

Theoretical study of the Diels–Alder reaction between the *S*-methylthiophenium ion and ethene

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The capability and activation of thiophene as a diene for the Diels–Alder reactions has been investigated by *ab initio* methods. The reactants and transition structures are optimized with RHF/3-21 + G*, RHF/6-31 + G* and MP2/6-31 + G*. Energies are evaluated with the same level of theory and by single point calculations employing MP2/6-31 + G*/RHF/6-31 + G* and MP3/6-31 + G*/MP2/6-31 + G* methods. The *ab initio* calculated geometries are compared with experimental data, where available. The relative reactivity of buta-1,3-diene, thiophene and the *S*-methylthiophenium ion were estimated by comparing their FMO energy gap with ethene as the dienophile. The predicted activation energies are in full agreement with the qualitative determination of reactivity and suggest that thiophene is not a suitable diene for the Diels–Alder reaction. For the *S*-methylthiophenium ion, the predicted activation energy may be reached under normal reaction conditions. Thus *S*-methylthiophenium should be a suitable diene for the Diels–Alder reactions.

Introduction

Searching for simple, readily available starting materials known as 'syntones' for the preparation of complex organic compounds is a worthy target of organic chemists.¹ On the other hand, many organic materials can be derived from reactions that transform intermediates into useful products. The Diels–Alder reaction is a general reaction that can combine two linear molecules and produce six membered rings with pre-determined geometry.² The knowledge of the theoretical aspects, synthetic studies, mechanisms³ and reaction conditions is fairly well developed. Thus, most research targets the development of suitable dienophiles and dienes for this reaction.

By describing the dienes for Diels–Alder reactions as a group of organic compounds having two conjugated double bonds, it is possible to substitute heterocyclic aromatic compounds as dienes. Heterocyclic aromatic species when used as dienes should engage in a cycloaddition reaction with ethene derivatives to produce the corresponding bicyclic compounds. Heteroatoms are ordinarily easy to eliminate from the product leaving the mono-six-membered ring. This is similar to the conventional Diels–Alder open chain reaction between dienophile and diene.

One particularly interesting heterocyclic aromatic compound, with respect to elimination of the heteroatom from the bicyclic adduct, is thiophene. Unfortunately, thiophene does not readily undergo cycloaddition reactions with ordinary dienophiles.⁴ This behaviour is explained by the extraordinary high aromaticity of the thiophene ring, the highest of all heterocyclic five-membered aromatic compounds.⁵ Recently, we demonstrated that the aromaticity of the thiophene ring is destroyed by its transformation to the *S*-methylthiophenium ion.⁶ Here we present our theoretical study of ethene addition to the *S*-methylthiophenium ion with the intention of demonstrating the suitability of the *S*-methylthiophenium ion as a way of activating thiophene for the Diels–Alder reaction.⁷

Computational methodology

Geometric optimizations were carried out without using symmetry or any other structural restrictions. All calculations are performed with GAUSSIAN92⁸ at the restricted Hartree–Fock⁹ level with 3-21 + G¹⁰ and 6-31 + G*¹¹ as basis sets

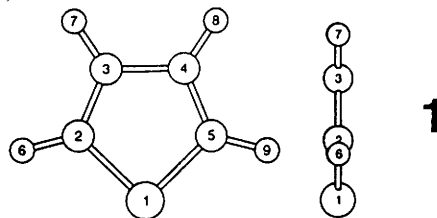
and applying second-order Møller–Plesset (MP2)¹² theory with a 6-31 + G* basis set. For all structures the vibrational analysis was performed with the same basis set used for optimization. Each transition structure gives only one imaginary harmonic vibrational frequency, corresponding to the motion of forming new C–C bonds for concerted transition structures. The activation energies were estimated from MP3/6-31 + G* calculations on the MP2/6-31 + G* optimized geometries.

Results and discussion

The mechanism of Diels–Alder reactions¹³ has been at the centre of considerable dispute, but recent theoretical studies at the correlated level support a concerted mechanism¹⁴ which will be considered here. The geometries of the reactants, thiophene and the *S*-methylthiophenium ion, are first optimized by AM1 MOPAC¹⁵ semi-empirical methods and finally with *ab initio* methods. The obtained structures are presented in Tables 1 and 2. The *ab initio* calculated structural parameters agree well with the experimental structure of thiophene determined by microwave spectroscopy.¹⁶ The bond distance is maximally 0.02 Å and bond angle is at the most 0.7° off the experimental value.

The geometric parameters calculated with different theoretical models for the *S*-methylthiophenium ion are not in as good agreement as for thiophene. Although the predicted bond distances are within 0.02 Å, the bond angle agreement is 2.0° (*a*216 calculated by RHF with 3-21 + G* and 6-31 + G* basis sets) and the dihedral angle agreement is 5.0° (for *d*4516). This difficulty in obtaining good values for dihedral angles is a common problem for many modelling approaches. As expected, by considering the position of the lone pairs, the sulfur atom in all predicted cases is pyramidal with the methyl substituent being *ca.* 70° out of plane. To the best of our knowledge the structure of the *S*-methylthiophenium ion is not experimentally known, but there are X-ray data available¹⁷ for the 5-methyldibenzothiophenium ion indicating that this value is correct. In the X-ray structure the methyl group is 68–69° out of plane. If the lone pair, because of sp³ hybridization and improper symmetry, is not delocalized into the buta-1,3-diene segment, the system will be non-aromatic. This was shown to be true in the X-ray structure of thiophenium bismethoxycarbonylmethylide¹⁸ pointing to increased localization of the bonds in

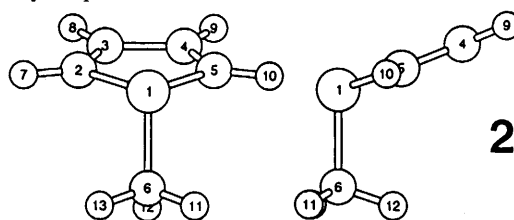
Table 1 Geometric parameters^a of thiophene (1)



	$r_{12}/\text{\AA}$	$r_{23}/\text{\AA}$	$r_{34}/\text{\AA}$	$r_{26}/\text{\AA}$	$r_{37}/\text{\AA}$	$a_{123}/^\circ$	$a_{234}/^\circ$	$a_{512}/^\circ$	$a_{623}/^\circ$	$a_{237}/^\circ$
I ^b	1.723	1.352	1.439	1.069	1.070	112.0	112.3	91.4	127.0	123.9
II ^c	1.725	1.348	1.437	1.071	1.074	111.9	112.5	91.3	127.7	123.7
III ^d	1.717	1.380	1.421	1.083	1.086	111.6	112.4	92.0	128.0	124.2
IV ^e	1.71	1.37	1.42 ^b	1.08	1.08 ^c	111.3	112.3 ^d	92.1	128.4	124.2

^a r Bond distance; a bond angle. ^b **I** RHF/3-21 + G*. ^c **II** RHF/6-31 + G*. ^d **III** MP2/6-31 + G*. ^e **IV** Obtained by microwave spectroscopy in the gas phase.¹⁶

Table 2 Geometric parameters^a of the *S*-methylthiophenium ion 2



	$r_{12}/\text{\AA}$	$r_{23}/\text{\AA}$	$r_{34}/\text{\AA}$	$r_{16}/\text{\AA}$	$r_{27}/\text{\AA}$	$r_{38}/\text{\AA}$
	$a_{123}/^\circ$	$a_{234}/^\circ$	$a_{215}/^\circ$	$a_{216}/^\circ$	$a_{723}/^\circ$	$a_{238}/^\circ$
	$d_{1234}/^\circ$	$d_{2345}/^\circ$	$d_{4516}/^\circ$	$d_{7216}/^\circ$	$d_{7234}/^\circ$	$d_{7238}/^\circ$
I ^b	1.770	1.330	1.479	1.827	1.069	1.70
	110.5	113.5	91.7	103.0	129.0	123.7
	2.5	0.0	107.0	75.7	179.3	-1.0
II ^c	1.769	1.327	1.472	1.827	1.071	1.073
	110.0	113.8	92.0	105.0	129.9	123.3
	3.4	0.0	110.6	73.5	178.7	-1.4
III ^d	1.763	1.356	1.457	1.824	1.084	1.084
	109.6	113.8	92.7	104.5	130.2	122.7
	4.7	0.0	112.0	73.9	177.9	-2.6

^a r Bond distance; a bond angle; d dihedral angle. ^b **I** RHF/3-21 + G*. ^c **II** RHF/6-31 + G*. ^d **III** MP2/6-31 + G*.

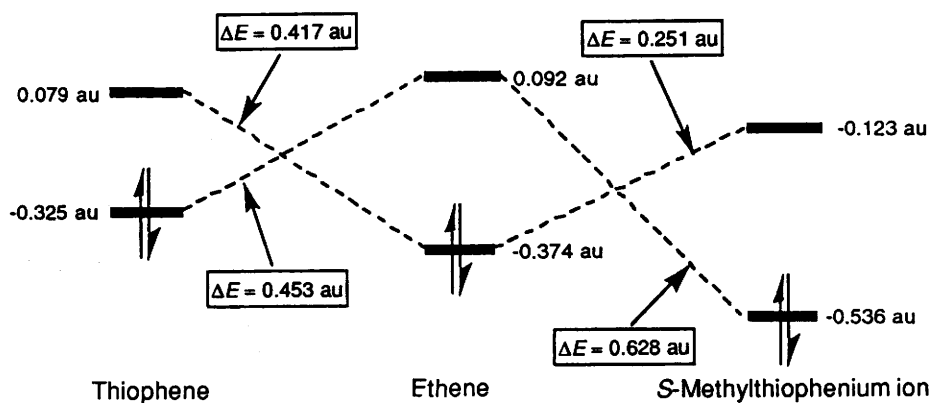


Fig. 1 Correlation of frontier molecular orbitals of thiophene and *S*-methylthiophenium ion with ethene calculated with the MP2/6-31 + G* method (1 au = 4.360×10^{-18} J)

the thiophene ring. The bond distances are $r_{12} = 1.75 \text{ \AA}$, $r_{23} = 1.33 \text{ \AA}$ and $r_{34} = 1.44 \text{ \AA}$. These findings are comparable with our results presented in Table 2. If compared to the structural parameters of thiophene and the *S*-methylthiophenium ion, the localization of bonds is increased in the latter. Furthermore, the r_{12} bond is much longer in the *S*-thiophenium ion indicating a considerable loss of aromaticity. Consequently, this non-aromatic system should be very reactive as a diene for Diels–Alder reactions, despite

published findings inferring that these species inhibit the progress of cycloaddition reactions.¹⁹

One very simple way to compare the reactivity of thiophene and the *S*-methylthiophenium ion as dienes in Diels–Alder reactions is to determine their frontier orbital energy and correlate them with the ethene frontier molecular orbitals (Fig. 1). According to frontier molecular orbital (FMO)²⁰ theory the reactant pairs that have a smaller energy gap between the reactants will be more reactive, e.g. the energy gap between

ethene as dienophile and buta-1,3-diene for $LUMO_{\text{ethene}} - HOMO_{\text{buta-1,3-diene}}$ is $209.15 \text{ kcal mol}^{-1}$.[†] This is smaller than the other frontier orbital energy gap ($LUMO_{\text{buta-1,3-diene}} - HOMO_{\text{ethene}} = 265.65 \text{ kcal mol}^{-1}$). This is also an example of a 'normal' electron demand, LUMO dienophile-controlled Diels–Alder reaction.²¹ Both FMO energy gaps for ethene addition to thiophene ($LUMO_{\text{thiophene}} - HOMO_{\text{ethene}} = 284.26 \text{ kcal mol}^{-1}$ and $LUMO_{\text{ethene}} - HOMO_{\text{thiophene}} = 260.41 \text{ kcal mol}^{-1}$) are considerably higher than ethene addition to buta-1,3-diene. This predicts a less favourable cycloaddition reaction. For ethene addition to the *S*-methylthiophenium ion (2) the FMO energy gap for the $LUMO_{\text{S-methylthiophenium ion}} - HOMO_{\text{ethene}} = 157.50 \text{ kcal mol}^{-1}$ predicts this reaction to be favoured over ethene addition to both thiophene and buta-1,3-diene.

With FMO, in many cases, it is possible to determine the relative reactivity of a series of similar reactants for the same reaction. It is usually very difficult to determine which reaction will be experimentally feasible. The most reliable way is to determine the activation barrier for the reaction. With this approach one transition structure for ethene addition to thiophene (3) and two for *S*-methylthiophenium ion (4 and 5) were optimized. As mentioned above, high level *ab initio* calculations suggest that Diels–Alder reactions proceed through concerted, but not necessarily synchronous, mechanisms for the formation of the two new bonds.^{4,22}

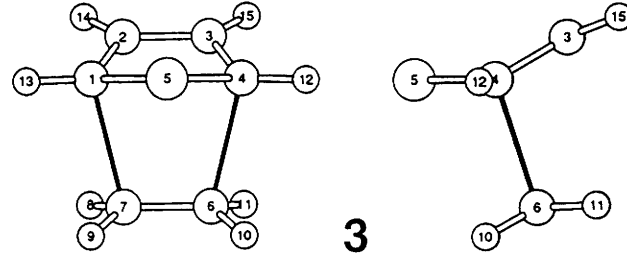
The geometries of transition structures for ethene addition to thiophene and the *S*-methylthiophenium ion are presented in Tables 3–5. The transition structure 3 (Table 3) is for the fully synchronous mechanism of the Diels–Alder reaction. The bond distance and bond angle disagreement between different methods is 1%, while the dihedral angle disagreement is slightly over 1%. This agreement between methods is high. Houk *et al.*²⁵ have studied the similarities of transition structures for Diels–Alder reactions obtained by different theoretical models.

The ability to predict geometric parameters for transition structures with polar dienes such as the *S*-methylthiophenium ion is not as good. As expected, the major difference in bond distance is obtained for newly forming bonds for the RHF/6-31+G* and MP2/6-31+G* theoretical models. Both structures 4 (Table 4) and 5 (Table 5) have a plane of symmetry that bisects the transition structures. Geometric parameters predicted by the MP2/6-31+G* method suggests the least compact transition structure. This is demonstrated by the

longer newly forming C–C bonds in comparison with RHF calculations (RHF/3-21+G* and RHF/6-31+G*). Other geometric parameters are similar to all theoretical models calculated.

As discussed earlier, the relative reactivity of a diene in a reaction with ethene can be determined by the FMO energy gap. It was determined that the *S*-methylthiophenium ion is more reactive than thiophene. It is not possible to determine the stereoselectivity of the ethene addition in regard to the methyl group; that can be obtained only by determining activation energies of the cycloaddition reactions. The total energies of the reactants and the transition structures for ethene addition to thiophene and *S*-methylthiophene are presented in Table 6. As expected, predicted activation energies (Table 7) with different theoretical models vary. To determine the best theoretical model the activation energy was first calculated for ethene addition to thiophene. Unfortunately we do not have experimentally available data for these activation barriers. In our previous study of ethene addition to buta-1,3-diene we selected MP3/6-31G*//MP2/6-31G* as a suitable theoretical

Table 3 Geometric parameters^a of transition structure 3

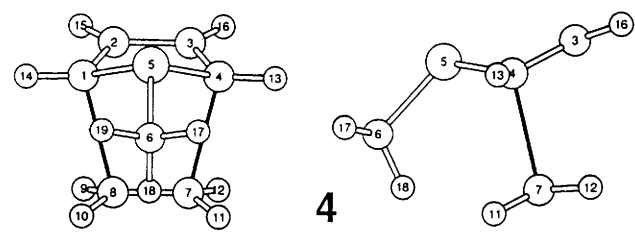


	$r_{12}/\text{\AA}$ $a_{123}/^\circ$ $d_{1234}/^\circ$	$r_{23}/\text{\AA}$ $a_{345}/^\circ$ $d_{2345}/^\circ$	$r_{45}/\text{\AA}$ $a_{345}/^\circ$ $d_{2346}/^\circ$	$r_{67}/\text{\AA}$ $a_{546}/^\circ$ $d_{3451}/^\circ$	$r_{46}/\text{\AA}$ $a_{467}/^\circ$ $d_{5467}/^\circ$
I ^b	1.412 111.4 0.0	1.372 109.6 -23.0	1.752 96.4 72.9	1.392 93.3 29.9	2.174 103.4 44.0
II ^c	1.412 111.3 0.0	1.369 109.0 -24.2	1.750 97.3 72.6	1.396 93.9 31.5	2.172 103.3 43.9
III ^d	1.424 111.0 0.0	1.382 109.3 -23.9	1.750 96.4 72.9 ^b	1.405 94.3 31.4	2.151 103.4 43.4

^a *r* Bond distance; *a* bond angle; *d* dihedral angle. ^b **I** RHF/3-21+G*. ^c **II** RHF/6-31+G*. ^d **III** MP2/6-31+G*.

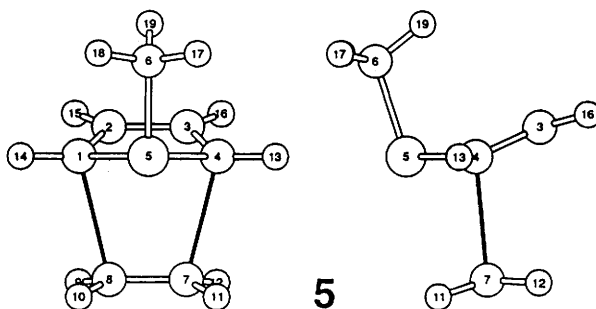
[†] 1 cal = 4.184 J.

Table 4 Geometric parameters^a of transition structure 4



	$r_{12}/\text{\AA}$ $a_{123}/^\circ$ $d_{1234}/^\circ$	$r_{23}/\text{\AA}$ $a_{345}/^\circ$ $d_{2345}/^\circ$	$r_{45}/\text{\AA}$ $a_{451}/^\circ$ $d_{3456}/^\circ$	$r_{56}/\text{\AA}$ $a_{456}/^\circ$ $d_{3478}/^\circ$	$r_{78}/\text{\AA}$ $a_{478}/^\circ$ $d_{5478}/^\circ$	$r_{47}/\text{\AA}$ $a_{547}/^\circ$ $d_{6547}/^\circ$
I ^b	1.392 112.8 0.0	1.396 104.8 -26.5	1.769 88.7 149.5	1.796 112.8 -64.0	1.376 104.0 41.7	2.265 95.4 49.9
II ^c	1.395 112.7 0.0	1.388 103.6 -28.4	1.767 88.5 152.0	1.802 112.9 -63.6	1.382 103.9 41.4	2.252 96.3 50.8
III ^d	1.404 113.0 0.0	1.403 103.9 -26.0	1.763 90.3 149.6	1.800 112.3 -63.8	1.384 103.9 41.0	2.326 95.5 50.4

^a *r* Bond distance; *a* bond angle; *d* dihedral angle. ^b **I** RHF/3-21+G*. ^c **II** RHF/6-31+G*. ^d **III** MP2/6-31+G*.

Table 5 Geometric parameters^a of transition structure **5**

	$r_{12}/\text{\AA}$ $a_{123}/^\circ$ d_{1234}	$r_{23}/\text{\AA}$ $a_{345}/^\circ$ d_{2345}	$r_{45}/\text{\AA}$ $a_{451}/^\circ$ d_{3456}	$r_{56}/\text{\AA}$ $a_{456}/^\circ$ d_{3478}	$r_{178}/\text{\AA}$ $a_{478}/^\circ$ d_{5478}	$r_{147}/\text{\AA}$ $a_{547}/^\circ$ d_{6547}
I ^b	1.385 112.3 0.0	1.396 108.9 -19.9	1.778 89.7 -77.4	1.817 103.6 -62.9	1.387 104.0 45.6	2.237 86.0 -177.8
II ^c	1.387 112.7 0.0	1.391 108.4 -21.6	1.778 87.7 -76.7	1.821 105.0 -62.5	1.390 103.9 45.6	2.229 86.8 -178.4
III ^d	1.393 113.0 0.0	1.407 108.7 -18.4	1.778 89.0 -78.8	1.825 102.9 -62.5	1.389 103.8 45.5	2.317 84.3 -179.0

^a r Bond distance; a bond angle; d dihedral angle. ^b **I** RHF/3-21 + G*. ^c **II** RHF/6-31 + G*. ^d MP2/6-31 + G*.

Table 6 Total energies (au) of the reactants and transition structure

Species	E_{al}^a	E_{all}^b	E_{alll}^c	E_{alv}^d	E_{av}^e
H ₂ CCH ₂	-77.607 92	-78.035 82	-78.290 50	-78.291 18	-78.311 72
1	-548.608 87	-551.296 42	-551.935 07	-551.937 28	-551.961 34
2	-587.734 81	-590.640 49	-591.397 08	-591.399 51	-591.440 56
3	-626.143 99	-629.245 14	-630.184 98	-630.186 49	-630.214 52
4	-665.285 97	-668.607 41	-669.671 75	-669.673 31	-669.715 86
5	-665.297 96	-668.615 15	-669.679 16	-669.680 53	-669.723 31

^a E_{al} RHF/3-21 + G*/RHF/3-21 + G*. ^b E_{all} RHF/6-31 + G*/RHF/6-31 + G*. ^c E_{alll} MP2/6-31 + G*/RHF/6-31 + G*. ^d E_{alv} MP2/6-31 + G*/MP2/6-31 + G*. ^e E_{av} MP3/6-31 + G*/MP2/6-31 + G*.

Table 7 Activation energies (kcal mol⁻¹) for the Diels–Alder addition of ethene to thiophene and *S*-methylthiophenium cation

TS	ΔE_{al}^a	ΔE_{all}^b	ΔE_{alll}^c	ΔE_{alv}^d	ΔE_{av}^e
3	45.68	54.65	25.47	26.33	36.73
4	35.62	43.23	9.93	10.90	22.85
5	28.09	38.38	5.28	6.37	18.18

^a ΔE_{al} RHF/3-21 + G*/RHF/3-21 + G*. ^b ΔE_{all} RHF/6-31 + G*/RHF/6-31 + G*. ^c ΔE_{alll} MP2/6-31 + G*/RHF/6-31 + G*. ^d ΔE_{alv} MP2/6-31 + G*/MP2/6-31 + G*. ^e ΔE_{av} MP3/6-31 + G*/MP2/6-31 + G*.

method for calculation of its activation barrier.²⁶ We can only assume that this model for neutral systems and MP3/6-31 + G*/MP2/6-31 + G* for charged systems will produce reliable activation barriers.

The minimal activation energy of only 5.28 kcal mol⁻¹ was observed using the MP2/6-31 + G*/RHF/6-31 + G* method for ethene addition to *S*-methylthiophenium *via* transition structure **5**. As mentioned above, this method highly underestimates the activation energy. Assuming that MP3/6-31 + G*/MP2/6-31 + G* gives reliable results, the activation energy for ethene addition to *S*-methylthiophenium ion is 18.18 kcal mol⁻¹. The reactivity with all applied theoretical models predicts that the *S*-methylthiophenium ion is much more reactive than thiophene. The same reactivity order is determined by FMO theory. Also, the predicted activation energies prefer ethene addition *via* transition structure **5** to *S*-methylthiophenium ion.

Is ethene addition to the *S*-methylthiophenium ion feasible? Activation energies below 20 kcal mol⁻¹ are easily obtained under ordinary reaction conditions. All computed activation energies with correlation methods predict ethene addition to the *S*-methylthiophenium ion to be experimentally feasible. The question which remains is the actual value of the activation energy. The predicted activation energy with the MP2/6-31 + G* method seems to be unrealistically low, while from our previous study the predicted energy with the MP3 method on MP2 geometries usually gives values which are a little bit too large.²⁷ Although in the case of ethene addition to *S*-methylthiophenium ion, the MP3/6-31 + G*/MP2/6-31 + G* method predicts the correct activation energy (in an isolated system),²⁶ it is not a perfect choice because the ethene addition is to a cation, not to a neutral molecule. Thus the activation energy of ethene to *S*-methylthiophenium ion is more likely to be between 5.28 and 18.18 kcal mol⁻¹.

Our own experimental results can confirm the predicted reactivity. We were not able to perform cycloaddition reactions between thiophene and either ethene or cyclohexene even at an elevated temperature (250 °C) in an autoclave. If methyl triflate is added to a carefully dried methylene dichloride solution of thiophene and cyclohexene at 40 °C, then quenched with methanol and worked up, then the cycloadduct can be isolated.† These results confirm our theoretical studies presented here.

† The synthetic procedure for the preparation of thiophene cycloadducts *via* *S*-methylthiophenium activation will be published elsewhere. Triflate = trifluoromethanesulfonate.

Conclusion

It has been shown that thiophene is not a very effective diene for the Diels–Alder reaction. By comparing FMO energy gaps it was determined that the reactivity of thiophene is far below that of buta-1,3-diene, which is already a very poor diene. The major reason for the low thiophene reactivity is its high aromaticity. To destroy thiophene's aromaticity, the thiophene can be transformed into the *S*-methylthiophenium ion. This system is shown to be non-aromatic by comparison of geometric parameters with thiophene. The FMO energy gap predicts a very high reactivity of *S*-methylthiophene, in agreement with the estimated activation energies for ethene addition. Because of this very low activation energy the reaction is of synthetic value for the preparation of thiophene cycloadducts.

Acknowledgements

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