 13) involved in their calculation. Total energy is, however, minimum for both the reactants and products and maximum for the TS which is confirmed by respective frequency calculations.

The profiles of the electrophilicity index are depicted in Figure 3 along with those of the dipole moment. In all cases, the electrophilicity goes down in the presence of the solvent. To check whether this is a generic result, more systems should be studied in the presence of various solvents. Even it is difficult to say at this stage whether μ is affected more than η in the presence of a solvent because the $\Delta\mu$ profile lies below the $\Delta\eta$ profile in the HF calculation but not in the DFT calculation. Although the dipole moment increases monotonically for reaction I and passes through a maximum at the TS for reaction II, ω pass through extrema in the TS in all cases. The chemical potential profile is a better indicator than the dipole moment profile in analyzing the electrophilicity patterns. Extremization of this index can be understood in the same terms for μ and η, it is easy to show from eq 9 that when both μ and η are extrema ω also attains an extremum value at that point.

Table 3 presents the $\Delta Q°$ and $\Delta Q^{\neq}$ values where the property Q is E, μ, η, and α (Pople and Sadlej) and $\Delta Q° = Q(\mathrm{P}) - Q(\mathrm{R})$ and $\Delta Q^{\neq} = Q(\mathrm{TS}) - Q(\mathrm{R})$. Reaction I is not favorable both thermodynamically (endothermic) and kinetically. Addition

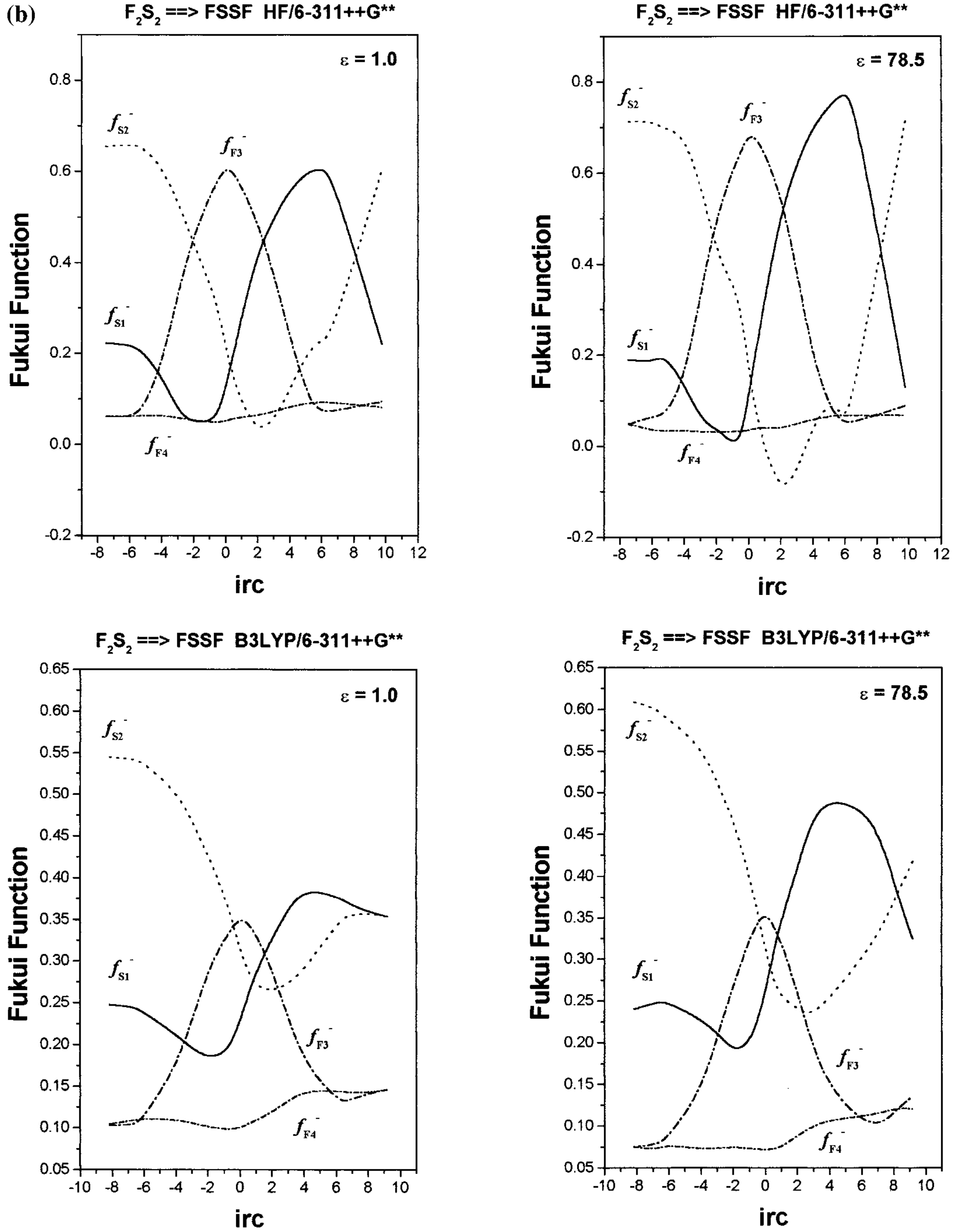

Figure 4. (b) Profiles of the nucleophilic Fukui function at site $k_1 f_k^-$ in vacuum and solvent for reaction II. See the text for details.

of solvent improves the situation in both accounts, in the sense that the reverse reaction becomes less favorable. Reaction II is, however, thermodynamically favorable (exothermic). Presence of the solvent makes the reaction more favorable both thermodynamically and kinetically.

Profiles of Local Reactivity Indices along a Reaction Path. Different local quantities like atomic valencies V_A and electrophilic and nucleophilic Fukui functions ($f_A^\pm$) are given in Table 4. Electrophilicity (ω) is a global reactivity parameter, its extremization around the TS results from the corresponding extremization of $f_k^\pm$ at the site k. For reaction I, ω minimizes around the TS mainly because of that of f_{N1}^+ and f_{H4}^+. Around the TS, ω is maximum for reaction II mainly because of the change in f_{F3}^+ along the IRC. V_A values do not provide and conclusive information. To understand the situation better, the profiles of different f_A^- quantities are presented in Figure 4. These profiles show the variation of the selectivity pattern during the progress of the reaction. It is interesting to note that the TS geometry can be approximately identified from the intersection point of f_{N1}^- and f_{H3}^- (only in the presence of solvent) for reaction I and from the first intersection point of f_{S1}^- and f_{S2}^- (better in the presence of solvent) for reaction II. HF and DFT calculations reveal identical trends in almost all cases, although the numerical values differ.

5. Concluding Remarks

Ab initio SCF and DFT calculations have been performed in order to gain insights into the effect of a solvent in the intramolecular rearrangement reactions like reactions I and II . Energy and polarizability profiles pass through maxima, and hardness profile passes through a minimum at the TS, indicating the validity of the principles of maximum hardness and minimum polarizability. In the solution phase, the reactions are both thermodynamically and kinetically more favorable. Electrophilic condensed Fukui functions can identify the particular atomic site responsible for extremization of the global electrophilicity index around the TS. Electronegativity profiles follow identical trends as those of the profiles of the electrophilicity index. Appreciable changes in various properties in the presence of the solvent are discernible for the species with large dipole moments. All species associated with these reactions become less electrophilic in aqueous solution.

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