AM1 Semiempirical study of reactivity of benzo[*b*]- and benzo[*c*]-thiophene as dienes in Diels–Alder reactions

Branko S. Jursic
Department of Chemistry, University of New Orleans, New Orleans, Lousiana 70148, USA

We have undertaken an AM1 semiempirical study to examine the capability of benzothiophene to function as a diene in Diels–Alder reactions. Two approaches are considered: the evaluation of the aromaticity of dienes and corresponding transition-state structures, and the estimation of activation barriers. The aromaticity was determined from the heats of hydrogenation. The study was performed for the addition of ethene, tetracyanoethene and maleic anhydride to benzothiophenes. The theoretical data were in full agreement with the experimental data demonstrating the capability of these methods correctly to predict the reactivity of benzothiophenes, and the feasibility of their cycloaddition reactions.

Introduction

Although thermal [4 + 2] cycloaddition reactions with derivatives of thiophene are allowed processes there are not many examples of Diels–Alder reactions in which thiophene is the diene.[1] To increase the reactivity of thiophenes in cycloaddition reactions, three approaches have been suggested: [1] use of highly reactive dienophiles, increasing the reactivity of thiophene either with electron-withdrawing or with electron-donating substituents, and carrying out the reaction under high pressure. These approaches have resulted in the preparation of thiophene-derived Diels–Alder adducts.[2]

Much of the reactivity of fused planar heterocycles is not well understood. Thus, while thiophene undergoes electrophilic substitution predominantly in the 2-position, benzo[*b*]thiophene reacts in the 3-position. It is well known that the annulation of aromatic rings onto the *b*-side and *c*-side of thiophene leads to systems with very different physical and chemical properties. Thus, while benzo[*b*]thiophene is a very stable aromatic system,[3] benzo[*c*]thiophene is very unstable and easily undergoes cycloaddition reactions.[4,5] The difference in reactivity is explained by the driving force induced by the aromatic character of the two intermediates.[6] In our semiempirical study we have calculated the aromaticity and activation energy of the Diels–Alder reaction.

Methodology

All calculations were performed on a DEC 7620 computer. Chem-3D Plus on a Macintosh IIfx was used as a graphical interface for drawing and visualizing all structures and for preparing input files for MOPAC.[7] The transition states are located, optimized and verified as described previously.[8,9] Vibrational and thermal analyses were performed on all optimized structures.

Results and discussion

We have previously performed an AM1 theoretical study of Diels–Alder reactions between cyanoethenes and cyclopentadiene,[10] and found that this method fails to predict correctly activation energies and the order of reactivity of the cyanoethenes. Nevertheless, AM1 has been found to be an effective method when studying the addition of dienophiles to heterocycles.[11] The AM1 method has proved useful for our previous work on the reactivity of thiophene, S-methylthiophenium ion,[12] and thiophene oxides[13] as dienes in Diels–Alder reactions. The AM1 semiempirical method correctly predicted the general trend of the reactivity and theoretical results in close agreement with the experimental data.

Although heterocyclic compounds are useful materials in organic synthesis,[14] except for a few of our papers[11-13,15] and one of Houk and co-workers[16] there are not many theoretical studies of heterocyclic compounds acting as dienes in Diels–Alder reactions. Similar studies with all-carbon dienes and dienophiles have been performed extensively.[17]

Diels–Alder reactions are generally assumed to be concerted cycloadditions. Although a stepwise radical mechanism has been proposed for Diels–Alder reactions,[18] it has been rejected following some high-level *ab initio* calculations.[19] Here the study was performed solely on the assumption that Diels–Alder reactions proceed through a concerted mechanism.

It is broadly accepted that aromaticity[20,21] can be defined as the ability to sustain an induced ring current (diatropic components).[22] This definition has its flaws.[23] The method that we used for estimating aromatic stabilization is based on AM1 MOPAC heats of formation. The most successful method performs calculations on the aromatic compound and on a linear, conjugated polyene containing the same number of double bonds.[24] The disadvantage of this method is that it assigns a resonance stability of zero to a conjugated polyene. The isodesmic reaction approach has also been calculated by applying the resonance stability of benzene. The resonance stability approach can use either experimental thermochemical data or energies obtained by MO calculations.[25] We compared the heats of hydrogenation of benzo[*b*]thiophene, benzo[*c*]thiophene and their respective transition-state structure to determine the difference in resonance stability. AM1 calculations predicted both reactions to be exothermic (Table 1). Benzo[*b*]thiophene is predicted to be 9–10 kcal mol^{-1} more stable than benzo[*c*]thiophene. If the transition-state structures of the two reactions have the same energy, that indicates a higher reactivity for benzo[*c*]thiophene, although this is not always necessary. We have optimized transition-state structures for the addition of ethene to both benzothiophenes (Fig. 1). As one can see, the transition-state structure with benzo[*c*]thiophene **2** is for a synchronous concerted mechanism of cycloaddition, because both reactants share a plane of symmetry which is maintained in the transition-state structure. Furthermore, dihedral angles defined by the carbon atoms of the benzene ring, the two carbons shared with thiophene, and the dihedral ring, defined by the carbons directly involved in new CC bond formation, are zero. For transition-state structure **1** the reactants' planes of symmetry are not parallel, therefore the

Table 1 Heats of hydrogenation of benzothiophenes and differences in their resonance stability (kcal mol^{-1})

Compound	ΔE	ΔE + ZPVE[a]	$\Delta\Delta E$	$\Delta\Delta E$ + ZPVE[a]
Benzo[*b*]thiophene	−52.87	−19.12	−8.77	−9.79
Benzo[*c*]thiophene	−61.64	−28.91		

[a] ZPVE, zero point vibrational energy.

Table 2 AM1 Estimated heats of hydrogenation (kcal mol^{-1}) of transition structures **1** and **2** and the differences in their resonance stability

Compound	ΔE	$\Delta\Delta E$ + ZPVE[a]	$\Delta\Delta E$	$\Delta\Delta E$ + ZPVE[a]
1	−113.3	−83.28		
2	−97.54	−67.35	−15.76	−15.88

[a] ZPVE, zero point vibrational energy.

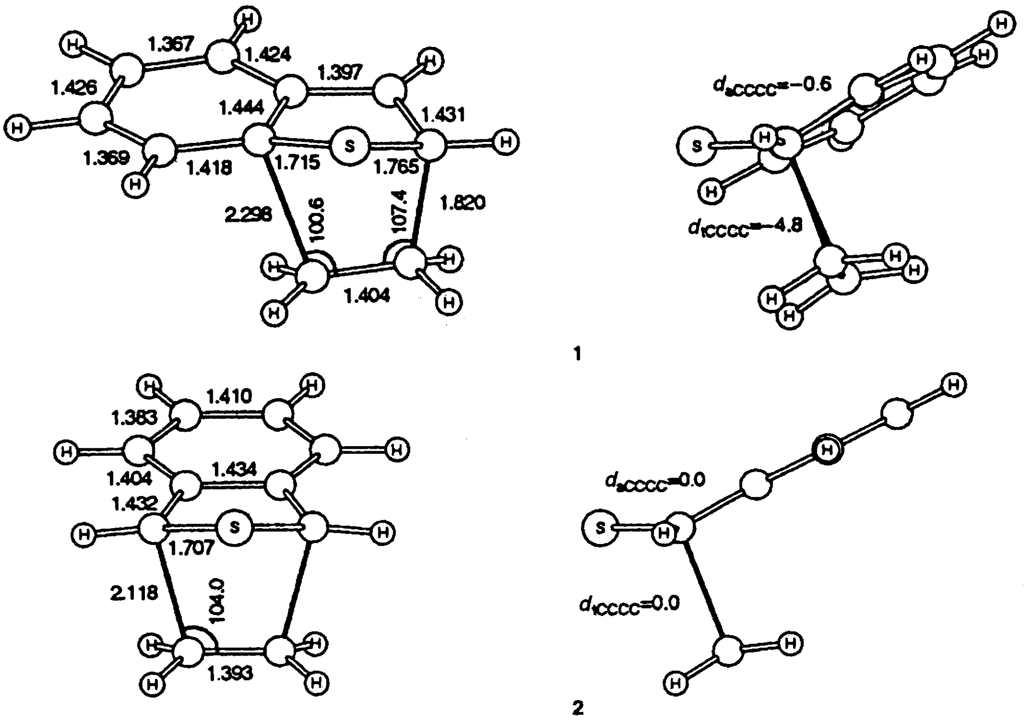
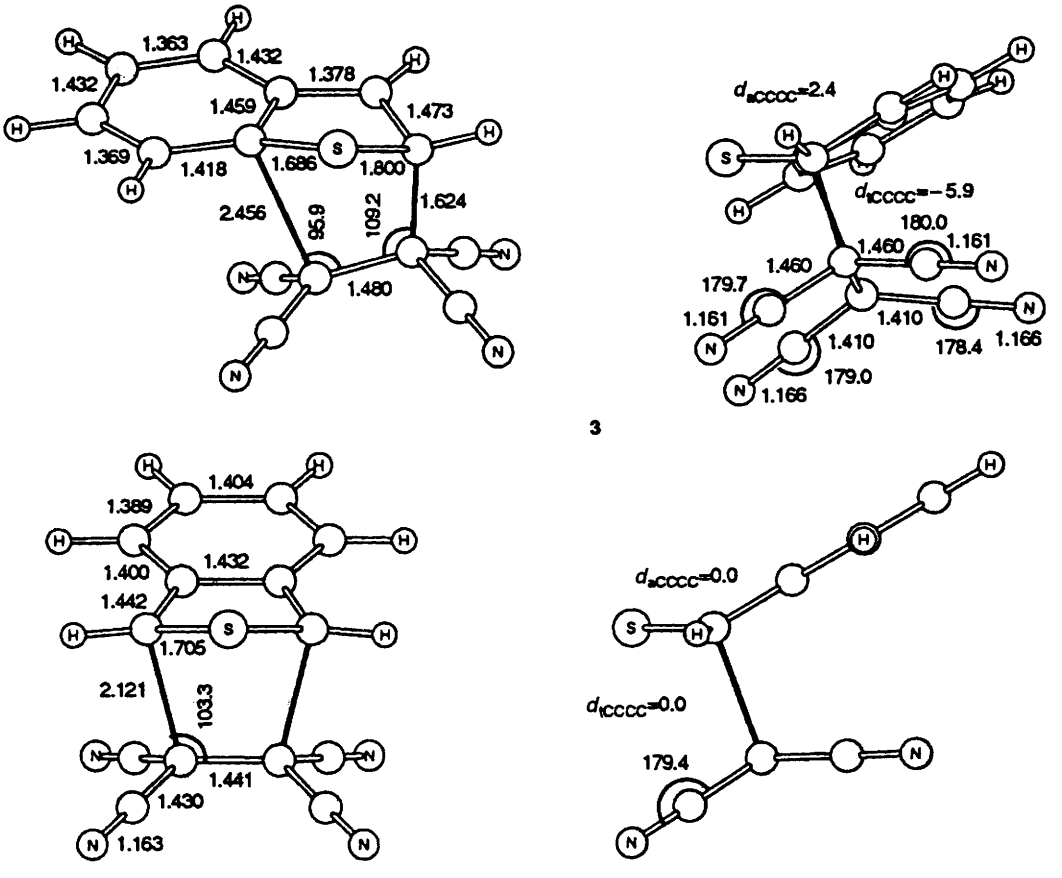


Fig. 1 Transition-state structures for addition of ethene to benzo[*b*]thiophene (**1**) and benzo[*c*]thiophene (**2**)

transition state is for an asynchronous cycloaddition reaction. The CC bond in formation should be considerably longer, not only because of steric interaction between the methylene moiety of ethene and benzene ring, but also because the aromaticity of the benzo[*b*]thiophene has been destroyed. The bond length is 2.298 Å in comparison with about 2.0–2.1 Å for a typical CC bond in the formation of an all-carbon Diels–Alder transition-state structure. To demonstrate the lost aromaticity we determined the hypothetical heat of hydrogenation of the transition-state structures.[17]

The heat of hydrogenation for a transition-state structure is strictly a theoretical value, because it cannot be experimentally determined. In the course of the cycloaddition reaction three double bonds are retained, while two are transformed into two new CC single bonds. Three molecules of hydrogen were added to transition states **1** and **2**, subsequently; these structures were optimized by keeping the forming CC bonds the lengths given in structures in **1** and **2**, respectively. The calculated heats of hydrogenation are the differences between the heats of formation for these structures and the transition states plus three molecules of hydrogen (Table 2). As expected in the transition-state structure for benzo[*c*]thiophene, the aromatic ring stays intact giving transition-state structure **2** more resonance stability than transition state **1** containing benzo[*b*]thiophene. The AM1 estimated difference in resonance stability is around 15–16 kcal mol^{-1}. Another way to determine the difference in reactivity of the two benzothiophenes is by comparison of their heat of formation (Table 3). The difference in heat of formation is 7.06 kcal mol^{-1} clearly indicating benzo[*c*]thiophene to be more reactive. One can also use the heat of formation of two isomeric transition-state structures. Structure **2** is predicted to be for 8.46 kcal mol^{-1} lower in energy than **1** indicating the higher aromatic character of **2** and higher reactivity of benzo[*c*]thiophene as a diene in Diels–Alder reactions.

To determine the feasibility of the reaction we have estimated the activation barriers for the reactions (Table 3). Although AM1 calculation favours benzo[*c*]thiophene by 8.37 kcal mol^{-1}, the activation energy is too high to be achievable under normal reaction conditions. As for all intermolecular Diels–Alder reactions, the activation volume of the reaction is negative, thus by applying high pressure the reaction may be forced towards



3

4

Fig. 2 Transition-state structures for the addition of tetracyanoethene to benzothiophenes

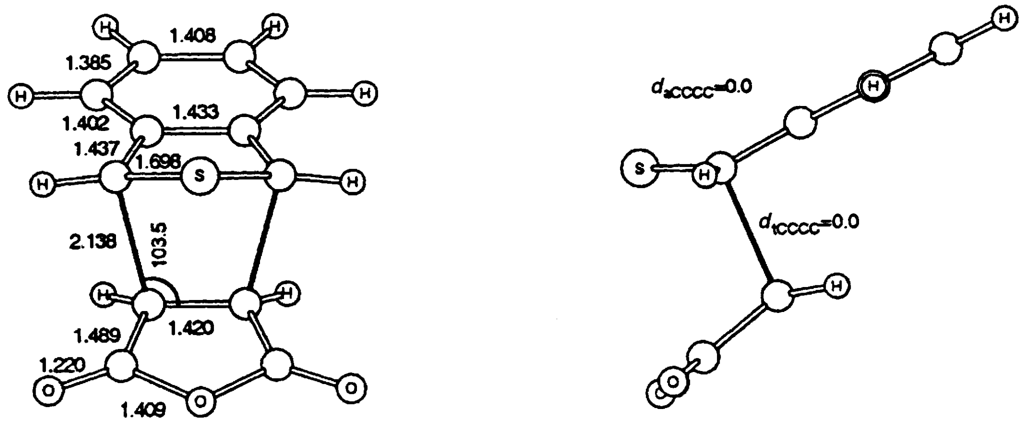
Table 3 Heats of formation and activation energies (kcal mol^{-1}) for reactants and transitions states

	Heat of formation	
Molecular species	E	ZPVE[a]
Ethylene	16.47	32.05
Benzo[*b*]thiophene	42.36	73.50
Benzo[*c*]thiophene	49.42	73.50
Transition-state structure **1**	110.83	106.91
Transition-state structure **2**	102.37	106.83
	Activation energy	
Transition state	ΔE	ΔE + ZPVE[a]
1	52.00	53.36
2	36.48	37.76

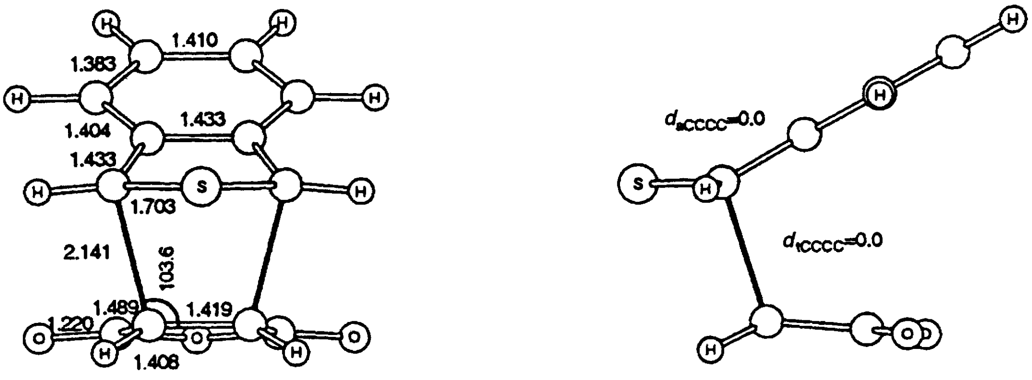
[a] ZPVE, zero point vibrational energy.

the desired direction. In comparison with the AM1-calculated activation energy for addition of ethene to thiophene (44.15 kcal mol^{-1})[13] it appears that the reactivity of benzo[*c*]thiophene should be higher than thiophene as dienes for the Diels–Alder reaction. There is no experimental evidence indicating that addition of ethene to thiophene or benzo[*c*]thiophene is feasible. Continuing the theoretical study of the ability of benzothiophenes as dienophiles for Diels–Alder reactions we chose to investigate very strong dienophiles such as tetracyanoethene. If the transition state **3** for the addition of tetracyanoethene to benzo[*b*]thiophene is similar to that for the ethene addition (Fig. 1); then the AM1 optimization of the transition-state structure requires a special approach. The newly forming bond distances are initially kept stationary as in transition-state structure **1** and the structure is optimized with 'EF' and 'GNORM = 0.01' keywords. Further optimization was performed with 'NLLSQ', 'XYZ' and 'GNORM = 1' keywords allowing the bonds undergoing formation to be optimized. Final optimization was performed with 'TS' and 'GNORM = 0.01' keywords and verified by vibrational analysis. Using the above described procedure for optimizing the transition-state structure, the two-step mechanism for the cycloaddition was determined to be approximately 5 kcal mol^{-1} higher in energy and will not be discussed here. Owing to considerable steric and π–π[26] repulsion interactions between two nitrile groups of the ethene moiety and the benzene group of benzo[*b*]thiophene moiety of **3**, there is considerable higher asynchronicity than in **1**. The calculated bond orders for the two newly forming CC bonds indicate that one bond is almost formed (0.775) while the other is just beginning to be formed (0.252) with overall asynchronicity of 0.523.[29] The transition-state structure **4** for addition at tetracyanoethene to benzo[*c*]thiophene preserves the planes of symmetry that bisect the transition-state structure, making the addition synchronous. The bond orders for both bonds undergoing formation are 0.453. The transition structure **3** is more advanced (sum of CC forming bond orders is 1.027) than transition structure **4** (sum of CC forming bond orders is 0.906), because the reaction is endothermic according to the Hammond postulate,[30] therefore the reaction through **4** should have a lower reaction barrier.

Heats of hydrogenation of the transition structures are obtained by the same procedure discussed above for **1** and **2**. There are two interesting points that can be addressed in terms of the heat of hydrogenation of transition-state structures **3** and **4** and their comparison with transition-state structures **1** and **2**.



6



7

Fig. 3 The transition-state structures for addition of maleic anhydride to benzo[*c*]thiophene

Table 4 Heats of hydrogenation (kcal mol^{-1}) of transition-state structures **3** and **4**

Compound	ΔE	ΔE + ZPVE[a]	$\Delta\Delta E$	$\Delta\Delta E$ + ZPVE[a]
3	−52.28	−27.24		
4	−24.2	0.65	−28.08	−27.89

[a] ZPVE, zero point vibrational energy.

Table 5 Activation energies (kcal mol^{-1}) for the addition of tetracyanoethene to thiophene (**5**) and benzothiophenes

Transition-state structure	ΔE	ΔE + ZPVE[a]
3	54.96	55.05
4	40.15	38.83
5	47.81	46.64

[a] ZPVE, zero point vibrational energy.

Table 6 Activation barriers for addition of maleic anhydride to benzo[*c*]thiophene (kcal mol^{-1})

Transition structure	ΔE	ΔE + ZPVE[a]
6	20.30	19.68
7	22.03	21.34

[a] ZPVE, zero point vibrational energy.

Both transition states with tetracyanoethene have considerably higher aromaticity than those with ethene (comparison of energies in Tables 3 and 5). The aromatic theory of the Diels–Alder transition state was first pointed out by Evans in 1939.[31] Its application to a wide variety of reactions was not fully appreciated until after the pioneering work of Woodward and Hoffmann[32] and was formulated by Dewar[33] and Zimmerman.[34] According to theory, higher aromaticity of the transition state causes a lower activation barrier of the reaction. Heats of the hydrogenation indicated transition-state structure **4** as the more aromatic and consequently the one with the lower activation energy. To confirm this finding the activation barriers for these reactions were calculated (Table 5). The activation energies are those expected on the basis of the heats of formation. The activation energy for the addition of tetracyanoethene to benzo[*b*]thiophene is very high because of the severe disruption of the aromatic benzene system. In the case of addition to benzo[*c*]thiophene, the aromaticity is high because the double bond constituent of the five-membered ring is incorporated into the aromatic system in contrast with the isolated double bond formed when the dienophile is added to thiophene. Therefore, the addition of tetracyanoethene to benzo[*c*]thiophene has the lowest activation energy, which is in full agreement with the experimental evidence.[4,5]

Continuing the study of Diels–Alder reactions with benzothiophenes we now present our results for the addition of maleic anhydride to benzo[*c*]thiophene. The transition-state structures are for a synchronous concerted mechanism (Fig. 3). The newly formed CC bonds in the two isomeric transition-state structures are almost identical suggesting the possibility of similar activation barriers for the isomeric cycloaddition reactions. Although the predicted activation energies (Table 6) are very similar, *exo* maleic anhydride (**6**) addition is preferred by 1.66 kcal mol^{-1}. The activation energy, 20 kcal mol^{-1}, indicates the experimental feasibility of a cycloaddition reaction.

These theoretical studies are supported by experimental data. Benzo[*c*]thiophene undergoes a cycloaddition reaction with maleic anhydride under mild, normal reaction conditions (refluxing in acetic anhydride).[35] The major product of the reaction is not the usual *endo* adduct, as predicted by AM1 calculations, but the *exo* isomer. However, there is no experimental evidence to indicate that the reaction operates *via* cycloaddition with ethene or any other electron-rich dienophile. In this way our theoretical studies are consistent with the experimental results presented herein.

Conclusions

Two different approaches for determining the suitability of benzothiophenes as dienophiles for Diels–Alder reactions were employed: determination of the heats of hydrogenation and estimation of reaction barriers. AM1 calculations of heats of hydrogenation for benzothiophenes indicate that benzo[*b*]thiophene is the more stable isomer. The heats of hydrogenation of the transition-state structures with ethene and tetracyanoethene as the dienophile were used to determine the higher aromaticity of the transition-state structures with benzo[*c*]thiophene. The activation energy for the addition of maleic anhydride to benzo[*c*]thiophene is predicted to be around 20 kcal mol^{-1}, and the *exo* isomer is preferred. Thus, the reaction is predicted to be experimentally feasible with the formation of the *exo*-isomer as the major product. The addition of ethene has a high activation energy therefore, forcing reaction conditions are necessary. This theoretical study is in excellent agreement with the experimental data.

Acknowledgements

This work was supported by a generous contribution from Mr and Mrs Timmons. The author thanks Mr D. Coupe for his help with preparation of the data.

References

1 S. Rajappa, 'Thiophenes and their Benzo Derivatives: (ii) Reactivity', in *Comprehensive Heterocyclic Chemistry*, eds. A. R. Katritzky and C. W. Rees, Pergamon, New York, 1984, p. 741 and references therein.

2 D. D. Callander, P. L. Coel and J. C. Tatlow, *J. Chem. Soc., Chem. Commun.*, 1966, 143; D. D. Callander, P. L. Coel, J. C. Tatlow and A. J. Uff, *Tetrahedron*, 1969, **25**, 25; P. L. Coel, G. M. Pearl and J. C. Tatlow, *J. Chem. Soc. C*, 1971, 604; D. Del Mazza and M. G. Reinecke, *Heterocycles*, 1980, **14**, 647; J. M. Barker, P. R. Huddleston and S. W. Shutler, *J. Chem. Soc., Perkin Trans. 1*, 1975, 2483.

3 D. H. Hartough and S. L. Meisels, *Chem. Heterocycl. Compd.*, 1954, **7**, 1.

4 R. Mayer, S. Richter and K. Gewald, *J. Pract. Chem.*, 1963, **20**, 244.

5 B. Iddon, *Adv. Heterocycl. Chem.*, 1972, **14**, 331.

6 S. Gronowitz, *J. Heterocycl. Chem.*, 1994, **31**, 641 and references therein.

7 All calculations were carried out with MOPAC version 6.0. *Quantum Chemistry Program Exchange (QCPE)*, 1990, Program No. 455.

8 For a detailed explanation of input files and keywords for transition-state[9] computation by MOPAC see: B. S. Jursic and Z. Zdravkovski, *J. Mol. Struct. (Theochem.)*, 1994, **303**, 177.

9 The transition state has to have only one imaginary frequency and that has become the major criterion for determining the transition state. For a review of transition-state theory see: W. J. Albery, 'Transition-State Theory Revisited' in *Adv. Phys. Org. Chem.*, 1993, **28**, 139; R. A. Marcus, 'Skiing the Reaction Rate Slopes', in *Science*, 1992, **256**, 1523; I. W. M. Smith, 'Probing the Transition State' in *Nature (London)*, 1992, **358**, 279.

10 B. S. Jursic and Z. Zdravkovski, *J. Mol. Struct. (Theochem.)*, 1994, **309**, 249.

11 B. S. Jursic and Z. Zdravkovski, *J. Heterocycl. Chem.*, 1994, **31**, 1429.

12 B. S. Jursic and D. Coupe, *J. Heterocycl. Chem.*, in press.

13 B. S. Jursic, *J. Heterocycl. Chem.*, submitted.

14 For an excellent book on heterodienophile in Diels–Alder reactions see: D. L. Boger and S. N. Weinreb, *Hetero Diels–Alder Methodology in Organic Synthesis*, Academic Press, New York, 1987; S. M. Weinreb and R. R. Staib, *Tetrahedron*, 1982, **38**, 3087; A. Hassner, K. S. K. Murthy, R. Maurya, W. Dehaen and O. Friedman, *J. Heterocycl. Chem.*, 1994, **31**, 687.

15 B. S. Jursic and Z. Zdravkovski, *J. Org. Chem.*, 1994, **59**, 3015; B. S. Jursic and Z. Zdravkovski, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1877; B. S. Jursic and Z. Zdravkovski, *J. Phys. Org. Chem.*, 1994, **7**, 634; B. S. Jursic and Z. Zdravkovski, *J. Mol. Struct. (Theochem.)*, 1995, **331**, 215; **331**, 229; 1995, **332**, 39.

16 For a theoretical study of the addition of ethene to oxazole and isoxazole performed at the MP2/6-31*//RHF/3-21g theory level see J. Gonzalez, E. C. Taylor and K. N. Houk, *J. Org. Chem.*, 1992, **115**, 3753.

17 For a recent review see K. N. Houk, Y. Li and J. Evanseck, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 682 and references therein; O. Kikuchi, *Tetrahedron*, 1971, **27**, 2791; M. V. Basilevsky, V. A. Tikhanov and I. E. Chenlov, *Theor. Chim. Acta*, 1971, **23**, 75; J. W. McIver Jr., *Acc. Chem. Res.*, 1974, **7**, 72; M. V. Basilevsky, A. G. Shamov and V. A. Tikhanov, *J. Am. Chem. Soc.*, 1977, **99**, 1369; M. J. S. Dewar, S. Olivella and H. S. Rzepa, *J. Am. Chem. Soc.*, 1978, **100**, 5650 and references therein; M. J. S. Dewar, S. Olivella and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1986, **108**, 5771; J. Pancir, *J. Am. Chem. Soc.*, 1982, **104**, 7424; K. N. Houk, Y.-T. Lin and F. K. Brown, *J. Am. Chem. Soc.*, 1986, **108**, 554; F. K. Brown and K. N. Houk, *Tetrahedron Lett.*, 1984, **25**, 4609; K. N. Houk, R. J. Loncharich, J. F. Blake and W. L. Jorgensen, *J. Am. Chem. Soc.*, 1989, **111**, 9172; W. L. Jorgensen, D. Lim and J. F. Blake, *J. Am. Chem. Soc.*, 1993, **115**, 2936.

18 M. J. S. Dewar, S. Olivella and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1986, **108**, 5771; M. J. S. Dewar, *Acc. Chem. Res.*, 1992, **25**, 537 and references therein.

19 K. N. Houk and Y. Li, *J. Am. Chem. Soc.*, 1993, **115**, 7478.

20 For an historical account of early consideration of aromaticity, see J. P. Snyder, *Nonbenzenoid Aromatics*, vol. 1, Academic Press, New York, 1969, ch. 1.

21 It has been proposed that the word aromatic be discontinued, see: D. Lloyed and D. R. Marshall, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 404.

22 For a review of the criteria used to define aromatic character see: A. J. Jones, *Rev. Pure Appl. Chem.*, 1968, **18**, 253; L. J. Schaad and B. A. Hess Jr., *J. Am. Chem. Soc.*, 1972, **94**, 3068; L. J. Schaad and N. A. Hess Jr., *J. Chem. Educ.*, 1974, **51**, 640.

23 R. B. Mallion, *Pure Appl. Chem.*, 1980, **52**, 1541.

24 M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, 1969, **91**, 789; H. Kollmar, *J. Am. Chem. Soc.*, 1979, **101**, 4832.

25 P. George, M. Trachtman, C. W. Bock and A. M. Brett, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1222; P. George, M. Trachtman, C. W. Block and A. M. Brett, *Tetrahedron*, 1976, **32**, 1357.

26 Orbital repulsion interactions, as an explanation of the reactivity in transition-state structures, were first suggested by Coxon and co-workers,[27] later used by Houk and co-workers,[28] and us[15] to explain different reactivity of heterodienophiles in Diels–Alder reactions.

27 J. M. Coxon, S. T. Grice, R. G. A. R. Maclagon and D. G. McDonald, *J. Org. Chem.*, 1990, **55**, 3804.

28 M. A. McCorrick, Y.-D. Wu and K. N. Houk, *J. Org. Chem.*, 1993, **58**, 3330; M. A. McCorrick, Y.-D. Wu and K. N. Houk, *J. Am. Chem. Soc.*, 1992, **114**, 1499.

29 For determination of synchronicity through bond orders of newly forming bonds, see B. S. Jursic and Z. Zdravkovski, *J. Org. Chem.*, 1994, **59**, 7732; for characterization of the progress of chemical reaction by bond orders see: G. Lenday, *J. Phys. Chem.*, 1994, **98**, 6098 and references therein.

30 G. S. Hammond, *J. Am. Chem. Soc.*, 1955, **77**, 334; W. J. Le Noble, A. R. Miller and S. D. Hamann, *J. Org. Chem.*, 1977, **42**, 338; A. R. Miller, *J. Am. Chem. Soc.*, 1978, **100**, 1984.

31 M. G. Evans, *Trans. Faraday Soc.*, 1939, **35**, 824.

32 R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**, 395; R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, 1970.

33 M. J. S. Dewar, *Tetrahedron Suppl.*, 1966, **8**, 75; M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 761.

34 H. E. Zimmerman, *J. Am. Chem. Soc.*, 1966, **88**, 1564; H. E. Zimmerman, *J. Am. Chem. Soc.*, 1966, **88**, 1566; H. E. Zimmerman, *Acc. Chem. Res.*, 1971, **4**, 272; Zimmerman was the first to apply the antiaromaticity idea in pericyclic reactions, H. E. Zimmerman, *Tetrahedron*, 1983, **38**, 753.

35 M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, 1966, **88**, 4112; R. H. Schlesinger and G. S. Ponticello, *J. Am. Chem. Soc.*, 1967, **89**, 7138; R. H. Schlessinger and G. S. Ponticello, *Tetrahedron Lett.*, 1968, 3017.

Paper 4/06050D
Received 4th *October* 1994
Accepted 25th *January* 1995