Ab Initio Study of Heterodienophile Addition to Oxazole

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The Diels–Alder additions of formaldehyde, formaldehyde imine, (*Z*)-diazene, (*E*)-diazene and nitrosyl hydride to oxazole have been investigated by frontier molecular orbital theory and by *ab initio* methods. The former cannot account for steric and other electronic interactions in the transition states and is of limited value in predicting the reactivity of these dienophiles. The transition state structures of all possible isomers for the concerted cycloadditions were located at the restricted Hartree Fock 3-21G level and the energies evaluated by means of the second-order Møller–Plesset perturbation theory with the 6-31G* basis set. The heteroatom lone pairs play a decisive role in directing the regioselectivity of these additions.

Of all five-membered aromatic heterocyclic dienes, the most susceptible toward [4 + 2] cycloaddition reactions is oxazole.[1] Since the initial report that alkyloxazoles undergo Diels–Alder reactions with maleic anhydride,[2] extensive efforts have been invested to define the scope and synthetic utility of the [4 + 2] cycloadditions of oxazole derivatives known as the Kondrat'eva reaction. These studies have been the subject of several reviews.[3] The course and facility in which the Kondrat'eva reaction proceeds, depend on the oxazole/dienophile substitution, as well as the reaction conditions. Alkenic dienophiles provide pyridine derivatives through fragmentation of the initial [4 + 2] bicyclic adduct followed by oxidation.

Despite the early recognition that heterocyclic azadine systems are typically electron-deficient,[4] little effort has been devoted to the exploration of the potential participation of electron-deficient oxazoles in inverse electron demand ($LUMO_{diene}$-controlled) Diels–Alder reactions with electron rich dienophiles. Here we present our *ab initio* study of the hetero Kondrat'eva reaction.[5] The frontier molecular orbital (FMO) approach was used to explain the relative reactivity of the heterodienophiles, and the regioselectivity of their addition to oxazole. The FMO results are compared with the reaction activation barriers calculated at the MP2/6-31G*//RHF/3-21G theory level. The influence of the orientation of the heterodienophile lone pair in the transition structure on calculated activation barrier will be discussed.

Methods

Geometry optimizations were carried out at the restricted Hartree-Fock level using the GAMESS program.[6] For each reaction, the reactants, transition structures and the products were fully optimized with the 3-21G[7] basis set. Each transition structure gave only one imaginary harmonic vibrational frequency, corresponding to the motion forming the new C–C and C–X bonds for the concerted transition structures. The activation energies were estimated from MP2/6-31G* [8] calculations on the RHF/3-21G optimized geometries. Although there is not much data available on the theoretical study of the addition of any kinds of heterodienophile to dienes, a few of them have been studied with the same theoretical model.[9] Our previous *ab initio* study of heterodienophile addition to some five-membered heteroaromatic compounds was performed at the same level.[10] To be able to compare the literature results with the results presented in this paper the same theory level of *ab initio* calculations was chosen. In addition, it was shown, in the case of the Diels–Alder reaction of butadiene with ethylene, that the geometries of the concerted transition states generated by various semiempirical,[11] and *ab initio* theory levels,[12] including MCSCF methods,[13] are very similar. The optimized bond lengths usually agree to within a few hundredths of an ångstrøm. The bond lengths of the forming C–C bonds show the largest variation, ranging from 2.20 to 2.28 Å. Inclusion of electron correlation tends to shorten the forming C–C bond.

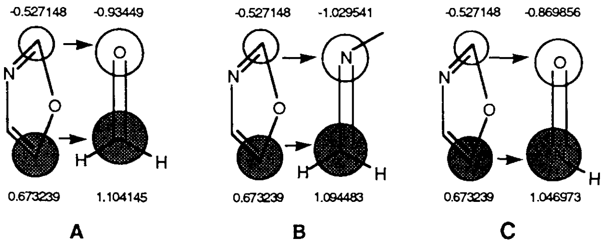

Fig. 1 RHF/6-31G atomic orbital coefficients for HOMO (oxazole) – LUMO (heterodienophile) interactions

Results and Discussion

The Frontier Molecular Orbital Approach.—Reactivity. This approach suffers from many disadvantages that originate from the fact that the frontier orbitals are calculated for the separated reactants, and thus they do not encounter the interactions of the substituents on the diene and the dienophile present in the transition structures. That is in many cases crucial for the prediction of the relative reactivity and sometimes even the regioselectivity of the reaction. Having these drawbacks in mind, FMO can, in a majority of cases, predict the relative reactivity of a series of dienophiles in the reaction with the same diene and was used in this case of heterodienophile addition to oxazole. According to FMO,[14] the most reactive pair in the Diels–Alder reaction is the one that has the smallest gap between the HOMO energies of one reactant with LUMO energy of the other reactant. These differences calculated at the MP2/6-31G*//3-21G level are presented in Fig. 1. According to these energy gaps, the reactivity of the dienophiles studied is in the order nitrosyl hydride (0.4439 eV), (*Z*)-diazene (0.4878 eV), (*E*)-diazene (0.4907 eV), formaldehyde (0.4922 eV), ethylene (0.538 eV) and formaldehyde imine (0.5212 eV). All heterodienophile additions to oxazole are normal electron demand Diels–Alder reactions—HOMO diene and LUMO dienophile

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Table 1 α-Eigenvalues (eV) for LUMO and HOMO of oxazole and heterodienophiles calculated by MP2/6-31G*//RHF/3-21G

Compound	HOMO	LUMO	ΔE_I[a]	ΔE_{II}[b]
Oxazole	−0.3536	0.1588		
Ethylene	−0.3748	0.1844	0.5336	0.538
Formaldehyde	−0.4392	0.1386	0.598	0.4922
Formaldehyde imine	−0.4189	0.1676	0.5777	0.5212
(*Z*)-Diazene	−0.4032	0.1342	0.562	0.4878
(*E*)-Diazene	−0.3997	0.1371	0.5585	0.4907
Nitrosyl hydride	−0.4272	0.0903	0.586	0.4439

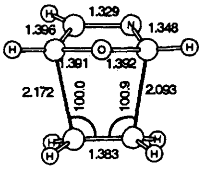
[a] $\Delta E_I = E_{LUMO(oxazole)} - E_{HOMO(dienophile)}$. [b] $\Delta E_{II} = E_{LUMO(dienophile)} - E_{HOMO(oxazole)}$.

controlled additions. Only the reference example, ethylene addition to oxazole is HOMO dienophile controlled and it is an example of an inverse electron demand Diels–Alder reaction.

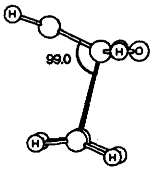
Regioselectivity. An important outcome of computational studies of cycloaddition reactions is their accurate prediction of the regioselectivity. The regioselectivity of a reaction can be predicted by various qualitative methods. In the present case of addition of an asymmetric dienophile (formaldehyde, formaldehyde imine and nitrosyl hydride) to oxazole, frontier orbitals, specifically the LUMO of the dienophile and HOMO of oxazole, is used for prediction of regioselectivity of the addition. The RHF/6-31G* frontier orbital of oxazole, formaldehyde, formaldehyde imine and nitrosyl hydride in the orientation of the highest molecular orbital overlap are presented in Fig. 1. According to the frontier orbitals the dienophile and the diene will be oriented in such a way that maximal overlap between the frontier orbitals is possible. The heteroatom in formaldehyde and formaldehyde imine, and the oxygen of nitrosyl hydride will make a bond with the oxazole carbon that is between oxygen and nitrogen (Fig. 1). However, FMO is powerless in predicting the position of the N–H dienophile bonds, *i.e.*, whether they will be *exo* or *endo* in the adducts.

In order to confirm the FMO prediction of the reactivity and regioselectivity and select the *endo* and *exo* isomer in the hetero Kondrat'eva reaction, the transition structures were generated, and activation barriers were evaluated by *ab initio* calculations.

Geometries of the Transition State Structures.—A concerted, but not necessarily synchronous, reaction mechanism was assumed. Owing to the asymmetry of the dienes, the dienophiles, or both, asynchronous transition structures were generated in all cases. As expected, the bond formed between the oxazole-carbon and the dienophile-heteroatom always is shorter than the newly forming carbon–carbon bond.



1 a



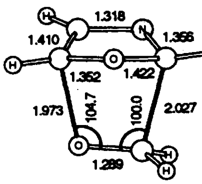
1 b

The geometry of transition structure **1** of ethylene addition to oxazole is quite similar to that between cyclopentadiene and ethylene.[15] Of course, in the case of ethylene addition to cyclopentadiene a synchronous transition structure was generated owing to the plane of symmetry for both reactants. Since there is no such symmetry in the case of oxazole, all transition structures for the diene addition to oxazole are expected to be asynchronous. The two newly forming C–C bonds in structure **1** are considerably shorter than in the case of ethylene addition to cyclopentadiene (0.033 Å and 0.112 Å).[15] According to the Hammond postulate, this suggests that the transition structure is closer to the structure of the product, and that the activation barrier is higher compared with the cyclopentadiene addition.[15,16]

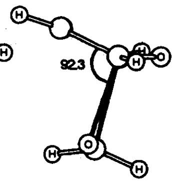
For the formaldehyde addition to oxazole two regioisomeric transition structures (**2** and **3**) were located. They are both asynchronous, with higher degree of asynchronicity (Δr = 0.149 Å) for structure **3**, where the newly forming C–O bond is between C-2 of oxazole and the oxygen of formaldehyde, than for structure **2** (Δr = 0.054 Å), where the newly forming C–O bond is between C-5 of oxazole and oxygen of formaldehyde. There is one more further interesting structural feature that should be mentioned. The newly forming C–O and C–C bonds are in one plane in transition structure **3**, while the C–O bond is pushed inside a little towards the transition structure. The behaviour of structure **2** is absolutely understandable since the shorter newly forming C–O bond brings the transition structure closer to the product, which must be reflected in the angle presented in **2b**. That is not quite so in **3** which indeed has a shorter C–O bond being formed, and according to this approach, one would expect a smaller angle. However, the angle in **3b** is 95.3°, compared with an angle of 92.3 ° in **2b**. This can be explained with the strong n–n lone-pair repulsion interactions between the oxygen of formaldehyde and the nitrogen of oxazole in transition structure **3**, thus pushing the newly forming C–O bond away.

If this explanation is correct, the effect of the n–n repulsion interactions should be even more pronounced in the transition states of formaldehyde imine addition to oxazole. Four isomeric transition structures were located. Because of asymmetry of both the dienophile, and the diene, all four transition structures are asynchronous. Similarly to the addition of formaldehyde, the newly forming bond with the heteroatom is shorter. Again, the bond undergoing formation with the oxazole C-2 carbon is much shorter and, in the case of the C–N bond, is even shorter if the hydrogen is in the *endo* position. This structure **6a** has the highest degree of asynchronicity of all four transition structures (Δr = 0.329 Å). On the other hand, the transition structure with C-2 oxazole C–C bond formation and an *exo* hydrogen, **5**, is almost synchronous (Δr = 0.035 Å). It is interesting to take a closer look at the angle between the forming C–N bond and the oxazole ring. The angle closely follows the degree of bond formation, thus for structures **4** and **6** with an *endo* N–H, the bond is smaller and so is the angle (94.4° *vs.* 97.0°), than in transition structures **5** and **7** with an *exo* N–H (97.0° *vs.* 103.0°). One would expect that the angle in structure **6** would be lower than in structure **4** because the newly forming C–N bond is at a more advanced stage, but it seems that there is very strong repulsion with the nitrogen lone pair. When the nitrogen lone pair is oriented toward the transition structure the angle is considerably higher.

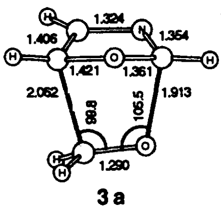
In the diazene addition to oxazole, again, four transition state structures were obtained, two for the (*Z*)-diazene addition and two for the (*E*)-diazene addition. In the case of (*Z*)-diazene addition, **8** and **9**, the higher asynchronicity is obtained when the hydrogens are in the *exo* position (Δr = 0.135 Å for *exo vs.* 0.079 Å for *endo*). The newly forming bond at C-5 is more sensitive to the position of hydrogen: 2.014 Å *vs.* 2.086 Å for the *endo* and *exo* isomers, respectively, while the difference in the bond forming at C-2 is smaller. This is understandable taking into account the fact that the repulsive interactions between the diazene nitrogen lone pair are smaller with the nitrogen lone pair from oxazole, than with the C–C π-system, on the one hand, and the attractive interactions between the hydrogen and the C–C π-system when in the *endo* position on the other. In transition structure **8** the atoms forming the new bonds are in one plane



2a



2b



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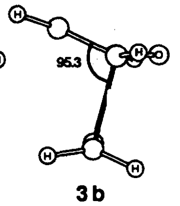

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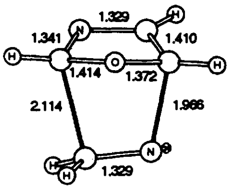

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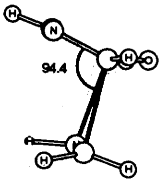

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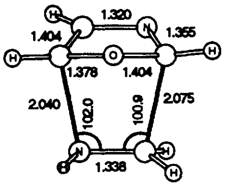

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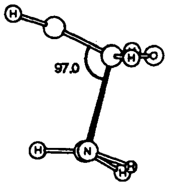

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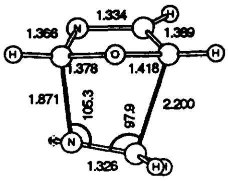

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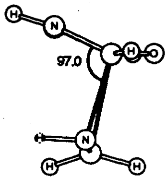

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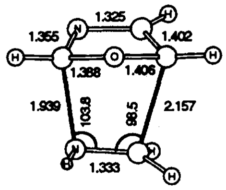

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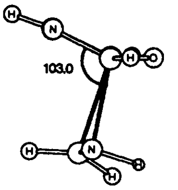

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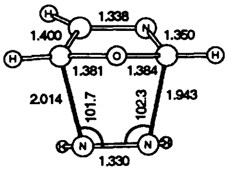

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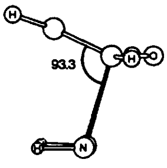

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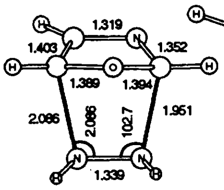

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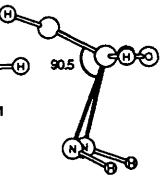

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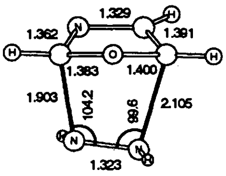

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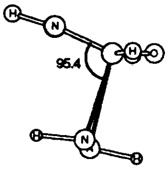

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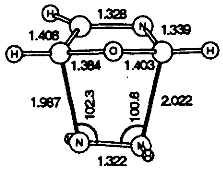

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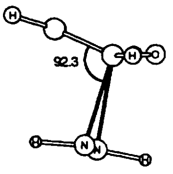


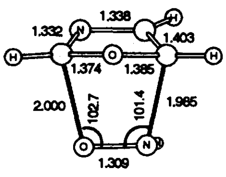
11b

but in **9**, as in the formaldehyde addition, the two newly forming bonds are not planar. This distortion is even more pronounced in transition structures **10** and **11**, owing to the stronger non-bonding interactions in these structures. Transition state **10** has the highest asynchronicity ($\Delta r = 0.202$) of all diazene additions. This is a result of the highly attractive interactions between the oxazole nitrogen lone pair and diazene hydrogen, and the repulsive interactions of the diazene nitrogen lone pair and the C–C π-system of oxazole, which gives rise to the longest C–N forming bonds of all the transition structures.

Transition state structures **12–15** were obtained for the addition of nitrosyl hydride to oxazole. The absence of one hydrogen on the dienophile is responsible for more synchronous structures (Δr = 0.004 to 0.095 Å) otherwise the pattern is similar to those in the previous cases. For example, although it is expected that the bond forming with oxygen would be shorter than that with nitrogen, in **12** and **14** it is not so, owing to the hydrogen interactions with either the oxazole π-system and/or the nitrogen lone pair. Structure **15**, which is practically synchronous, has the greatest deformation from planarity of the newly forming bonds and the greatest angle (98.5°), in order to accommodate the lone-pair interactions of the nitrosyl hydride oxygen and nitrogen, with the oxazole nitrogen lone pair and oxazole π-system.

Energetics of the Transition Structures.—Geometry considerations can give only qualitative estimates of the reactivity and regioselectivity. A quantitative picture can be obtained from the energy barriers for each of these transition states and reactions. The calculated total energies for the reactants and transition structures, and the activation energies are given in Tables 2 and 3, respectively.

As expected, the Hartree–Fock energies are always higher than those obtained at the second-order Møller–Plesset level where electron correlations are taken into account. Since correlation energies are very important for transition-state calculations, we will limit our discussion of the energy barriers to the MP2/6-31G*//RHF/3-21G theoretical model. In the case of formaldehyde addition, both FMO and RHF predict that **2** is a more favourable transition state, but MP2 finds that **3** has a



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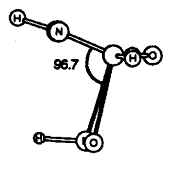

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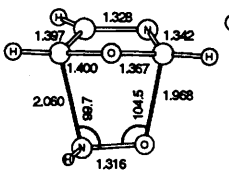

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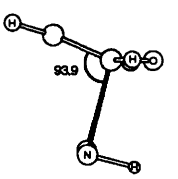

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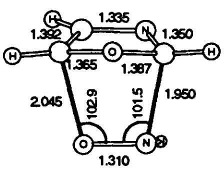

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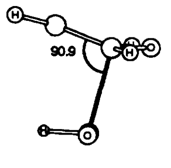

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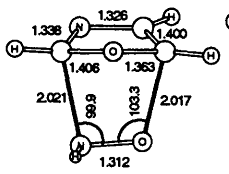

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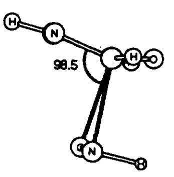

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Table 2 Total energies (au) of reactants and transition states for the Diels–Alder reaction of heterodienophiles to oxazole

Species	RHF/6-31G*// RHF/3-21G	MP2//6-31G*// RHF/3-21G
Oxazole	−244.628 653 672 8	−245.345 654 997 4
Ethylene	−78.031 694 347 1	−78.284 102 982 5
Formaldehyde	−113.865 285 682 6	−114.166 811 960 1
Formaldehyde imine	−94.027 857 544 8	−94.313 392 761 1
(*Z*)-Diazene	−109.982 146 521 3	−110.303 160 839 6
(*E*)-Diazene	−109.993 382 164 4	−110.313 168 249 9
Nitrosyl hydride	−129.782 751 090 5	−130.123 570 914 0
1	−322.593 489 591 1	−323.604 207 188 1
2	−358.419 843 160 1	−359.481 365 963 0
3	−358.426 680 024 3	−359.477 837 176 0
4	−338.584 359 404 8	−339.633 222 849 9
5	−338.579 116 334 2	−339.627 419 743 6
6	−338.590 846 127 9	−339.633 138 033 3
7	−338.584 284 571 0	−339.626 440 818 1
8	−354.543 785 899 0	−355.635 378 238 0
9	−354.530 962 473 4	−355.620 422 613 8
10	−354.551 167 430 1	−355.641 576 213 9
11	−354.549 667 031 0	−355.641 010 738 9
12	−374.353 224 268 8	−375.461 585 272 5
13	−374.346 523 508 1	−375.451 930 523 6
14	−374.350 796 011 3	−375.464 924 092 3
15	−374.344 225 835 2	−375.458 489 025 6

Table 3 Calculated activation energies (kcal mol^{-1}) for the Diels–Alder reaction of heterodienophiles to oxazole

TS	RHF/6-31G*//RHF/3-21G	MP2/6-31G*//RHF/3-21G
1	41.95	16.03
2	46.49	19.52
3	42.20	21.73
4	45.27	16.20
5	48.56	19.85
6	41.20	16.26
7	45.32	20.46
8	42.05	8.43
9	50.10	17.82
10	44.47	10.82
11	45.41	11.18
12	36.51	4.79
13	40.71	10.85
14	38.03	2.70
15	42.15	6.74

lower reaction barrier. This difference in the energy barriers of 2.21 kcal mol^{-1},* as already discussed, can be attributed to the lone-pair repulsion interactions between the formaldehyde oxygen and the oxazole nitrogen in **3** on one hand, and the formaldehyde hydrogen and oxazole nitrogen attraction interactions in **2**, on the other.

The energies of **4** and **6** are quite similar, and are favoured over the respective isomers **5** and **7** for the same reasons. In the lower level energy isomers, there are no formaldehyde imine nitrogen lone pair repulsive interactions, only hydrogen attractive interactions, unlike in **5** and **7** where the formaldehyde imine nitrogen lone pair adversely interacts with the oxazole nitrogen lone pair and/or diene π-system.

These interactions are especially pronounced in the (*Z*)-diazene addition, where the price for the *exo* hydrogen addition is 9.4 kcal mol^{-1} over the *endo* hydrogen addition. In the (*E*)-diazene cycloaddition the isomer where the diazene hydrogen can interact with the nitrogen lone pair of oxazole has a lower energy barrier.

There are four possible isomers for the nitrosyl hydride addition to oxazole. Of these four, three have lower energy barriers than any of the reactions considered here. The most favoured species is the adduct **14** in which the formation involves dienophile hydrogen and diene nitrogen lone pair interactions. As expected, the repulsion interaction between the dienophile oxygen and diene nitrogen are responsible for the high energy barrier in **13**.

The first reported hetero Kondrat'eva reaction in the literature is the cycloaddition of diethyl azodicarboxylate to oxazole.[17] Although azodicarboxylate is an activated dienophile, these calculations indicate that the diazene and nitrosyl hydride cycloadditions with oxazole should be feasible under moderate reaction conditions. In both cases, *endo* addition would be energetically preferred over *exo* addition, and in the latter the hydrogen would preferentially bind on the carbon next to the nitrogen of oxazole.

Conclusions

The limitations of frontier molecular orbital theory are apparent not only when predicting the reactivity of the series of dienophiles, but also in predicting their regioselectivity. Hartree–Fock theory gives reasonable geometries but is inadequate for calculating energy barriers because it does not take into account the electron correlations which are especially important in the process of bond formation involving heteroatoms with lone pairs.

A qualitative picture of the reactivity and regioselectivity is obtained from the geometries of the transition structures, but the energy barriers are the only reliable quantitative indicators. Lone-pair repulsion interactions, as well as dienophile hydro-

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* 1 cal = 4.184 J.

gen–diene heteroatom lone pair and/or diene π-system attractive interactions, account for the discrepancy in the FMO and *ab initio* predictions of the reactivities of all heterodienophiles and the regioselectivities of these reactions.

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