Density functional theory study of ethene and acetylene addition to oxazole and protonated oxazole

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The suitability of the electron deficient oxazole for an inverse Diels–Alder reaction is presented. The qualitative reactivities have traditionally been evaluated by using the frontier molecular orbital (FMO) energy gaps between the reactants. The transition-state structures for the reaction of oxazole and protonated oxazole with ethene, acetylene and their methyl derivatives have been calculated with *ab initio*, DFT and AM1 semiempirical methods and their results were compared and discussed. A new approach, Becke3LYP/6-31 + G*//AM1 for obtaining activation energies has been introduced and compared with the traditional calculations.

Introduction

Oxazole is the most reactive heterocyclic five-membered aromatic compound as a diene in the Diels–Alder reaction. Since it was first discovered by Kondrateva in 1957,[1] it has been broadly used for the preparation of valuable heterocyclic compounds,[2] *e.g.* the pyridoxals have been synthesized that are the active form of vitamin B_6.[3] Despite an early recognition of the practical scope of the reaction, little effort has been devoted to exploring the potential of electron deficient oxazoles in the inverse Diels–Alder reaction.[4] There are numerous examples of employing the Diels–Alder reaction in the preparation of valuable alkaloids. For example, Weinreb and Levin completed synthesis of eupolauramine, an azaphenanthrene alkaloid, by using the intramolecular alkene–oxazole Diels–Alder reaction.[5]

Houk and co-workers performed an *ab initio* study of the reactivity of the oxazole in comparison to isoxazole.[6] Actually, they preferred the theoretical study of the addition of ethene to oxazole and isoxazole using the MP2/6-31G*//RHF/3-21G theory level. We have used the same level of theory for the theoretical study of heterodienophile addition to oxazole.[7] Now we would like to present the density functional theory (DFT) study of ethene and acetylene addition to free and protonated oxazole.

Methods

The initial optimizations of the reactants, transition-state structure search and transition-state optimizations were performed by using the computational package AM1[8] in MOPAC 6.0.[9] Further optimizations were carried out with both *ab initio* and DFT methods with GAUSSIAN 92/DFT.[10] The closed-shell Hartree–Fock (RHF)[11] self-consistent field and second-order Møller–Plesset perturbation theory[12] *ab initio* methods were also employed. Five different DFT methods were used for calculations: local SVWN (Slater[13] local spin density exchange functional with the correlation functional of Vosko *et al.*[14]); two hybrid Becke3LYP (Becke's 3 parameter functional[15] with the non-local correlation provided by the expression of Lee *et al.*[16]) and Becke3P86 (Becke's 3 parameter functional[15] with the non-local correlation provided by the Perdew 86 expression[17]) and two non-local BLYP (Becke's 1988 exchange functional[15] with LYP correlation functional[16]) and BP86 (Becke's 1988 exchange functional[15] with Perdew's gradient-corrected functional[17]). The output, after optimizing the transition structure[18] with the AM1 semiempirical method,† was transferred into a Gaussian input file with the MOPAC keywords 'aigout 1scf'. The initial optimization with GAUSSIAN was performed with 'rhf sto-3G‡ opt = (ef,ts, calcfc) scf = direct'. After one step, the optimization was aborted, and the input file was modified to the 'DFT or *ab initio* method 6-31 + G*[21] opt = (ef,ts,readfc) scf = direct' while keeping the file name constant and linking calculations in the chain with the '--link1--' command. It is possible to use the 'rfo' keyword instead of 'ef'. It usually performs more efficiently (faster); however, in our case the AMl optimized transition structures are very similar to the DFT optimized structures. They are usually in the correct curvature, as the lowest mode is to be followed uphill. Finally, all transition states were characterized by vibrational frequency analyses, as they have only one imaginary frequency.

Results and discussion

In the past there has been considerable dispute about the mechanism of the cycloaddition reaction. The researchers were divided between the concerted, the stepwise and the transition-state structure mechanisms that are similar to the biradicals. For example, the ethene addition to butadiene with the aromatic transition state is considered to occur by a typical concerted synchronous mechanism in the formation of two new C–C bonds.[22] Usually, the semiempirical methods support the biradicaloid mechanism[23] of addition. Recently, both high levels of *ab initio*[24,25] and DFT[26] calculations were performed, which support the synchronous concerted mechanism of cycloaddition reactions. Thus, the multiconfiguration SCF (MCSCF) calculations performed by Bernardi *et al.* predicted the biradical transition structure to be 2 kcal mol^{-1} higher.[24] The QCISD(T)6/-31G* *ab initio* calculations were performed by Houk and Li: the results obtained favour the synchronous concerted mechanism by 6 kcal mol^{-1} over the biradical mechanism.[25] These results are in excellent agreement with the experimental estimation of 2–7 kcal mol^{-1}.§ Although butadiene is not a suitable analogue to oxazole and the

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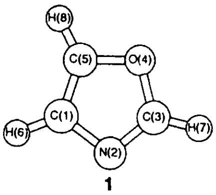
† For the procedure to find and verify the transition-state[19] structure by semiempirical methods see B. S. Jursic and Z. Zdravkovski, *J. Mol. Chem.* (*Theochem.*), 1994, **303**, 177 and references therein.

‡ Initial calculations were performed at minimal basis set, STO-3G,[20] in which one imaginary frequency mode was obtained. To be sure that the transition structure is one that combines the reactants and the cycloaddition product, one and only one imaginary frequency was visualized with a graphical program.

§ 1 cal = 4.184 J.

Table 1 Geometric parameters for oxazole **1** calculated by *ab initio* and DFT methods

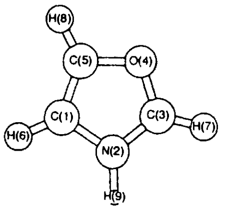


1

Method[a]	r21/Å	r32/Å	r43/Å	r51/Å	∠321/degrees	∠432/degrees	∠512/degrees	μ/D
I	1.388	1.270	1.329	1.335	104.1	114.9	108.7	1.61
II	1.377	1.295	1.350	1.359	104.3	114.3	109.1	1.66
III	1.393	1.295	1.359	1.357	104.2	114.6	109.2	1.60
IV	1.386	1.292	1.351	1.355	104.1	114.7	109.2	1.62
V	1.405	1.308	1.380	1.369	104.1	114.6	109.4	1.56
VI	1.399	1.306	1.372	1.368	104.0	114.8	109.4	1.59
VII	1.392	1.305	1.364	1.364	104.0	114.6	109.4	1.53
VIII[32]	1.395	1.292	1.357	1.353	103.9	115.0	109.7	1.50[33]

[a] I = RHF/6-31+G*; II = SVWN/6-31+G*; III = Becke3LYP; IV = Becke3P86; V = BLYP; VI = BP86; VII = MP2; VIII = microwave structure.

Table 2 Geometric parameters for protonated oxazole **2** calculated with *ab initio* and DFT methods



2

Method[a]	r21/Å	r32/Å	r43/Å	r54/Å	r51/Å	∠321/degrees	∠432/degrees	∠512/degrees
I	1.397	1.295	1.281	1.071	1.328	108.1	110.5	105.1
II	1.378	1.319	1.307	1.361	1.354	109.1	109.2	105.1
III	1.395	1.320	1.311	1.379	1.352	108.8	109.7	105.2
IV	1.388	1.316	1.306	1.371	1.350	108.8	109.6	105.2
V	1.405	1.334	1.328	1.395	1.363	109.0	109.5	105.4
VI	1.400	1.331	1.323	1.387	1.263	109.0	109.5	105.2
VII	1.388	1.324	1.319	1.376	1.360	109.2	109.4	105.0

[a] I = RHF/6-31+G*; II = SVWN/6-31+G*; III = Becke3LYP; IV = Becke3P86; V = BLYP; VI = BP86; VII = MP2.

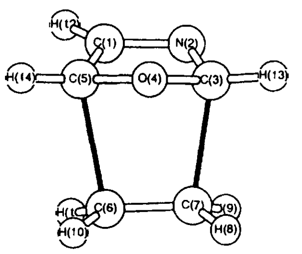
computational results obtained cannot be transfered to the ethene–oxazole system, we believe that a concerted mechanism for the studied reactions is a reasonable assumption.[27]

The relative reactivity of oxazole in reaction with the ethene and acetylene might be evaluated on the basis of the frontier molecular orbital (FMO)[28] energy gap. The FMO energy gaps are calculated with RHF/6-31+G* for the oxazole–ethene reaction: $\mathrm{LUMO}_{\mathrm{ethene}} - \mathrm{HOMO}_{\mathrm{oxazole}} = 281.24$ kcal mol^{-1} and $\mathrm{LUMO}_{\mathrm{oxazole}} - \mathrm{HOMO}_{\mathrm{ethene}} = 283.42$ kcal mol^{-1}. The energy gap between ethene as a dienophile and buta-1,3-diene as a diene is $\mathrm{LUMO}_{\mathrm{ethene}} - \mathrm{HOMO}_{\mathrm{butadiene}} = 209.15$ kcal mol^{-1}. This is smaller than the other FMO energy gap ($\mathrm{LUMO}_{\mathrm{butadiene}} - \mathrm{HOMO}_{\mathrm{ethene}} = 265.65$ kcal mol^{-1}) indicating that it is a normal LUMO dienophile controlled reaction.[29] These results predict a lower reactivity for the oxazole if it is compared with the butadiene as a diene for the Diels–Alder reaction. Similar results were obtained for the reactant pair oxazole–acetylene with FMO energy gaps: $\mathrm{LUMO}_{\mathrm{acetylene}} - \mathrm{HOMO}_{\mathrm{oxazole}} = 273.90$ and $\mathrm{LUMO}_{\mathrm{oxazole}} - \mathrm{HOMO}_{\mathrm{acetylene}} = 305.16$ kcal mol^{-1}.

By protonating the pyrazole nitrogen, considerable amounts of positive charge should be located in the oxazole ring, thereby, the LUMO energy should be lower. Now, the FMO energy gaps in the reaction of H–oxazole with ethene are: $\mathrm{LUMO}_{\mathrm{ethene}} - \mathrm{HOMO}_{\mathrm{H\text{-}oxazole}} = 426.67$ kcal mol^{-1} and $\mathrm{LUMO}_{\mathrm{H\text{-}oxazole}} - \mathrm{HOMO}_{\mathrm{ethene}} = 177.89$ kcal mol^{-1}. The FMO energy gap for acetylene addition to the protonated oxazole shows the same behaviour: $\mathrm{LUMO}_{\mathrm{acetylene}} - \mathrm{HOMO}_{\mathrm{H\text{-}oxazole}} = 419.32$ kcal mol^{-1} and $\mathrm{LUMO}_{\mathrm{H\text{-}oxazole}} - \mathrm{HOMO}_{\mathrm{acetylene}} = 199.62$ kcal mol^{-1}. These energy gaps suggest that the acid-catalysed cycloaddition reaction with oxazole should be feasible with a very low activation barrier. The reaction can be facilitated if it is performed with an electron-donating dienophile like (*Z*)-but-2-ene and but-2-yne. In these cases, the FMO energy gaps are $\mathrm{LUMO}_{\mathrm{H\text{-}oxazole}} - \mathrm{HOMO}_{(Z)\text{-}\mathrm{but\text{-}2\text{-}ene}} = 153.17$ kcal mol^{-1} and $\mathrm{LUMO}_{\mathrm{H\text{-}oxazole}} - \mathrm{HOMO}_{\mathrm{but\text{-}2\text{-}yne}} = 166.67$ kcal mol^{-1}.

Of course, the best estimation of the reactants' reactivity is obtained by evaluating their activation energies. Recently we have studied the suitability of the DFT methods for predicting the cycloaddition activation energies.[30] The best results were obtained with the hybrid Becke3LYP DFT method. Similarly, we have applied DFT methods for the study of the *ab initio* problematic systems.[31] In all calculations the hybrid DFT methods, Becke3LYP and Becke3P86, produced geometries that are almost indistinguishable from the experimental results which were proven to be more accurate than the MP2 *ab initio* calculations.[31] The structural parameters of oxazole and protonated oxazole were calculated by both *ab initio* and DFT methods and are presented in Tables 1 and 2, respectively. The geometry of oxazole was determined by microwave spectroscopy.[32] The molecule is planar; this is supported by all of our calculations. The geometry obtained by the RHF/6-31+G* method differs greatly from the experimental value, predicting shorter bond distances with an average difference of 0.02 Å. The

Table 3 Geometric parameters for transition state structures 3 or 4 with *ab initio* and DFT methods



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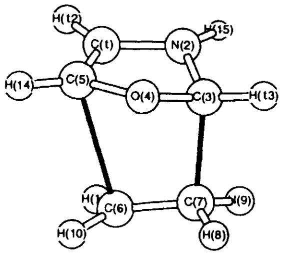
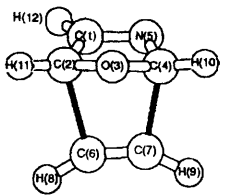


4

Method[a]	$r21$/Å	$r32$/Å	$r43$/Å	$r51$/Å	$r54$/Å	$r76$/Å	$r56$/Å	$r73$/Å	∠765/degrees	∠673/degrees
Transition-state structure 3										
I	1.309	1.340	1.348	1.400	1.348	1.391	2.189	2.072	98.7	100.3
II	1.333	1.338	1.367	1.396	1.351	1.381	2.304	2.100	97.4	101.6
III	1.329	1.360	1.384	1.411	1.368	1.403	2.239	2.050	97.6	101.7
IV	1.329	1.349	1.373	1.403	1.359	1.392	2.250	2.075	97.8	101.3
V	1.341	1.378	1.411	1.423	1.384	1.419	2.285	2.014	96.4	102.9
VI	1.342	1.366	1.398	1.415	1.375	1.407	2.296	2.058	96.8	102.3
Transition-state structure 4										
I	1.355	1.370	1.340	1.356	1.347	1.391	2.546	1.898	92.7	104.2
II	1.359	1.350	1.333	1.369	1.348	1.363	2.641	2.169	95.0	101.6
III	1.361	1.386	1.366	1.378	1.360	1.398	2.572	1.933	92.4	105.0
IV	1.359	1.370	1.351	1.372	1.353	1.383	2.580	2.000	93.3	103.7
V	1.371	1.405	1.391	1.390	1.374	1.414	2.613	1.906	91.2	106.3
VI	1.370	1.386	1.371	1.385	1.369	1.396	2.634	2.003	92.5	104.6

[a] I = RHF/6-31+G*; II = SVWN/6-31+G*; III = Becke3LYP; IV = Becke3P86; V = BLYP; VI = BP86.

Table 4 Geometric parameters for transition state structure 5 calculated with *ab initio* and DFT methods[a]



5

Method	$r21$/Å	$r32$/Å	$r43$/Å	$r51$/Å	$r54$/Å	$r62$/Å	$r74$/Å	∠621/degrees	∠762/degrees	∠745/degrees
I	1.404	1.347	1.342	1.308	1.340	2.160	2.094	94.6	100.9	99.0
II	1.397	1.349	1.364	1.332	1.339	2.313	2.116	90.7	98.2	97.7
III	1.413	1.365	1.378	1.329	1.359	2.240	2.074	93.4	99.3	99.4
IV	1.405	1.357	1.368	1.329	1.349	2.250	2.096	92.6	99.3	98.6
V	1.423	1.381	1.404	1.342	1.375	2.300	2.044	92.8	97.7	100.3
VI	1.416	1.373	1.392	1.343	1.364	2.311	2.083	92.0	98.0	99.3
VII	1.413	1.369	1.385	1.338	1.367	2.170	2.001	93.4	99.8	99.3

[a] I = RHF/6-31+G*; II = SVWN/6-31+G*; III = Becke 3LYP; IV = Becke 3P86; V = BLYP; VI = BP86; VII = MP2.

MP2/6-31+G* predicts the structural parameters to be closer to the experimental values, yet the most accurate calculations are obtained by the Becke3LYP/6-31+G* and Becke3P86/6-31+G* methods. The non-local DFT methods BLYP and BP86 overestimate the bond distances for identical values, unlike RHF which underestimates them. A satisfied geometry of oxazole is obtained by a local SVWN (LSDA) DFT method (Table 1). Geometric parameters for protonated oxazole are calculated with the same *ab initio* and DFT methods (Table 2) and follow similar patterns. Unfortunately, there are no experimental results to compare with the calculations. Nevertheless, the MP2/6-31+G* and Becke3LYP or Becke3P86 are in close agreement with one another. We believe that the structure obtained with the DFT hybrid method is the most accurate, as in the case of the oxazole structure.

The structural parameters for the transition-state structures 3 and 4 for ethene addition to oxazole and protonated oxazole are presented in Table 3. As expected, the transition-state structures are for concerted but not for synchronous cycloaddition reactions. Geometries of transition-state structure 3 determined by various DFT methods and RHF calculations turns out to be quite similar, except that the carbon–heteroatom bond distances calculated with RHF *ab initio* methods are too short. Two hybrid methods, Becke3LYP and Becke3P86, agree with the geometries of 3, while the non-local methods overestimate the bond distances. Transition-state structure 4 differs considerably from 3. The molecule is positively charged owing to protonation of the oxazole nitrogen. According to the Mulliken charges calculated by Becke3LYP/6-31+G*, the higher charge density is located on the carbon C-3 (0.561) in comparison to the carbon C-5 (0.313). Owing to the higher atomic C-3 orbital contribution to the LUMO of protonated oxazole in comparison to the C-5 atomic orbital contribution, the transition-state structure 4 exhibits substantial asynchronicity. The degree of predicted asynchronicity varies from method to method. Thus the highest asynchronicity was predicted with the RHF/6-31+G* (Δr = 0.648 Å) and the lower one with SVWN/6-31+G* (Δr = 0.472 Å). The hybrid DFT method predicts the transition-state structures which are intermediate (Table 3).

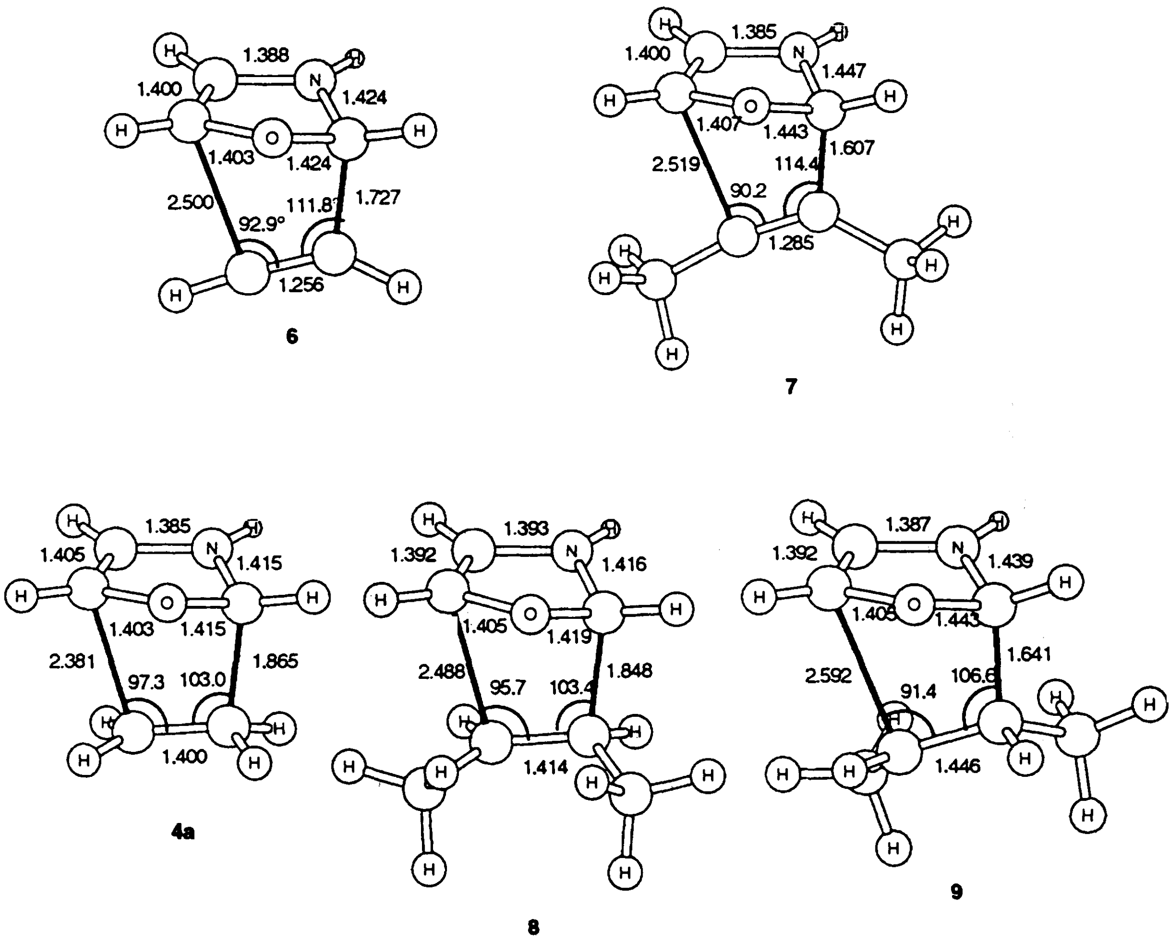


Fig. 1 Transition-state structures for ethene, acetylene, (*Z*)-but-2-ene and but-2-yne addition to protonated oxazole generated by AM1 method

The transition-state structure for acetylene addition to oxazole **5** (Table 4) in many ways resembles that of **3**. It is slightly asynchronous with new forming bond distances between 2.04 and 2.30 Å. Here, the case of higher asynchronicity was obtained with the non-local BLYP/6-31+G* DFT method (Δr = 0.253 Å), while the RHF/6-31+G* method predicts that the two new forming bond distances are almost identical (Δr = 0.067 Å, Table 4). Nevertheless, all predicted transition-state structures are very similar. The highest similarity is obtained with MP2 *ab initio* and Becke3LYP DFT methods.

Transition-state structures for addition of but-2-yne and (*Z*)-but-2-ene to protonated oxazole **2** were optimized by the AM1 semiempirical method (Fig. 1). Recently, we demonstrated that transition-state structures for the Diels–Alder reactions obtained by the AM1 and Becke3LYP DFT methods do not differ notably.[34] Here we are confirming this finding with an example of ethene addition to **2**. The predicted asynchronicity is Δr = 0.516 Å (Fig. 1) corresponding to Δr = 0.580 Å obtained by Becke3LYP/6-31+G* (Table 3). The structure obtained with the AM1 calculation is more compact and is farther from the reactants. According to the Hammond postulate,[35] it is expected that the single point energy evaluation on this structure might produce slightly higher energies than the full DFT optimization. All other transition structures **6–9** are generated by AM1 calculations for concerted asynchronous cycloaddition. Note that the transition structures for the alkyne addition to protonated oxazole are much more asynchronous than the corresponding transition structures of the reaction of alkenes (Fig. 1).

Based on the FMO energy gap calculated with RHF/6-31+G* we have concluded that the ethene addition to oxazole **1** is less feasible than the ethene addition to butadiene. The opposite is expected if the reaction is performed with protonated oxazole **2**. To confirm this finding, we have estimated the activation energies by the *ab initio* and DFT methods. Total energies of the reactants and transition-state structures are presented in Table 5. The activation energies are presented in Table 6. Experimentally it was determined that the activation energy for ethene addition to butadiene is 25.1 kcal mol^{-1}.[36] Our previous study of the ethene addition to butadiene with Becke3LYP/6-31G** predicted the activation energy to be 22.43 kcal mol^{-1}. Here we have estimated the activation energy for the ethene addition to butadiene by Becke3LYP/6-31G* on the AM1 geometries. Now, the estimated activation energy (23.31 kcal mol^{-1}) is much closer to the experimental value. As we have demonstrated earlier,[30] neither local nor non-local DFT methods produce reasonable activation energies. It is known that MP2 calculations underestimate activation energies for the Diels–Alder reactions.[37] The best estimation of the activation energies are obtained with Becke3LYP DFT methods. According to these calculations, the activation energy for the ethene addition to oxazole is 25.15 kcal mol^{-1}. Knowing that the same method underestimates the activation energy for the ethene addition by *ca.* 3.0 kcal mol^{-1}, it is reasonable to expect that the actual reaction barrier is *ca.* 28 kcal mol^{-1}. The Becke3LYP calculations are in agreement with the FMO method that predicts oxazole to be less reactive than butadiene. As expected from FMO evaluations, the activation energy for ethene addition to protonated oxazole decreases to 11.85 kcal mol^{-1}. The addition of acetylene to oxazole has the highest activation energy (26.48 kcal mol^{-1}). The order of reactivity is the same as it was predicted with the FMO method.

Although the local DFT method (SVWN) predicts reasonable geometries of both the reactants and the transition-state structures, the estimated activation energies are very low.

Table 5 Total energies of the reactants and the transition states

	E_{I}[a]	E_{II}[b]	E_{III}[c]	E_{IV}[d]	E_{V}[e]	E_{VI}[f]	E_{VII}[g]
A[h]	−78.035 82	−78.130 37	−78.593 25	−78.877 72	−78.544 18	−78.584 51	−78.291 18
B[i]	−76.823 07	−76.860 44	−77.333 11	−77.575 63	−77.300 18	−77.325 68	−77.073 26
1	−244.640 22	−244.764 84	−246.081 19	−246.722 01	−246.014 43	−246.086 25	−245.365 08
2	−244.988 87	−245.098 78	−246.422 93	−247.065 25	−246.353 81	−246.426 50	−245.700 61
3	−322.607 18	−322.891 22	−324.634 36	−325.569 50	−324.519 34	−324.641 95	
4	−322.978 88	−323.241 98	−324.997 30	−325.932 74	−324.880 36	−325.002 38	
5	−321.385 77	−321.614 42	−323.368 92	−324.261 41	−323.271 46	−323.378 42	−322.402 07

[a] I = RHF/6-31 + G*. [b] II = SVWN/6-31 + G*. [c] III = Becke3LYP/6-31 + G*. [d] IV = Becke3P86/6-31 + G*. [e] V = BLYP/6-31 + G*. [f] VI = BP86/6-31 + G*. [g] VII = MP2/6-31 + G*. [h] A = Ethene. [i] B = Acetylene.

Table 6 Activation energies (kcal mol^{-1}) for ethene and acetylene addition to oxazole

TS	ΔE_{I}[a]	ΔE_{II}[b]	ΔE_{III}[c]	ΔE_{IV}[d]	ΔE_{V}[e]	ΔE_{VI}[f]	ΔE_{VII}[g]
3	43.21	2.50	25.15	18.97	24.64	18.08	
4	28.75	−8.05	11.85	6.42	11.06	5.42	
5	48.65	6.81	28.48	22.73	27.08	21.03	22.76

[a] I = RHF/6-31 + G*. [b] II = SVWN/6-31 + G*. [c] III = Becke3LYP/6-31 + G*. [d] IV = Becke3P86/6-31 + G*. [e] V = BLYP/6-31 + G*. [f] VI = BP86/6-31 + G*. [g] VII = MP2/6-31 + G*.

Thus, for the transition state **4**, negative activation energies were obtained. The BP86 correlation functional seems to suffer from the same problem as the MP2 *ab initio* method in underestimating the activation energies at almost the same level. The Becke3LYP DFT method was proven by Houk and co-workers[38] and Schleyer and co-workers[39] to be reliable for the estimation of activation energies for the Cope rearrangement.

We have also estimated the activation barriers for the addition of the alkynes and alkenes to the protonated oxazole by Becke3LYP/6-31 + G* on the AM1 geometries (Table 7). As demonstrated in the example of ethene addition to butadiene the Becke3LYP/AM1 energies are higher than the one obtained by the full Becke3LP calculations. In fact, they may be closer to the experimental energies. Because the reaction is LUMO diene and HOMO dienophile controlled by substituting methyl groups on ethene and acetylene, the activation energies are decreased. It is also predicted that the *endo* addition is preferred over the *exo* addition, known as Alder's rule.

Conclusions

The reactivity of oxazole in the LUMO diene controlled Diels–Alder reaction with ethene and acetylene derivatives were studied by DFT and *ab initio* methods. It was demonstrated by both estimation of the FMO energy gaps and evaluation of the activation energies that oxazole is less reactive than butadiene. The reactivity is predicted to be increased if oxazole is protonated. Thus, a further increase of the reactivity is obtained by substituting methyl groups on the dienophiles. The acetylenes are found to be less reactive than the ethenes.

Of all the DFT methods Becke3LYP has been proven to produce the best results. Energies obtained by the SVWN local DFT method are far too low and energies obtained by the BP86 and Becke3P86 are the same as MP2. It has been demonstrated that the geometries obtained with different DFT methods and MP2 *ab initio* calculations do not differ considerably, although AM1 calculations predict more compact transition-state structures than both of the *ab initio* and DFT calculations. The Becke3LYP energy evaluation on those structures is even better than when the full Becke3LYP calculations are performed. This might be the method of choice when a larger system of interest is used by the experimental organic chemist; therefore it should be investigated.

Table 7 Activation energies (kcal mol^{-1}) for the alkene and the alkyne addition to oxazole calculated by Becke3LYP/AM1

ΔE_{A}[a]	ΔE_{B}[b]	ΔE_{C}[c]	ΔE_{D}[d]	ΔE_{E}[e]	ΔE_{F}[f]	ΔE_{G}[g]
26.67	12.58	31.05	18.29	10.91	11.82	16.45

[a] A = Ethene + oxadiazole. [b] B = Ethene + protonated oxazole. [c] C = Acetylene + oxazole. [d] D = Acetylene + protonated oxazole. [e] E = (*Z*)-But-2-ene + protonated oxazole, *endo* addition. [f] F = (*Z*)-But-2-ene + protonated oxazole, *exo* addition. [g] G = But-2-yne + protonated oxazole.

Acknowledgements

The author is grateful to the Louisiana Educational Quality Support Fund for a grant (ENH-TR-42) which provided the computational facilities. We appreciate the numerous and very constructive comments of one of the reviewers.

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Paper 5/02968F
Received 9*th May* 1995
Accepted 1*st November* 1995