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A Density Functional Study of the Claisen Rearrangement of Allyl Aryl Ether, Allyl Arylamine, Allyl Aryl Thio Ether, and a Series of Meta-Substituted Molecules through Reactivity and Selectivity Profiles

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The Claisen rearrangement of allyl phenyl ether, allyl phenylamine, and allyl phenyl thioether, together with the family of H, CH₃, OCH₃, Cl, F, and CN, meta-substituted molecules, is studied within a density functional framework with B3LYP exchange-correlation energy functionals and 6-311G** basis set. Reactants, intermediates, and products have equilibrium configurations (with no imaginary frequency), and the two transition states possess one imaginary frequency each corroborating the proposed mechanism of a [3,3]-sigmatropic rearrangement. The energy profile for the systems containing oxygen and nitrogen atoms mirrors the hardness profile along the reaction path in agreement with the maximum hardness principle. However, the molecules with sulfur atom do not follow the maximum hardness principle. This is explained in terms of the participation of the highest occupied molecular orbital (HOMO) in the reaction. The minimum polarizability principle is obeyed in all cases.

Introduction

The [3,3]-sigmatropic reaction is one of the widely used reactions in synthetic organic chemistry.¹ Among these reactions the Claisen rearrangement² has been found to be the most useful in which an oxygen atom is present in the reacting system.³ Ryan and O'Connor⁴ have confirmed the reaction mechanism of the Claisen rearrangement in terms of a [3,3]-sigmatropic rearrangement when they studied the reaction of ¹⁴C-labeled allyl phenyl ether. The reactant passes through an intermediate to go to the product. There are two transition states associated with this reaction. For the special case of the allyl phenyl ether, the intramolecular nature of this reaction has also been established⁵ by a crossover experiment. Effects of solvent,⁶ substituents,⁷ catalysts,⁸ and also the kinetic isotope effects⁹ in the Claisen rearrangement have been studied. In this paper various reactivity indices defined in density functional theory have been used to study the Claisen rearrangement of the allyl phenyl ether, allyl phenylamine, and allyl phenyl thioether, together with the corresponding H, CH₃, OCH₃, Cl, F, and CN, meta-substituted molecules.

Density functional theory (DFT)¹⁰ has been found to be successful in providing insights into the chemical reactivity and selectivity respectively in terms of global reactivity parameters such as electronegativity¹¹ χ and hardness¹² η and local ones, such as Fukui function¹³ $f(r)$ and local softness¹⁴ $s(r)$. While Pauling¹⁵ introduced the concept of electronegativity as “the power of an atom in a molecule to attract electrons to itself”, the concept of hardness was put forward by Pearson in his hard–soft acids and bases (HSAB) principle which states that¹⁶ “hard

likes hard and soft likes soft”. Another hardness-based principle is the maximum hardness principle^{17–19} (MHP), which states that¹⁷ “there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible”. The MHP has been found to be successful¹⁹ in analyzing molecular vibration and internal rotation, different types of chemical reactions, aromaticity, clusters with a magic numbers of atoms, extra stability of a closed-shell species, dynamical problems, electronic excitation in atoms²⁰ and molecules,²¹ etc.

For an N -electron system with total energy E and external potential $v(\vec{r})$, electronegativity χ and hardness η are respectively defined as the following first-order²² and second-order²³ derivatives, viz.,

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \quad (1)$$

and

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} \quad (2)$$

In the present work we study the variations of various descriptors of reactivity and selectivity as given above, along the reaction path of the Claisen rearrangement of allyl phenyl ether, allyl phenylamine, and allyl phenyl thioether. For this purpose, a density functional route has been adopted to optimize the geometries of the reactant, the product, the intermediate, and the two transition states and then different quantities are calculated for the optimized structures.

In connection with the MHP, Chattaraj and Sengupta²⁴ have proposed a minimum polarizability principle (MPP) which says that “the natural direction of evolution of any system is toward a state of minimum polarizability”. Both, the MHP and MPP

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TABLE 1: Total Energy (au) and Relative Energy (kcal/mol) of the Claisen Rearrangement Reactions of Allyl Phenyl Ether and Allyl Phenyl Amine

reaction	methods	reactant	transition state 1	intermediate	transition state 2	product
allyl-phenyl ether	RHF/3-21G	-419.1239	51.7	18.4	95.8	-6.1
	RHF/6-31G*	-421.4617	56.0	9.3	88.5	-7.1
	B3LYP/6-31G*	-424.1634	36.5	12.6	68.6	-7.7
	MP2/6-311G** // RHF/6-31G*	-423.0168	32.6	21.3	63.8	-16.3
	MP2/6-31G* // RHF/3-21G	-422.7688	32.3	10.0	68.5	-11.7
	present work ^a	-424.1107	34.4	11.7	62.8	-9.6
	RHF/3-21G	-399.4050	61.4	30.4	101.3	-5.9
allyl phenylamine	RHF/6-31G*	-401.6351	65.0	22.1	99.0	-6.3
	B3LYP/6-31G*	-404.3005	44.2	24.5	79.5	-6.9
	MP2/6-311G** // RHF/6-31G*	-403.1731	48.0	23.1	76.2	-11.4
	MP2/6-31G* // RHF/3-21G	-402.9314	37.3	22.3	80.4	-9.2
	present work ^a	-404.2309	44.5	25.2	71.8	-7.4

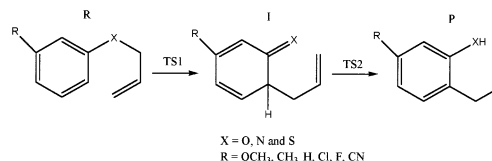
^a Including the zero-point energy correction.**TABLE 2: Relative Energy (kcal/mol), Hardness (kcal/mol), and Polarizability (in au) for the Studied Claisen Rearrangements**

reactions	X: relative			relative			relative		
	<i>E</i>	η	α	<i>E</i>	η	α	<i>E</i>	η	α
OCH ₃ - ϕ -X-allyl									
R	0.0	58.9	184.2	0.0	66.2	174.1	0.0	63.2	203.5
TS 1	42.9	50.1	230.8	34.8	45.8	227.8	32.5	39.7	267.9
I	21.2	52.1	184.7	9.4	49.6	179.0	22.0	35.7	239.1
TS 2	68.4	47.4	207.6	60.4	46.0	200.3	60.5	36.5	258.1
P	-7.0	63.8	185.6	-9.2	66.3	177.9	-1.6	64.2	201.1
CH ₃ - ϕ -X-allyl									
R	0.0	60.4	178.3	0.0	66.4	168.5	0.0	63.3	197.3
TS 1	43.9	49.3	224.8	33.9	45.8	220.1	32.3	40.7	255.5
I	23.7	51.3	179.8	9.9	52.5	171.0	22.4	36.5	226.0
TS 2	70.8	45.8	201.7	61.5	44.6	191.5	62.6	35.0	246.4
P	-7.4	63.4	179.7	-9.7	67.0	171.9	-1.7	66.6	194.6
H- ϕ -X-allyl									
R	0.0	60.7	161.0	0.0	67.1	151.3	0.0	63.4	179.8
TS 1	44.5	48.5	207.2	34.4	45.2	202.3	33.0	40.2	236.7
I	25.2	50.6	162.5	11.7	51.5	153.8	24.2	36.0	207.5
TS 2	71.8	45.1	183.9	62.8	43.9	173.7	63.9	34.3	227.6
P	-7.4	63.5	162.3	-9.6	67.4	154.5	-1.6	66.8	176.9
Cl- ϕ -X-allyl									
R	0.0	61.0	177.7	0.0	66.4	167.9	0.0	62.2	196.6
TS 1	44.7	48.9	225.3	34.0	45.6	220.6	32.5	40.0	257.3
I	25.3	50.3	180.7	11.3	51.7	172.5	23.3	35.7	229.9
TS 2	71.9	45.1	202.8	62.7	44.2	193.9	63.2	34.5	251.1
P	-7.2	63.1	178.9	-9.5	66.9	171.1	-1.6	65.6	194.1
F- ϕ -X-allyl									
R	0.0	62.2	161.3	0.0	68.3	151.7	0.0	62.5	180.6
TS 1	44.8	49.5	207.8	34.0	46.2	203.2	32.3	40.6	238.1
I	24.9	51.8	162.7	10.4	53.4	154.3	22.7	36.6	208.2
TS 2	71.2	46.6	184.2	61.7	45.8	174.5	62.4	36.0	229.5
P	-7.0	64.8	162.7	-9.3	68.5	155.0	-1.5	66.0	177.9
CN- ϕ -X-allyl									
R	0.0	53.8	191.0	0.0	59.5	181.1	0.0	57.2	208.8
TS 1	45.4	46.5	240.8	35.0	44.4	233.4	32.9	37.7	275.7
I	27.5	46.3	193.6	14.4	47.3	183.5	25.2	32.8	248.5
TS 2	73.6	41.2	217.6	65.0	40.4	208.5	64.7	31.2	270.6
P	-7.4	55.9	193.0	-9.6	60.4	184.8	-1.9	59.9	207.3

have been extensively studied in the recent years.^{25,26} Therefore, in this work the change in the static electric dipole polarizability along the reaction path has also been studied.

Computational Details

Equilibrium geometries of the reactant, the two transition states, the intermediate and the product associated with the Claisen rearrangement of all the studied molecules, are obtained by optimization within a density functional framework using a 6-311G** basis set. The B3LYP exchange-correlation functionals²⁷ are used for this purpose. Vibrational frequencies are also calculated at the B3LYP/6-311G** level mainly to check the number of imaginary frequencies (NIMAG) and for calculating the zero-point energies.

**Figure 1.** General scheme of the Claisen rearrangement.

Hardness η is calculated as the half of the HOMO–LUMO gap, i.e.,

$$\eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \quad (3)$$

This definition comes from eq 2 with a finite difference approximation in addition to Koopmans' theorem.

The static electric dipole polarizability has been calculated by analytical differentiation of the dipole moment with respect to the electric field and for this work only the following mean value $\langle\alpha\rangle$ is interesting

$$\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (4)$$

All calculations have been accomplished with the GAUSSIAN 98 program.²⁸

Results and Discussion

The general scheme of the studied reactions is presented in Figure 1. The Claisen rearrangement for the studied molecules goes from the reactant R to the product P through an intermediate I and two transition states TS1 and TS2. All of them have been fully characterized. Before discussing the results for all systems in detail, a comparison with other calculations for the molecules of allyl-phenyl ether and allyl-phenylamine is made in Table 1. For the other reactions no literature data are available for comparison. One can see that the results obtained in this work compare very well with the other ones. The noted differences between the results of our calculations and that of the B3LYP/6-31G* reported in ref 29 is due to the inclusion of the zero-point energy in our calculations. Test calculations on the allyl-vinyl ether show a complete agreement when the zero-point energy is not considered. In Table 2 the relative energy (relative to that of the reactants), the hardness, and the dipole polarizability for all the species are provided. The calculated free energies differ from the reported relative energies in less than 1 kcal/mol. For all the allyl phenyl ether derivatives the product is more stable than the reactant by about 9 kcal/mol, for the amine derivatives this energy difference is about 7 kcal/mol and decreases significantly to around 2 kcal/mol for the thioether derivatives. The meta-substitution has little influence

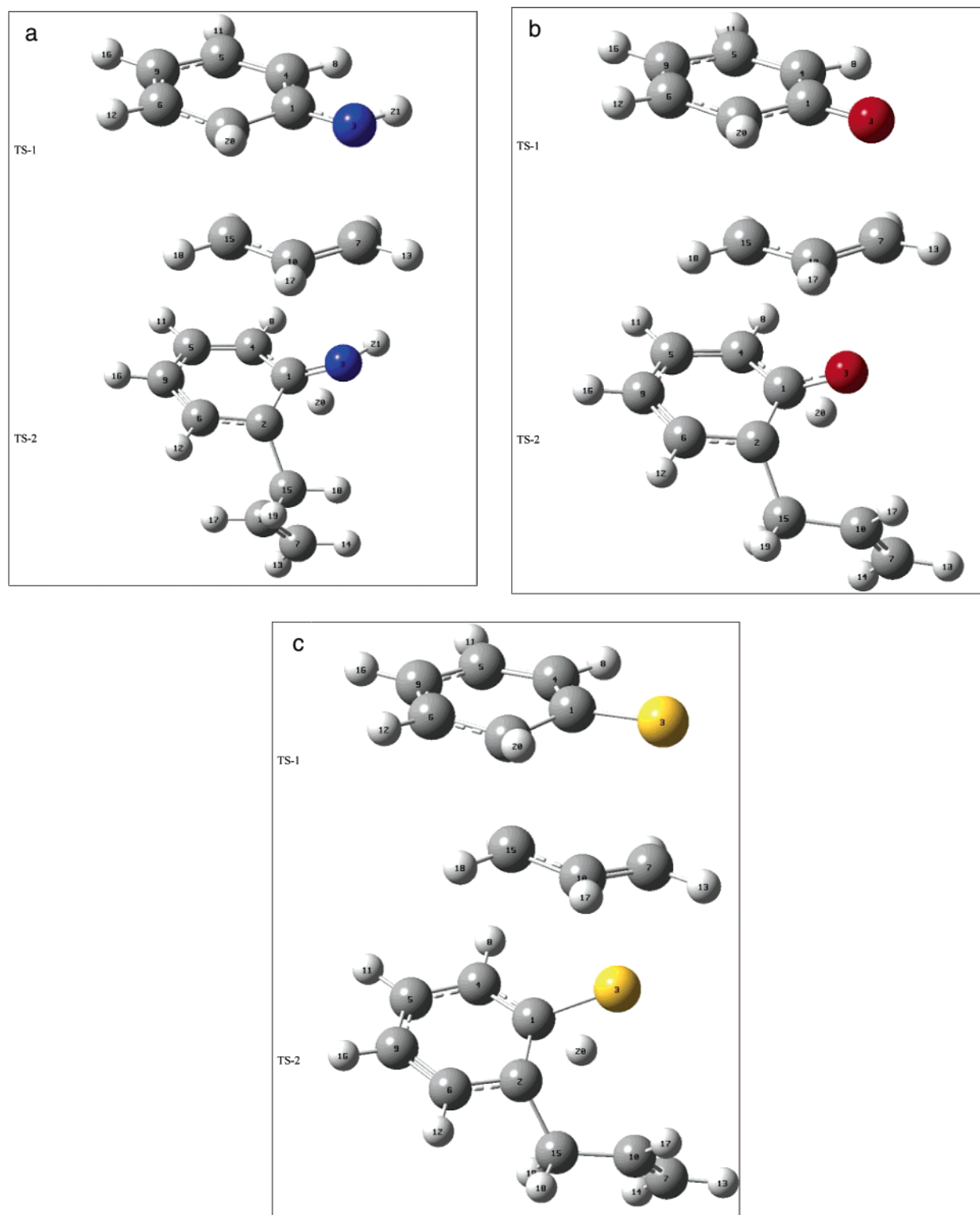


Figure 2. Geometries of the transition states for the N-, O-, and S-substituted species.

on the reaction energy. The barrier heights to pass from the reactant to the intermediate are higher for the amine-substituted molecules, and they are very similar for the ether and thioether substituted molecules. However, the intermediates of the ether substituted molecules are clearly more stable than the others. The generic feature of all the reactions is the barrier height to the second transition state which is very similar for the ether and thioether substituted molecules, between 60.0 and 65.0 kcal/mol, whereas the amine-substituted molecules present a barrier height between 70.0 and 75.0 kcal/mol. In Figure 2 the structure

of the transition state for some representative species are presented. In the first transition state the distance $X-C7$ ($X = N, O$, and S) varies from 2.22 Å (N) and 2.16 Å (O) to 2.58 Å (S). This is expected due to the larger size of the sulfur atom. However, the other important distance $C2-C15$ is smaller for the sulfur substituted molecule (2.10, 2.24, and 1.99 Å for the N -, O -, and S -substituted molecule, respectively). For the second transition state, the important $C1-C2$ and $C2-H_{20}$ bond lengths do not change in an important way with the nature of the heteroatom. On the contrary, the $C1-X$ and $X-H_{20}$ bond

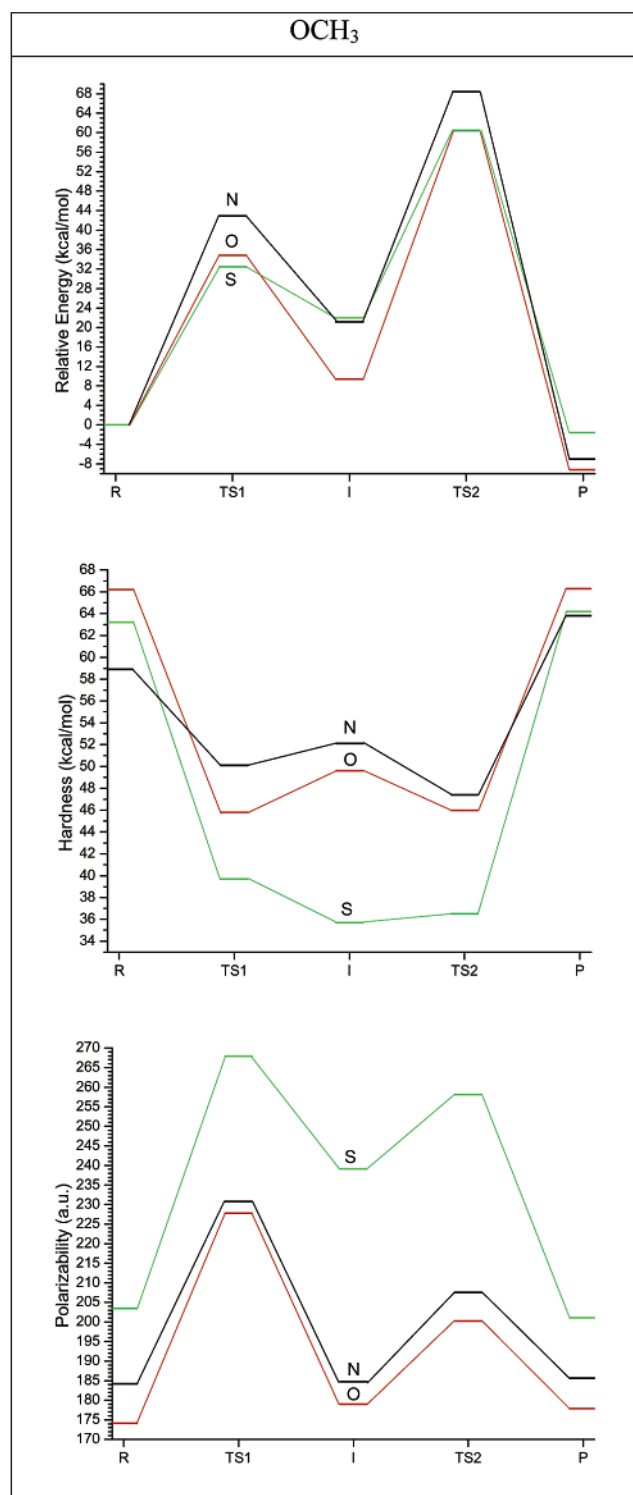


Figure 3. Relative energies, hardnesses and polarizabilities for the species participating in the Claisen rearrangement of the *m*-OCH₃ substituted allyl-phenyl ether, allyl-phenylamine, and allyl-phenyl thioether.

lengths change considerably. For instance, the C1–X bond length is 1.32, 1.29, and 1.73 Å for the N-, O-, and S-substituted species, respectively. In general, the meta-substituents do not affect in an important way the structure of the transition states.

From Figures 3–8 one can see that the hardness values follow the maximum hardness principle for the ether and amine substituted molecules without exception. The hardness profile mirrors the energy profile as it is expected. However, for the thioether substituted molecules there is at least one transition

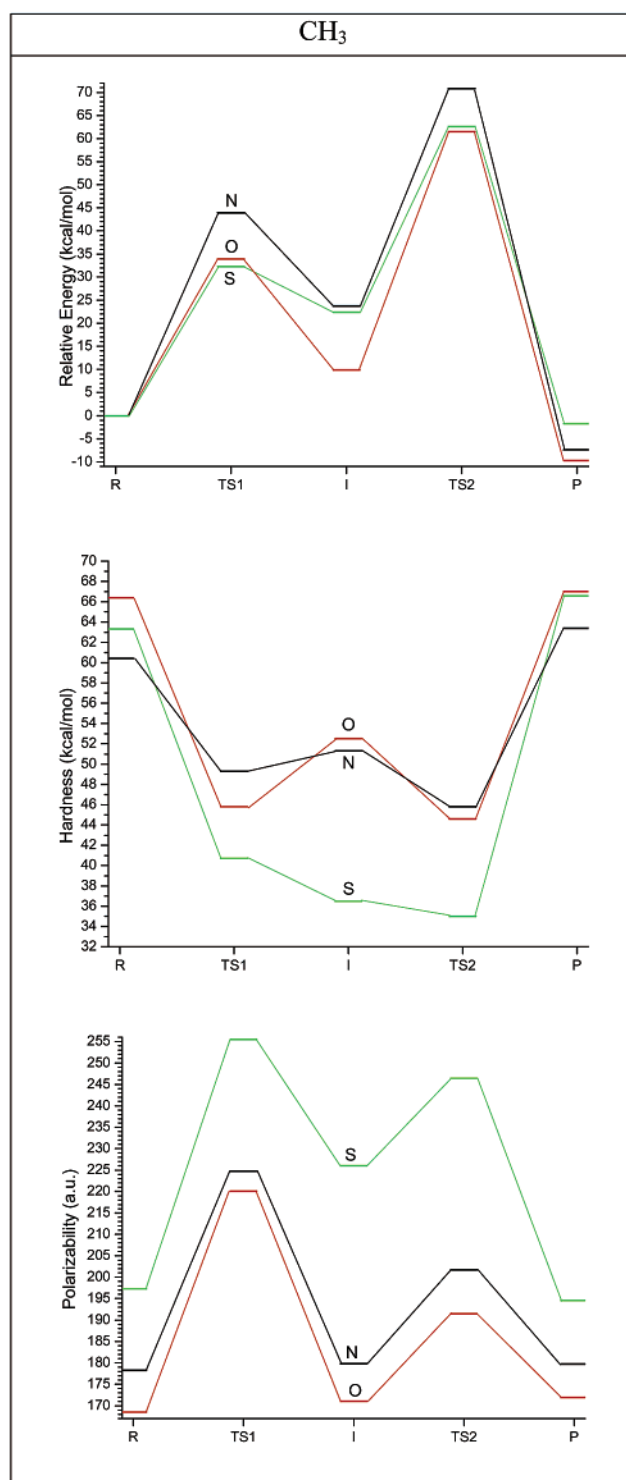


Figure 4. Relative energies, hardnesses, and polarizabilities for the species participating in the Claisen rearrangement of the *m*-CH₃-substituted allyl-phenyl ether, allyl-phenylamine, and allyl-phenyl thioether.

state with a higher hardness than the intermediate. On the other hand, the minimum polarizability principle is followed for all the reactions with nitrogen, oxygen, and sulfur atoms. Taking into consideration that the calculated dipole polarizabilities can have an error of about 5 au the discussion should be done only in the global aspects and one should not expect to have a clear-cut conclusion about the small difference between the dipole polarizabilities of the reactants and the products. However, higher polarizability values for the transition states are clearly

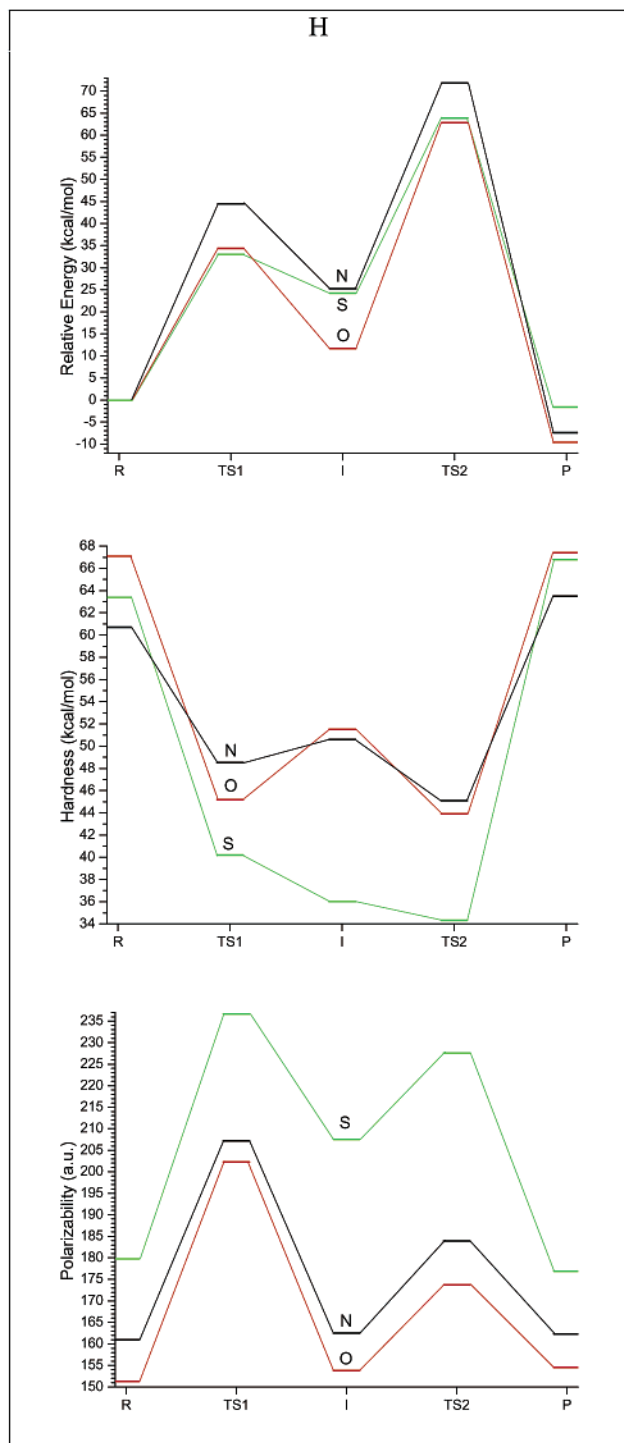


Figure 5. Relative energies, hardnesses, and polarizabilities for the species participating in the Claisen rearrangement of the allyl-phenyl ether, allyl-phenylamine, and allyl-phenyl thioether.

delineated. From Figures 3–8 it is transparent that the minimum polarizability principle is followed in all cases, whereas the maximum hardness principle fails for the sulfur containing molecules. The reason for this behavior can be understood by analyzing the nature of the HOMO in each case. For the operational definition of the global hardness (eq 3) one sees that the hardness carries information about the HOMO and LUMO. Therefore, in the cases where these orbitals are not changing in an important way during the reaction one cannot expect the operational hardness to be a good reactivity index. In fact, this is the case for the Claisen rearrangement of the

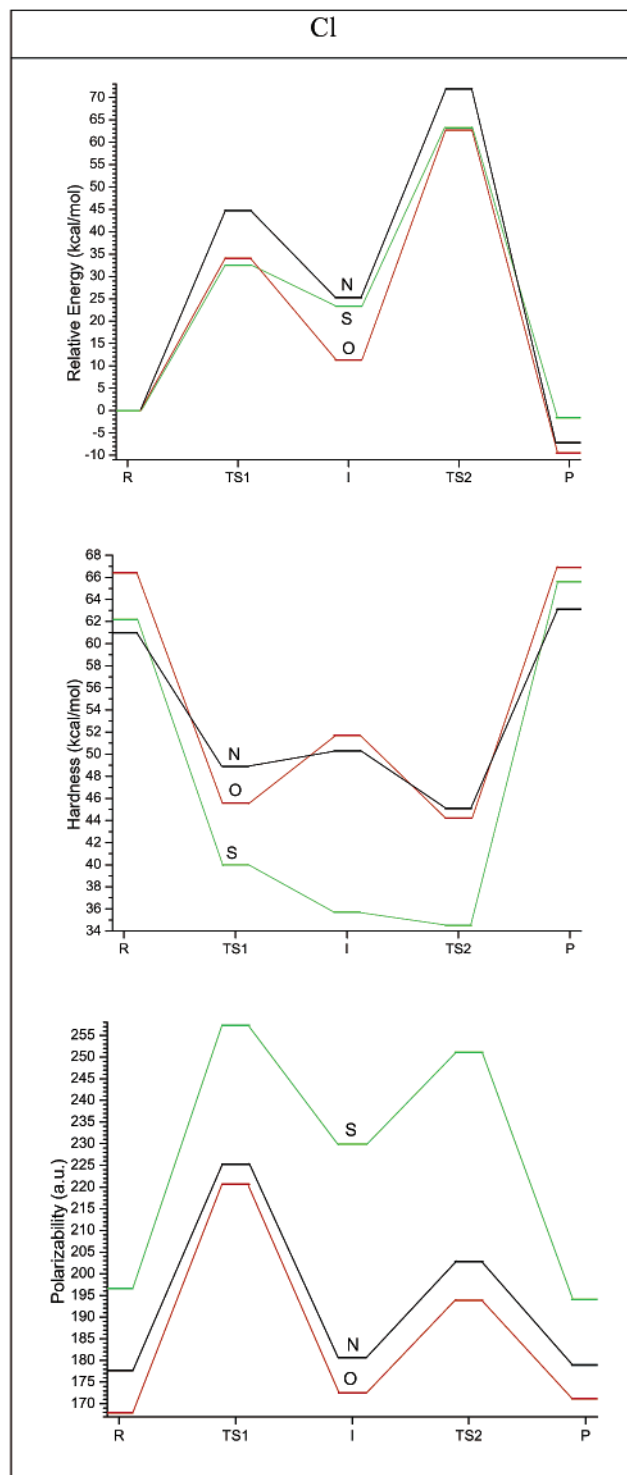


Figure 6. Relative energies, hardnesses, and polarizabilities for the species participating in the Claisen rearrangement of the *m*-Cl-substituted allyl-phenyl ether, allyl-phenylamine, and allyl-phenyl thioether.

allyl phenyl thioether and substituted molecules. In Figure 9, the HOMO and LUMO orbitals for the transition structures, TS1, of the Claisen rearrangement of the allyl phenyl ether, allyl phenylamine, and allyl phenyl thioether are displayed. It is obvious that for the allyl phenyl ether and allyl phenylamine the HOMO is important in the region of overlap between the phenyl and allyl moieties where the bond breaking and formation is occurring. However, the HOMO of the allyl phenyl thioether has no overlap between these two regions and it is more

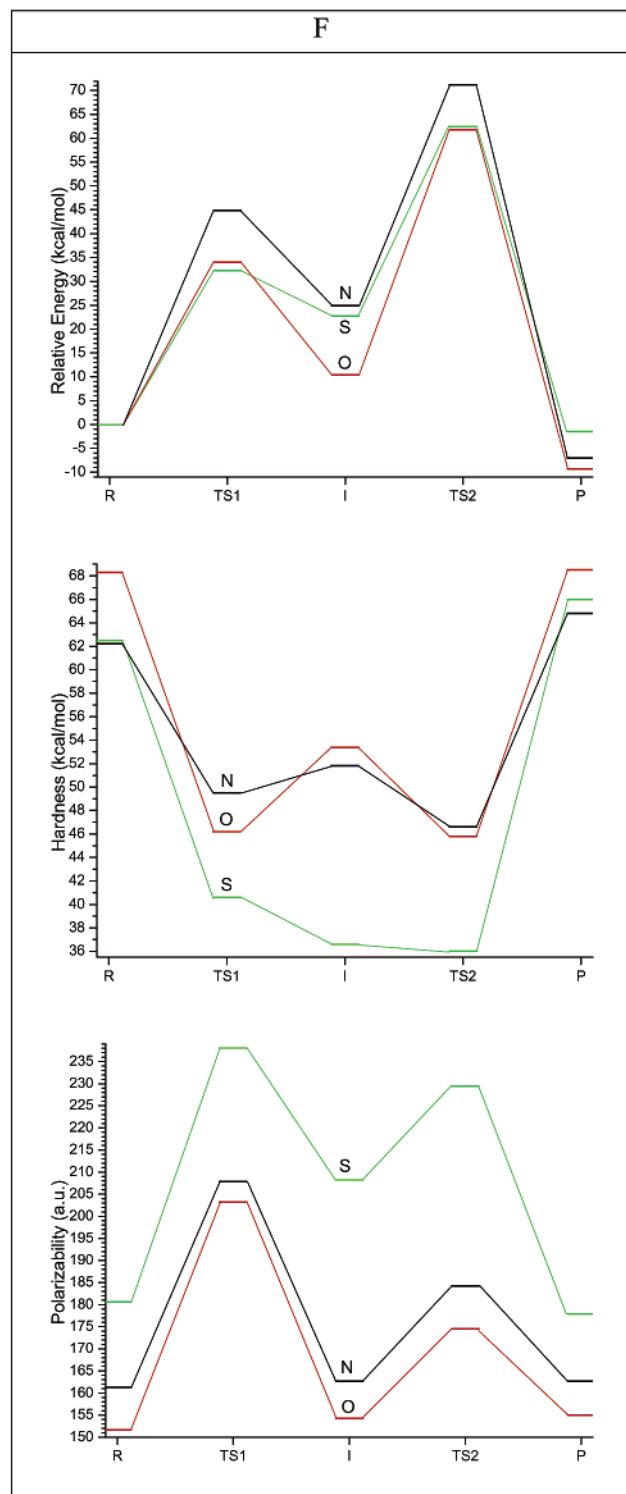


Figure 7. Relative energies, hardnesses, and polarizabilities for the species participating in the Claisen rearrangement of the *m*-F-substituted allyl-phenyl ether, allyl-phenylamine, and allyl-phenyl thioether.

concentrated in the electron lone pairs of the sulfur atom. The MPP is valid for these molecules as well. It is interesting to note that recently it has been numerically demonstrated that the MPP does not hold good for sulfur clusters³⁰ because the HOMO is more concentrated on the sulfur atom lone pairs and does not participate significantly in the bonding and accordingly an inverse relationship between the hardness and the polarizability has not been observed.

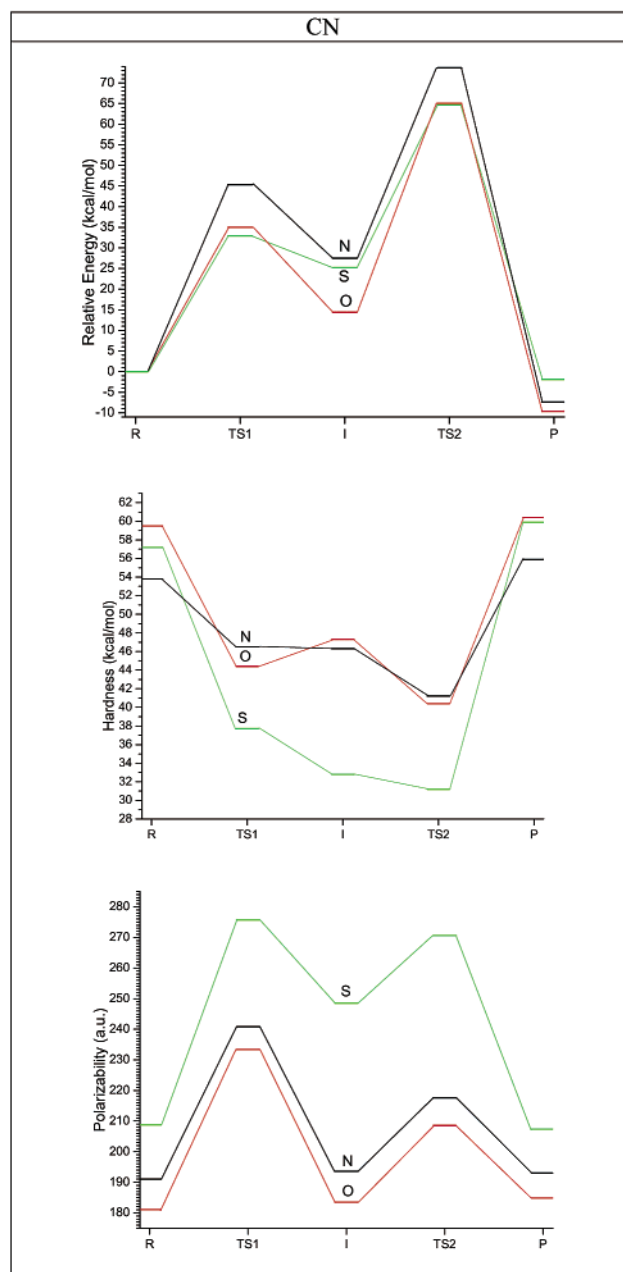


Figure 8. Relative energies, hardnesses, and polarizabilities for the species participating in the Claisen rearrangement of the *m*-CN-substituted allyl-phenyl ether, allyl-phenylamine, and allyl-phenyl thioether.

Since the polarizability profile mimics the energy profile and the hardness profile mirrors the latter one can, in principle, obtain all information regarding Claisen rearrangement (both thermodynamic and kinetic) in terms of the hardness/polarizability profile almost in the same way as would have been obtained from the corresponding energy profile. The effect of substitution can also be understood through the variation of these quantities along a reaction path. In as much as the insight into the feasibility of an unknown Claisen rearrangement could have been obtained through the study of the energetics of the said reaction a complementary approach would involve the associated hardness/polarizability study.

Concluding Remarks

DFT (B3LYP/6-311G**) calculations have been performed to understand the Claisen rearrangement of allyl phenyl ether,

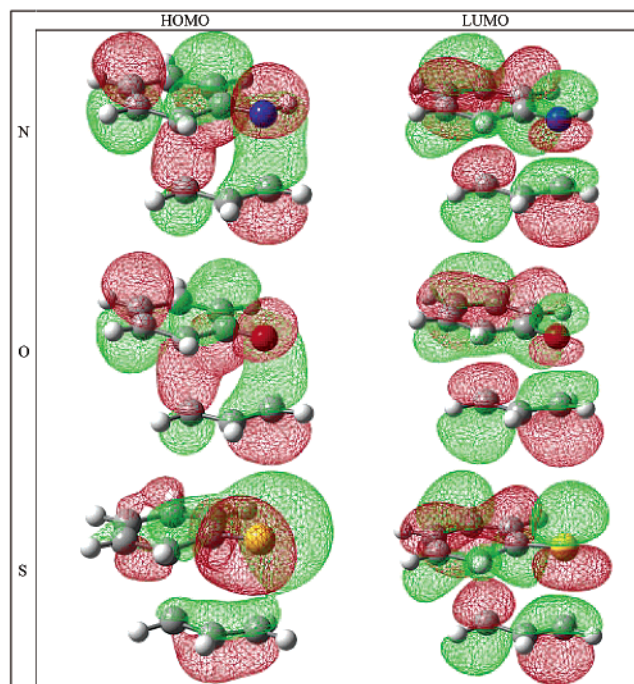


Figure 9. HOMO and LUMO 0.02 isosurfaces of the first transition state for the Claisen rearrangement of the allyl-phenyl ether, allyl-phenylamine, and allyl-phenyl thioether.

allyl phenylamine, allyl phenyl thioether and related meta-substituted molecules. In the case of the oxygen and nitrogen containing molecules the energy profile of the reaction is a perfect mirror image of the hardness profile, as expected from the maximum hardness principle. While the energy increases in the order $E_P < E_R < E_I < E_{TS1} < E_{TS2}$, the hardness decreases in the same order, viz., $\eta_P > \eta_R > \eta_I > \eta_{TS1} > \eta_{TS2}$, as it should.

The MPP is also followed. However, for the reactions of the sulfur containing molecules there is not a clear relationship between the hardness and the energy. This is due to the less important role of the HOMO in the reaction. For the sulfur containing molecules the HOMO is mainly concentrated in the region of the sulfur lone pair of electrons and not in the region where the bonds are being created or broken. The MPP is, however, found to be valid for this class of reactions as well.

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