XIII_669

JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 8, 753–760 (1995)

AB INITIO STUDY OF THE LOW REACTIVITY OF THIOPHENE IN DIELS–ALDER REACTIONS WITH CARBON DIENOPHILES

BRANKO S. JURSIC*, ZORAN DZRAVKOVSKI AND SCOTT L. WHITTENBURG
Department of Chemistry, University of New Orleans, New Orleans, Louisiana, USA

The utility of thiophene as a diene for Diels–Alder reactions was studied by *ab initio* methods. The reactivity was evaluated with three dienophiles, vinyl alcohol, ethylene and acrylonitrile. Qualitatively the reactivity was determined by comparison of the reactant's frontier orbital energies, bond orders and charge transfer in the transition states. Quantitatively the reactivity was determined by estimation of activation energy with RHF/6-31G*, MP2/6-31G*, MP3/6-31G*//MP2/6-31G*, and MP4/6-31G//MP2/6-31G* ab initio calculations. The results of the calculations predicts that the reactivity of thiophene with acrylonitrile is similar to butadiene and ethylene with a preferred formation of the endo isomer.

INTRODUCTION

Preparation of thiophene derivatives is well documented in organic literature, therefore it can be an excellent starting material in organic syntheses.[1] One reaction that is prevalent in organic synthesis is Diels–Alder cycloaddition.[2] Theoretically, thiophene seems to be an ideal diene for this reaction, especially because methods for sulfur elimination from the Diels–Alder adduct exist.[3] Unfortunately the thiophenes do not easily undergo cycloaddition reactions.[4] Nevertheless, there is a body of experimental results that suggest a few approaches that can facilitate a Diels–Alder reaction with thiophene as the diene.[4,5] Strong electron-withdrawing substituents on the thiophene considerably increase the reactivity with electron-rich dienophiles. Likewise, electron-donating substituents on thiophene activate electron-deficient dienophiles. Alternatively, the reaction conditions can be changed. For example, the reaction be force-driven towards completion under high pressure because the activation volume for the Diels–Alder reaction is negative.[6] We have been involved in both theoretical and experimental study of the Diels–Alder reaction with thiophene derivatives as a dienophile for preparation of valuable organic materials.[7]

COMPUTATIONAL METHODOLOGY

Geometry optimizations were carried out using GAUSSIAN 92[8] at the restricted Hartree–Fock theory[9] level with 3-21G[10] and 6-31G*[11] basis sets and applying second-order Møller–Plesset (MP2) theory with 6-31G* basis set. For all structures vibrational analyses were performed with the same basis set used for optimization. Each transition structure gives only one imaginary harmonic vibrational frequency, corresponding to the motion forming the new C–C bonds for concerted transition structures. The activation energies were estimated from MP3 and MP4[12]/6-31G* calculations on the MP2/6-31G* optimized geometries.

RESULTS AND DISCUSSION

We have performed the theoretical investigation with a relatively high level of theory with the aim of determining the reactivity of thiophene as a diene with ethylene and acrylonitrile. The mechanism of the Diels–Alder reaction is very well documented experimentally[13] and theoretically.[14] Although there are many theoretical studies, mostly at the semi-empirical level,[15] that support a biradical mechanism for the reaction, recent high level of *ab initio* calculations have indicated that a concerted mechanism may be at work.[14] In this paper only concerted mechanisms for the Diels–Alder reactions will be considered.

---

* Author for correspondence.

CCC 0894–3230/95/110753–08

Received 28 January 1995
Revised 14 June 1995

Prior to determining the geometries of the transition structures for concerted addition of the dienophiles to thiophene the geometries of the reactants calculated with MP2/6–31G* were generated (Figure 1). As expected, every reactant has all atoms in one plane and both ethylene and thiophene have a common plane of symmetry. The validity of the geometrical parameters can be ensured on the basis of extraordinary agreement between the theophene structure generated with MP2/6-31G* and the structure derived from microwave data (Figure 1).[16]

The reactivity of the reactants for Diels–Alder reaction can be determined by using the frontier molecular orbital (FMO) approach developed by Fukui.[17] According to this approach, a higher reactivity for the diene–dienophile reactive pair will be obtained in the case where two opposite frontier orbitals have similar energy. Better molecular orbital overlap will be obtained, leading to a transition structure with lower activation barrier. According to this approach, the addition will be HOMO thiophene-controlled except when very electron-rich dienophiles, such as vinyl ethers and alcohols, are used. Electron-rich dienophiles have a high energy HOMO orbital (Figure 2). It is well known that the energy difference of $\mathrm{LUMO}_{\mathrm{ethylene}} - \mathrm{HOMO}_{\mathrm{butadiene}}$ (209·15 kcal/mol) is smaller than for $\mathrm{LUMO}_{\mathrm{butadiene}} - \mathrm{HOMO}_{\mathrm{ethylene}}$ (265·65 kcal/mol). This is called a normal electron demand, LUMO dienophile-controlled Diels–Alder reaction.[18] The $\mathrm{LUMO}_{\mathrm{dienophile}} - \mathrm{HOMO}_{\mathrm{diene}}$ energy difference for ethylene (Figure 2) addition to thiophene is 313·12 kcal/mol (0·499 au) which is only 1·26 kcal/mol lower than the $\mathrm{LUMO}_{\mathrm{diene}} - \mathrm{HOMO}_{\mathrm{dienophile}}$ energy differences. According to this calculation, both modes of FMO interactions should be relevant for ethylene/thiophene reactions. Furthermore, the $\mathrm{LUMO}_{\mathrm{dienophile}} - \mathrm{HOMO}_{\mathrm{diene}}$ energy difference for ethylene addition to thiophene is 103·97 kcal/mol higher than in the case of ethylene addition to butadiene. These results indicate a considerably lower ability of thiophene to act as a diene for the Diels–Alder reaction. Ethylene addition to butadiene is not favored, thus ethylene addition to thiophene under ordinary reaction conditions should not be experimentally feasible due to the FMO energy gap.

Nevertheless, the FMO gap with ethylene as dienophile indicates that the cycloaddition reaction between thiophene and an electron-craving dienophile could exhibit a considerably lower energy difference between $\mathrm{HOMO}_{\mathrm{diene}} - \mathrm{LUMO}_{\mathrm{dienophile}}$. In fact, the energy difference between reactants using acrylonitrile as dienophile is now only 259·16 kcal (0·413 au). This is still 50 kcal/mol higher than in the case of ethylene addition to butadiene. We propose that this reaction

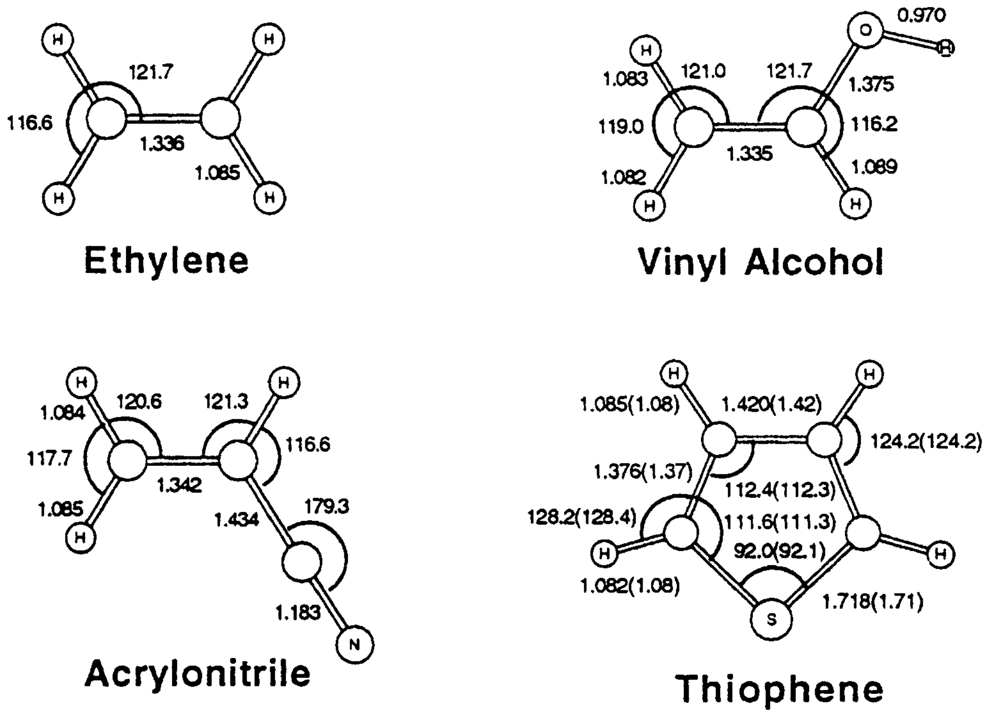


Figure 1. Geometries of the reactants generated with MP2/6-31G*. The experimental values for thiophene[16] are in parentheses

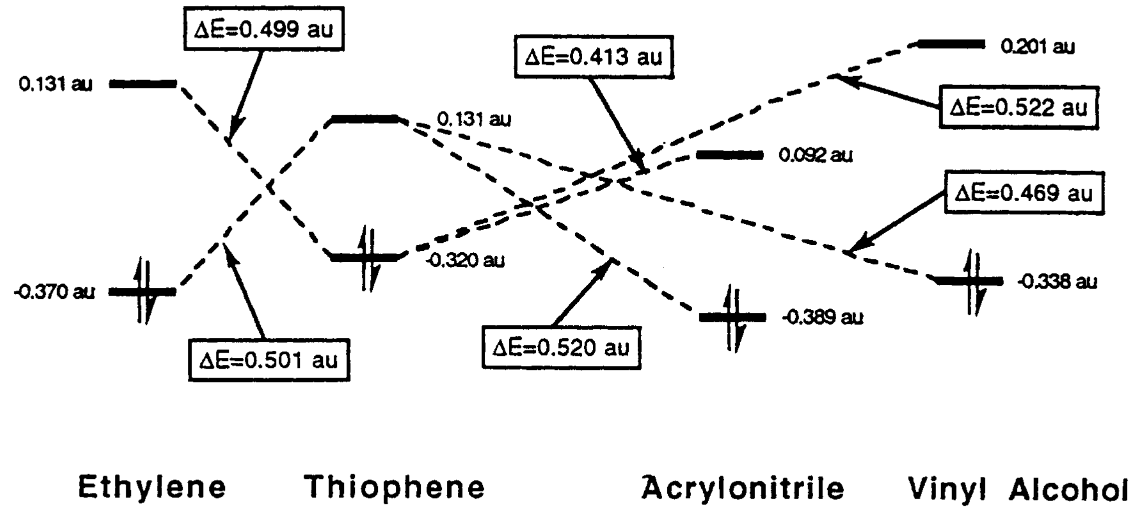


Figure 2. Frontier orbital energy correlation between thiophene and ethylene, acrylonitrile and vinyl alcohol calculated by MP2/6-31G*

might be possible under rather forceful reaction conditions.

Because the frontier orbital energy gap for ethylene addition to thiophene is nearly the same for $LUMO_{dienophile} - HOMO_{diene}$ and $LUMO_{diene} - HOMO_{dienophile}$ it is reasonable to expect that electron-donating as well as electron-withdrawing substituents might be suitable dienophiles. To test this assumption the frontier orbital energy gap between thiophene and vinyl alcohol was calculated. Indeed, the $LUMO_{diene} - HOMO_{dienophile}$ energy difference is now 294·30 kcal/mol and is only slightly lower than for plain ethylene addition. This suggests that electron-deficient dienophiles should be more practical for Diels–Alder reaction with thiophene.

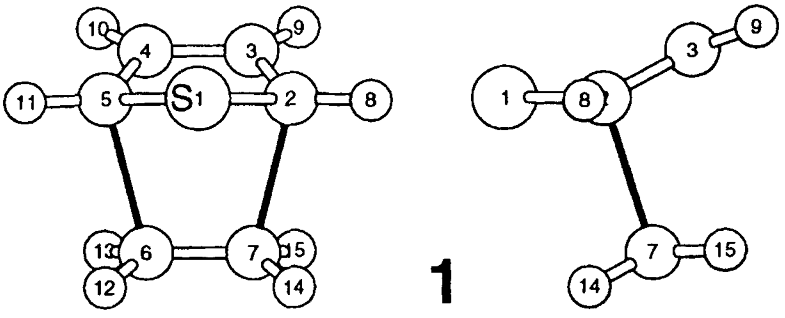
Although in many cases the FMO approach will give satisfactory results, in some cases it fails due to neglect of steric and electronic interactions of the reactants in the course of the reaction. A more reliable approach is comparisons of the charge separation in the transition structures, bond orders and, of course, the activation barriers of the reaction. Performing these studies requires knowledge of the geometries of the transition structures.

Geometries of the transition structures and bond orders

The transition structures generated with various *ab initio* methods are presented in Tables 1–3. As one would expect, the transition structures for ethylene addition to thiophene has a plane of symmetry bisecting the transition structure (Table 1). Thus, the transition structure describes concerted synchronous formation of two new C–C bonds. The agreement in geometric parameters between different theoretical models is very good. For example, for new forming bonds the maximal distance was predicted by RHF/3-21G* (2·177 Å) and the minimal distance was predicted by MP2/6-31G* (2·163 Å), a disagreement of only 0·6%. Other geometrical values (Table 1) are predicted with similar precision, as MP2/6-31G* predicts the most compact transition structure by comparing bond orders for new forming bonds.RHF/3-21G*, RHF/6-31G* to MP2/6-31G* predict bond orders of 0·282, 0·310 and 0·332 respectively. All other bond orders follow the same pattern. Thus, bond orders for r34 increase, and for r23, r45 and r67 decrease. We do not have a satisfactory explanation for this phenomenon.

There are two possible products to be formed from acrylonitrile addition to thiophene. Two isometric *endo* **2** and *exo* **3** transition structures are generated. As expected on the basis of symmetry of the reactants, the transition structures cannot result from a synchronous concerted cycloaddition, as in the case of ethylene addition. It is interesting to examine which of the two isomeric transition structures are more asynchronous. The geometric parameters of the *endo* transition structure **2** for acrylonitrile addition to thiophene (Table 2), as predicted by the different theoretical models, are not in as good an agreement as for transition structure **1**. For example, the disparity in the prediction of the bond length of new forming bonds r56 and r27 are in the range of 4·6% and 2·1%, respectively. Disagreement for the prediction of other geometrical parameters are also higher than for transition structure **1**. The asynchronicity of the transition structure can be judged by a couple of geometric characteristics. One of the simplest means compares the bond distances of two new form-

Table 1. Geometric parameters for ethylene addition to thiophene

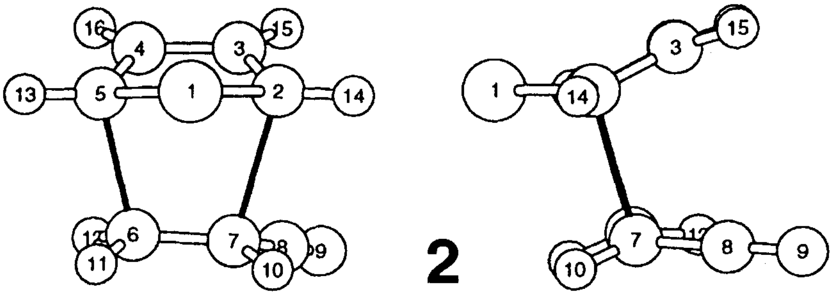


1

	r12	r23	r34	r45	r56	r67	a567	d2345	d3456	d4567
I	1·749	1·408	1·370	1·408	2·177	1·385	103·5	0·000	−73·0	66·2
IA	1·104	1·380	1·469	1·380	0·282	1·631				
II	1·750	1·410	1·367	1·410	2·175	1·392	103·3	0·000	−72·6	65·9
IA	1·098	1·358	1·489	1·358	0·310	1·598				
III	1·748	1·420	1·380	1·420	2·163	1·400	103·5	0·000	−72·9	66·5
IIIA	1·098	1·338	1·505	1·337	0·332	1·570				

I = RHF/3-21G*; = RHF/6-31G*; III = MP2/6-31G*; A denotes bond orders calculated on *ab initio* structures with AM1.

Table 2. Geometric parameters for *endo* acrylonitrile addition to thiophene



2

	r12 a567	r23 a789	r34 d2345	r45 d3456	r56 d4567	r67 d5678	r27 d6789	r78	r89
I	1·809	1·390	1·376	1·398	2·103	1·389	2·267	1·423	1·143
	105·9	179·7	−1·0	−73·5	64·2	−107·2	45·6		
IA	1·092	1·441	1·420	1·406	0·313	1·570	0·234	1·010	2·878
II	1·737	1·407	1·366	1·417	2·050	1·403	2·295	1·437	1·139
	105·9	179·3	−2·0	−75·2	66·0	−109·3	102·5		
IIA	1·132	1·355	1·510	1·309	0·386	1·501	0·278	1·006	2·879
II	1·737	1·416	1·381	1·428	2·006	1·411	2·315	1·429	1·185
	106·6	179·2	−3·7	−75·3	64·6	−104·7	51·5		
IIIA	1·134	1·343	1·521	1·293	0·425	1·463	0·286	1·018	2·857

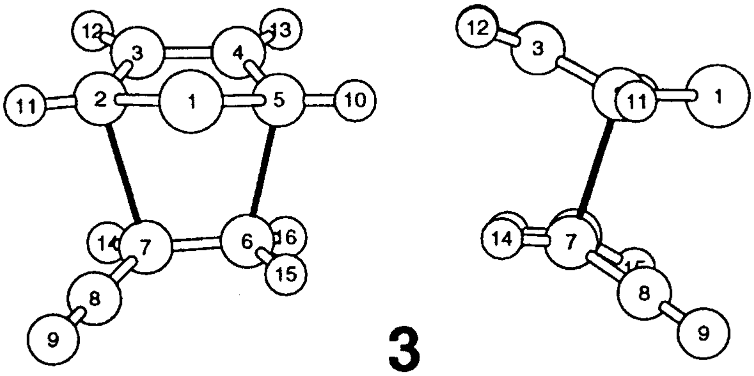
I = RHF/3-21G*; II = RHF/6-31G*; III = MP2/6-31G*; A denotes bond orders calculated on *ab initio* structures with AM1.

ing bonds. Thus, the transition structure **1** represents the synchronous concerted mechanism of ethylene addition to thiophene (Table 1). Although this approach might be useful to eliminate synchronicity of transition structure **2**, the comparison of asynchronicity between different transition structures in this way can be misleading and a better approach is by comparison of bond orders. Accordingly, the bond order differences for two new forming bonds r56 and r27 calculated on RHF/3-21G*, RHF/6-31G* and MP2/6-31G* geometries are 0·079, 0·108 and 0·139, respectively, for **2**.

The transition structure **3** for *exo* acrylonitrile addition to thiophene is as expected for asynchronous concerted cycloaddition reaction (Table 3). The geometry parameters predicted by different theoretical models are in similar agreement to the *endo* isomeric transition structure **2**. For example, the disagreement is maximal for bonds of formation r56 and r72 of 5·5% and 2·2%, respectively. The asynchronicity, again judged by the bond order differences for r56 and r27 calculated on RHF/3-21G*, RHF/6-31G* and MP2/6-31G* geometries are 0·075, 0·109 and 0·145, respectively. If we compare the bond orders for the *endo* transition structure **2** and *exo* transition structure **3**, the RHF/3-21G* predicted structure **2** is slightly more asynchronous (for 0·004) than expected if only sterical interactions between the CN group and the thiophene ring exist in **2**. It is well known that the electronic interactions between substituents prefer the *endo* dienophile addition (Alder's rule). By implementing a large basis set like 6-31G*, both RHF and MP2 calculations predict transition structure **3** to be less asynchronous than **2**. These results are 0·001 and 0·006, respectively, according to the bond orders. Attractive interaction between the dienophile and the diene can explain this difference in asynchronicity.

Combining bond orders and the Hammond postulate, one can select one of two isomeric cycloaddition reactions with lower activation energy. According to the Hammond postulate, the transition that is closer in geometry to the reactants will have lower activation energy.[19] The position of the transition structure on the reaction coordinate can be determined by comparing bond orders.[20] The sum of new forming bond orders calculated on MP2/6-31G* transition structures **2** and **3** are 0·711 and 0·733, respectively, indicating an early transition structure for **2** and lower activation energy.

Table 3. Geometric parameters for *exo* acrylonitrile addition to thiophene



3

	r12 a567	r23 a789	r34 d2345	r45 d3456	r56 d4567	r67 d5678	r27 d6789	r78	r89
I	1·806	1·391	1·375	1·400	2·108	1·390	2·270	1·424	1·142
	105·9	180·0	1·00	73·7	−64·0	−105·3	0·00		
IA	1·101	1·434	1·427	1·340	0·309	1·573	0·234	1·009	2·879
I	1·734	1·409	1·364	1·420	2·051	1·404	2·300	1·437	1·139
	106·0	197·1	2·00	75·5	−64·5	−107·2	155·0		
IIA	1·142	1·347	1·519	1·299	0·385	1·502	0·276	1·006	2·879
III	1·734	1·416	1·379	1·432	1·992	1·412	2·322	1·428	1·185
	99·5	180·0	4·00	75·6	−65·0	−103·8	124·2		
IIIA	1·143	1·331	1·537	1·263	0·439	1·449	0·294	1·020	2·857

I = RHF/3-21G*; II = RHF/6-31G*; III = MP2/6-31G*; A denotes bond orders calculated on *ab initio* structures with AM1.

Table 4. Charge transfer between thiophene and the dienophiles in the transition structures (RHF charge transfer at the MP2 geometries)

TS	RHF/3-21G*	RHF/6-31G*	MP2/6-31G*
1	0·0016	−0·0056	−0·0042
2	−0·0813	−0·1372	−0·1482
3	−0·0839	−0·1375	−0·1493

Table 6. Activation energies (kcal/mol) for the Diels–Alder reaction of the dienophile addition to thiophene

TS	ΔEa_{I}	ΔEa_{II}	ΔEa_{III}	ΔEa_{IV}
A[21]	50·8	23·3	32·8	27·4
1	52·9	26·0	36·2	30·1
2	49·5	20·4	32·3	24·6
3	50·6	21·3	33·2	25·4

A-ethylene addition to 1,3-butadiene; ΔEa_{I}-RHF/6-31G*; ΔEa_{II}-MP2/6-31G*; ΔEa_{III}-MP3/6-31G*//MP2/6-31G*; ΔEa_{IV}-MP4/6-31G*//MP2/6-31G*.

Determination of reactivity on the basis of charge transfer in transition structure

There is one more method that can be used to determine the position of the transition structure in regard to reactants–charge transfer from the diene to dienophile in the transition structure. Although it is well known that the Mulliken charges are coefficient-derived quantities, and consequently only represent the crudest of approximations of the electron density, we believe that relative charge transfer differences between similar transition structures should be possible. Comparison of Mulliken charges on the dienophile in two isomeric transition structures **2** and **3** (Table 4) suggest an early transition structure for **2** preferring the *endo* acrylonitrile addition. This is in full agreement with the previously discussed bond orders. In this respect it is not possible to compare the reactivity of ethylene as a dienophile with acrylonitriles.

Activation energies of the Diels–Alder reaction

The total energy of the species involved in a cycloaddition reactant between ethylene and acrylonitrile as dienophile with thiophene is presented in Table 5. Between Ea_{I} and Ea_{II} there is both a change in geometry and change in method. The energy increments between E_{II}, Ea_{III}, Ea_{IV} are interesting. For **1**, the fourth-order increment is larger than the third-order increment. This indicates the MP series may be diverging and is strong evidence that the biracial transition state might be very close to concerted transition structure in energy. For **2** and **3**, the fourth-order increment is only a little less than the third-order increment, indicating a slowly convergent series. This lack of convergence carries over to Table 6.

As predicted on the basis of frontier orbitals, the addition of acrylonitrile is strongly preferred to the addition of ethylene. The bond orders and charge transfer in transition structures **2** and **3** in combination with the Hammond postulate correctly predict that *endo* addition of acrylonitrile will have a lower activation energy. That is consistent with all of the applied theoretical models. As demonstrated earlier by others[14] and ourselves,[21] the predicted activation barrier varies with theoretical models. Thus, RHF/6-31* and MP3/6-31G*//mp2/6-31G* overestimate, while MP2/6-31G* underestimate, the activation energy. The closest calculated activation energy for ethylene addition to butadiene is obtained by MP4/6-31G*//MP2/60-31G*. The predicted value is only 1 kcal/mol different than the experimental value. Although MP4/6-31G*//MP2/6-31G* theoretical model predicts reliable results for ethylene addition to butadiene, this method might not be so accurate for thiophene as diene. Nevertheless, we believe that this theory level should give order of reactivity between the dienes and dienophiles. Comparing the activation energies calculated at the MP4/6-31G*//MP2/6-31G* levels reveals that addition of acrylonitrile to thiophene should have an activation energy similar to ethylene addition to butadiene. It also predicts that ethylene addition to thiophene should not be possible experimentally.

Table 5. Total energies (au) of the reactants and transition structure

Species	Ea_{I}	Ea_{II}	Ea_{III}	Ea_{IV}
ethylene	−78·03172	−78·28503	−78·30597	−78·31983
thiophene	−551·29035	−551·92498	−551·95018	−551·98954
nitrile	−169·76801	−170·29817	−170·30842	−170·34766
1	−629·23783	−630·16860	−630·19839	−630·26144
2	−720·97948	−722·19070	−722·20713	−722·29799
3	−720·97774	−722·18923	−722·20562	−722·29675

Ea_{I}-RHF/6-31G*; Ea_{II}-MP2/6-31G*; Ea_{III}-MP3/6-31G*//MP2/6-31G*; Ea_{IV}-MP4/6-31G*//MP2/6-31G*.

CONCLUSION

Our results suggest that thiophene is a very unreactive diene for Diels–Alder reactions. The reaction is only possible with very reactive electron-deficient dienophiles, like acrylonitrile, with the formation of a predominantly *endo* cycloadduct. Despite many disadvantages that the frontier orbital method has in predicting reactivity, the higher reactivity of acrylonitrile in comparison with ethylene was correctly predicted. Although it is not possible to predict stereoselectivity using FMO, by combination of the bond order-Hammond postulate and the charge transfer-Hammond postulate for isomeric transition structures of acrylonitrile to thiophene the stereoselectivity was predicted. Qualitative predictions were confirmed by estimating the activation barriers. The lower activation barrier predicted with MP4/6-31G*//MP2/6-31G* selects thiophene as a suitable diene for reaction only with electron-deficient dienophiles. It is also predicted that the *endo* cycloadduct should be a major product. The MP4/6-31G*//MP2/6-31G* *ab initio* calculations are in a qualitative agreement with experimental results.[2]

ACKNOWLEDGMENT

This work was supported by the National Science Foundation as computer time at the Pittsburgh Supercomputer Center (CHE 94-0015P) and by Mr and Mrs Timmons.

REFERENCES

1. A. I. Meyes, *Heterocycles in Organic Synthesis*, edited by E. C. Taylor and A. Weissberger, John Wiley & Sons, New York (1974); B. H. Lipshutz, *Chem. Rev.* **86**, 796 (1986); T. Masayoshi and Y. Gosei, *Kagaku Kyokaishi* **51**, 399 (1993); P. A. Jacobi, K. M. Touchette and H. G. Selnick, *J. Org. Chem.* **57**, 6305 (1992); A. R. Katritzky and C. W. Rees (Eds), *Comprehensive Heterocyclic Chemistry*, Vol. 1–8, Pergamon Press, New York (1984); W. Carruther, *Cycloaddition Reactions in Organic Synthesis*, Pergamon, New York (1990).
2. D. L. Boger and S. N. Weinreb, *Hetero Diels–Alder Methodology in Organic Synthesis*, Academic Press, New York (1987); R. R. Schmidt, *Acc. Chem. Res.* **19**, 250 (1986); S. N. Weinreb and R. R. Staib, *Tetrahedron* **38**, 3087 (1982); T. Kametani and S. Hibino, *Advances in Heterocyclic Chemistry*, Vol. 42, Chapter 2, Academic Press, New York (1987); J. Hamer (Ed.), *1,4-Cycloaddition Reactions*, Academic Press, New York (1967); M. E. Jung, K. Shishido, L. Light and L. Devis, *Tetrahedron Lett.* **4607** (1981); F. Jensen and C. Foote, *J. Am. Chem. Soc.* **109**, 6376 (1987); B. Nader, T. R. Bailey, R. W. Franck and S. M. Weinreb, *J. Am. Chem. Soc.* **103**, 7573 (1981); L. Le Coz, C. Veyrant-Martin, L. Wartski, J. Seyden-Penne, C. Bois and M. Philoche-Levisalles, *J. Org. Chem.* **55**, 4870 (1990); S. J. Danishefsky, E. Larson, D. Askin and N. Kato, *J. Am. Chem. Soc.* **107**, 1246 (1985); S. J. Danishefsky, H. G. Selznik, R. E. Zelle and M. P. Deninno, *J. Am. Chem. Soc.* **110**, 4368 (1988); S. J. Danishefsky, D. C. Myles and D. F. Harrey, *J. Am. Chem. Soc.* **109**, 862 (1987); M. Bednarsky and S. J. Danishefsky, *J. Am. Chem. Soc.* **108**, 7060 (1986); K. F. McCule, J. W. Benbow and S. J. Danishefsky, *J. Am. Chem. Soc.* **113**, 8185 (1991).
3. For the methods of desulfurization see: Ya. Gol'dfarb, B. P. Fabrichnyi and I. F. Shalavina, *Tetrahedron* **18**, 21 (1962).
4. For a historical account of early consideration of aromaticity, see J. P. Snyder, *Nonbenzenoid Aromatics*, Vol. 1, Chapter 1, Academic Press, New York (1969); It has been proposed that the word *aromatic* be discontinued, see D. Lloyd and D. R. Marshall, *Angew. Chem. Int. Ed. Engl.* **11**, 404 (1972); For a review of the criteria used to define aromatic character, see: A. J. Jones, *Rev. Pure Apl. Chem.* **18**, 253 (1968); L. J. Schaad and B. A. Hess Jr, *J. Am. Chem. Soc.* **94**, 3068 (1972); L. J. Schaad and B. A. Hess Jr, *J. Chem. Educ.* **51**, 640 (1974).
5. J. Rajappa, *Thiophenes and their Benzo Derivatives: (ii) Reactivity*, in *Comprehensive Heterocyclic Chemistry*, edited by A. R. Katritzky and C. W. Rees, Pergamon Press, New York (1984).
6. H. Kotsuki, S. Kitagawa, H. Nishizawa and T. Tokoroyama, *J. Org. Chem.* **43**, 1471 (1978).
7. B. S. Jursic and D. T. Coupe, *Tetrahedron* (submitted).
8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, *Gaussian 92*/DFT, Revision G.2, Gaussian, Inc., Pittsburgh PA (1993).
9. M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman and C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951).
10. R. Gomperts, J. L. Andres, K. Raghavachari and J. S. Binkley, **102**, 939 (1980); M. S. Gordon, J. S. Binkley, J. A. Pople, R. L. Gonzalez, D. J. Martin, D. J. Fox, J. Defrees, J. Baker, W. J. Hehre, *J. Am. Chem. Soc.* **104**, 2797 (1982).
11. M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem.Phys.* **77**, 3654 (1982).
12. P. Carsky, B. A. Hess, Jr and L. J. Schaad, *J. Comput. Chem.* **5**, 280 (1984).
13. For some reviews, see A. Wasserman, *Diels–Alder Reactions*, Elsevier, New York (1965); W. R. Roush, *Adv. Cycloaddit.* **2**, 91 (1990); G. Brieger and J. N. Bennett, *Chem. Rev.* **80**, 63 (1980).
14. K. N. Houk, Y.-T. Lin and J. D. Evanseck, *Angew. Chem. Int. Ed. Eng.* **31**, 682 (1992); W. L. Jorgensen, D. Lim and J. F. Blake, *J. Am. Chem. Soc.* **115**, 2936 (1993); Y. Li and K. N. Houk, *J. Am. Chem. Soc.* **115**, 7478 (1993), and references therein.
15. M. J. S. Dewar, S. Olivella and H. S. Rzepa, *J. Am. Chem. Soc.* **100**, 5650 (1978); M. J. S. Dewar and A. J. Pierini, *J. Am. Chem. Soc.* **106**, 203 (1984); M. S. J. Dewar, *J. Am. Chem. Soc.* **106**, 209 (1984); M. J. S. Dewar, S. Olivella and J. J. P. Stewart, *J. Am. Chem. Soc.* **108**, 5771 (1986); M. J. S. Dewar, Semiempirical Life Profile, in Seeman (Ed.), *Profile, Pathways and Dreams* (1992),

pp. 150–152; M. J. S. Dewar and C. Jie, *Acc. Chem. Res.* **25**, 537 (1992).

16. B. Back, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Andersen, *J. Mol. Spectrosc.* **7**, 58 (1961).
17. K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.* **40**, 2018 (1967); K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.* **42**, 2018 (1969); K. Fukui, *Angew. Chem. Int. Ed. Engl.* **21**, 801 (1982).
18. K. N. Houk, in *Pericyclic Reactions*, Vol. II, p. 203, edited by A. P. Marchand and R. E. Lehr, Academic Press, New York (1977); K. N. Houk, *Top. Curr. Chem.* **79**, 33 (1979).
19. G. S. Hammond, *J. Am. Chem. Soc.* **77**, 344 (1955); For analytical functions that describe the reaction coordinates and reproduce the Hammond behavior, see W. J. Le Noble, A. R. Miller and S. D. Hamann, *J. Org. Chem.* **42**, 338 (1977); A. R. Miller, *J. Am. Chem. Soc.* **100**, 1984 (1978).
20. For an excellent article concerning bond orders as a method for characterization of the reactivity, see G. Lendvay, *J. Phys. Chem.* **98**, 6098 (1994) and references therein.
21. B. S. Jursic and Z. Zdravkovski, *J. Comp. Chem.* (in press).