

# Comparison of AM1 and PM3 semiempirical to ab initio methods in the study of Diels–Alder reactions of butadiene and cyclopentadiene with cyanoethylenes

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## Abstract

Assuming a concerted synchronous mechanism with one transition state of the Diels–Alder reactions, the structures of the transition states and the activation energies for the reactions of butadiene and cyclopentadiene with cyanoethylenes were calculated by AM1 and PM3 semiempirical methods. The structural parameters were compared with those obtained by high level Gaussian calculations, whereas the activation energies were compared both with the ab initio calculations and those obtained experimentally. The structural properties calculated with PM3 methods are in general in better agreement with the ab initio calculations. The low level ab initio calculations are in many cases worse than the semiempirical methods. All predicted activation energies with both semiempirical methods are up to 300% higher than the experimental values. The predicted reactivity is also opposite to the experimental data. Only the very high level Gaussian calculations are in good correlation with experimental results. The predicted selectivity of the reaction is also opposite to the experimental facts. Two explanations are offered for this discrepancy: AM1 and PM3 methods cannot handle the calculation of the concerted Diels–Alder transition states and are not recommended to be used for that purpose, or this Diels–Alder reaction is not concerted but is stepwise.

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## 1. Introduction

The Diels–Alder reactions are the core of the pericyclic reactions. The mechanism of the reaction has been the subject of very extensive study and much disagreement. There is plenty of evidence that the Diels–Alder reaction of butadiene with ethylene follows a synchronous concerted mechanism and most organic chemists have regarded it as a typical synchronous

pericyclic reaction, involving a symmetrical aromatic transition state analogous to benzene [1–3]. It has been generally accepted that other cycloaddition reactions follow a similar course.

There is another group of scientists that does not share the same view on the mechanism of the Diels–Alder reactions. The first dispute came from the Dewar group in 1978 [4]. They performed an MINDO/3 study of the reaction of ethylene with butadiene and concluded that the reaction is not synchronous. They selected the very unsymmetrical biradicaloid transition state in which one of the bonds is almost completely formed while the other

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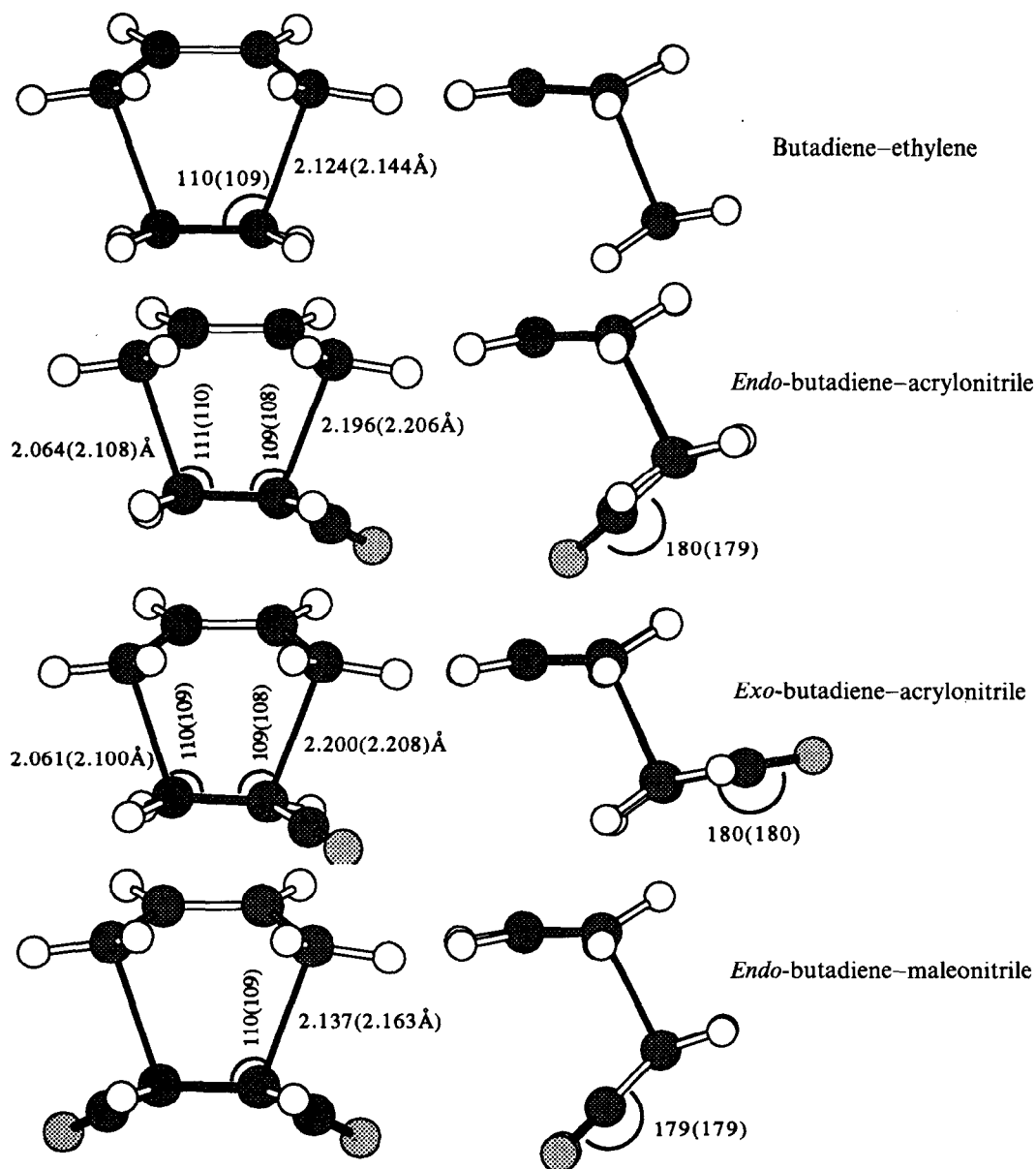


Fig. 1. (For figure caption see opposite page.)

is still weak. Other support for the biradicaloid Diels-Alder reactions has come later, almost exclusively from semiempirical methods [5]. We present here a study of the mechanism of the Diels-Alder reactions as a concerted synchronous pathway of transformation of the reactants to the products by the semiempirical AM1 method. We will show that the results obtained by AM1 in the

study of the Diels-Alder reactions can be compared to the low level Gaussian calculations while higher level Gaussian calculations show better agreement with the experimental values. We will also show that neither the AM1 nor the PM3 method can be used for predicting the reactivity of the Diels-Alder reactions if a synchronous mechanism is proposed which, in the chemical

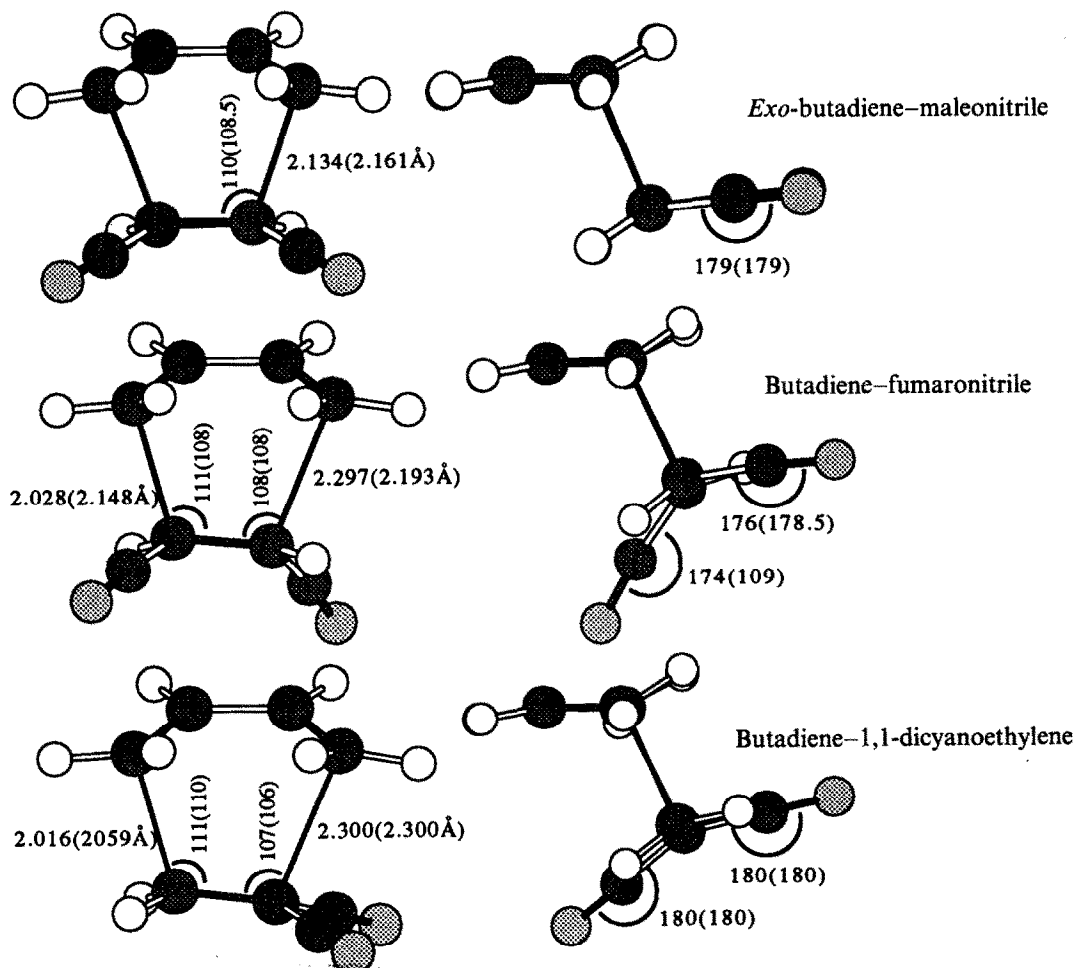


Fig. 1. The structures of the transition states generated by AM1 and PM3 (values in parentheses) in the reactions of 1,3-butadiene and cyanoethylenes.

community, is the broadly accepted mechanism for this reaction [6].

## 2. Procedures and methods

All calculations were performed on an IBM compatible 486 DX/2 66 MHz computer with 32 MB RAM and 512 MB HD and on a DEC 7620 computer. CHEM-X [7] was used as a graphical interface for drawing and visualizing all structures and for preparing input files for MOPAC 6.0 [8].

The reactants were optimized together at an intermolecular distance of more than 10 Å. The

search for the transition states and their verification [9] was performed as described previously [10]. Vibrational and thermal analyses were performed on all optimized structures.

## 3. Results and discussion

Two groups of Diels-Alder addition reactions were studied with regard to the selectivity and the reactivity. In the first group, the reaction of butadiene with ethylene, acrylonitrile, maleonitrile, fumaronitrile and 1,1-dicyanoethylene were studied. In the second group, instead of buta-

Table 1

The C–C distances (Å) in butadiene–cyanoethylene transition states generated by AM1, PM3 and RHF/3-21G methods<sup>a</sup>

Adduct	AM1	PM3	RHF/3-21G <sup>b</sup>
Butadiene–ethylene	2.124	2.144	2.210
<i>endo</i> -Butadiene–acrylonitrile	2.064 2.196	2.108 2.206	2.141 2.286
<i>exo</i> -Butadiene–acrylonitrile	2.061 2.200	2.100 2.208	2.123 2.306
<i>endo</i> -Butadiene–maleonitrile	2.137	2.163	2.217
<i>exo</i> -Butadiene–maleonitrile	2.134	2.161	2.219
Butadiene–fumaronitrile	2.028 2.297	2.148 2.193	2.246 2.196
Butadiene–1,1-dicyanoethylene	2.016 2.300	2.059 2.300	2.036 2.443

<sup>a</sup> In the asymmetric cyanoethylenes the first row represents the C–C bond distance where the cyano groups are not bound.

<sup>b</sup> Ref. 2.

diene, cyclopentadiene was used. The results of the AM1 and the PM3 studies will be discussed separately for each group and compared to experimental and ab initio data where available, and then together regarding their reliability to predict the correct reactivity and selectivity of the Diels–Alder reactions assuming the synchronous mechanism is the correct one.

### 3.1. Diels–Alder reaction of butadiene with the cyanoethylenes

The structures of the transition states in the synchronous mechanism of the Diels–Alder reactions obtained by AM1 and PM3 methods are presented in Fig. 1. The comparison of the structural properties of the transition states generated by the AM1 and PM3 methods show that the bond distances of the newly formed C–C bonds are a little longer when obtained by PM3 than by AM1. Consequently the bond angles for PM3 are a little smaller (Fig. 1). The RHF/3-21G Gaussian calculation data and structures are available for the same series of compounds [2]. The structural features of the Gaussian transition states are more similar to the ones generated by PM3 than by AM1. The C–C bond formation distances for

Table 2

The activation energies (kcal mol<sup>−1</sup>) of the reaction of butadiene with cyanoethylenes

Adduct	AM1	PM3	3-21G <sup>a</sup>	Exp.
Butadiene–ethylene	23.7	27.1	35.9	27.5 <sup>b</sup>
<i>endo</i> -Butadiene–acrylonitrile	24.9	28.4	33.7	
<i>exo</i> -Butadiene–acrylonitrile	24.4	27.9	33.1	
<i>endo</i> -Butadiene–maleonitrile	26.4	30.0	32.2	
<i>exo</i> -Butadiene–maleonitrile	25.4	29.4	31.8	
Butadiene–fumaronitrile	30.5	29.7	31.2	
Butadiene–1,1-dicyanoethylene	24.3	28.6	28.5	

<sup>a</sup> Ref. 2.

<sup>b</sup> Ref. 11.

AM1, PM3 and Gaussian RHF/3-21G generated transition states are presented in Table 1. If we assume that the RHF/3-21G generated structures of the transition states are the ones that closely resemble the real transition states, the transition state structures generated with both AM1 and PM3 should be satisfactory. Since we do not have experimental tools to determine the structure of the transition state, the major criteria for confirming the transition state calculations is the prediction of the reactivity through the calculation of the activation energies. The calculated activation energies assuming a concerted synchronous mechanism of the Diels–Alder reactions for butadiene–cyanoethylene with ab initio as well as the experimental values are presented in Table 2. Again when comparing the activation energies obtained by PM3 and 3-21G we can see a very strong similarity, but the selectivity and the reactivity do not follow the experimental data. Both semiempirical (AM1 and PM3) and ab initio (3-21G) methods predict that the *exo* isomers should have lower activation energies which is not consistent with the experimental evidence. In addition, the experimental activation energy for the reaction of butadiene with ethylene has been measured as 27.5 kcal mol<sup>−1</sup> [11] with reactivity increasing from ethylene to 1,1-dicyanoethylene. The 3-21G relative activation energies for the reaction of butadiene with the series of dienophiles ethylene, acrylonitrile, maleonitrile, fumaronitrile and 1,1-dicyanoethylene are 0.0, −2.8, −4.1, −4.7 and −7.4 kcal mol<sup>−1</sup>, respectively. This is in good

Table 3

Distances of the two newly formed C–C bonds (Å) in the transition states of cyclopentadiene dimerization

Type of dimerization	AM1	PM3	RHF/6-31G <sup>a</sup>
Endo	2.115	2.164	2.391
	2.091	2.147	2.031
Exo	2.186	2.184	2.302
	2.079	2.126	2.128

<sup>a</sup> Ref. 3.

correlation with the reactivity of the dienophiles. Contrary to the *ab initio* calculations, the predicted semiempirical activation energies for the butadiene–ethylene reaction are very close to the experimental value (27.1 kcal mol<sup>−1</sup> obtained by PM3; 27.5 kcal mol<sup>−1</sup> obtained experimentally), but its relative reactivity in the same series is 0.0, 0.7, 1.7, 6.8 and 0.5 kcal mol<sup>−1</sup> by AM1 and 0.0, 0.8, 2.3, 2.6 and 1.5 kcal mol<sup>−1</sup> by PM3. This prediction is almost totally opposite to the *ab initio* calculations and experimental data.

It is well established in the literature that cyclopentadiene exists at room temperature as a dimer which releases the monomer by distillation [12]. In many cyclopentadiene adducts the endo isomer is more stable than the exo [13]. The situation is the same with dicyclopentadiene. To determine the activation energies for the synchronous mechanism of the cyclopentadiene dimerization, AM1 and PM3 semiempirical calculations were performed. The generated structures are presented in Fig. 2. The transition states are more symmetrical than the one obtained with higher level *ab initio* 6-31G\* [3]. The distances of the newly formed bonds are presented in Table 3.

Major differences exist in the prediction of the activation energies of the dimerization (Table 4). Although the activation energy of the *ab initio* calculation at the RHF/6-31G\* level is higher [15] than the one calculated by both AM1 and PM3 methods, it favors correctly the endo isomer over the exo by 2.55 kcal mol<sup>−1</sup>. Both semiempirical methods predict the activation energies closer to the experimental but again they fail to predict the correct isomer (the exo isomer is favored by AM1 and PM3 methods by 2.2 and 1.7 kcal mol<sup>−1</sup>, respectively).

Table 4

Calculated and experimental activation energies (kcal mol<sup>−1</sup>) of cyclopentadiene dimerization

Type of dimerization	AM1	PM3	RHF/6-31G <sup>a</sup>	Exp
Endo	35.4	38.3	40.8	16.7 <sup>a</sup>
Exo	33.2	36.6	43.35	

<sup>a</sup> Ref. 14.

### 3.2. Diels–Alder reaction of butadiene with cyanoethylenes

In order to continue our evaluation of the AM1 and PM3 semiempirical methods in the study of the “synchronous” Diels–Alder reaction, we performed the calculation on the cyclopentadiene system where the experimental activation energies are available. The MOPAC generated structures are presented in Fig. 3. Although the *ab initio* calculations are only available for cyclopentadiene–acrylonitrile [3], it can be seen that the structural patterns are similar to those seen in the study of the butadiene–cyanoethylene Diels–Alder reaction. The structural parameters of the transition states calculated by PM3 are more similar to those calculated by 6-31G than by AM1 (Table 5). The calculated activation energies for the cyclopentadiene–cyanoethylene synchronous transition states of the Diels–Alder reaction follow the same pattern as for the butadiene–cyanoethylene synchronous mechanism (Table 6). Both methods, AM1 and PM3, predict that the most reactive cyclopentadiene–cyanoethylene pair is with ethylene, which is indeed the reaction with the highest activation energy.

The AM1 relative activation energies for the

Table 5

Distances of the newly formed C–C bonds (Å) in the cyclopentadiene–acrylonitrile generated synchronous transition states

Type of the addition	AM1	PM3	RHF/6-31G <sup>a</sup>
Endo	2.059	2.100	2.091
	2.189	2.209	2.316
Exo	2.052	2.084	2.091
	2.084	2.210	2.325

<sup>a</sup> Ref. 3.

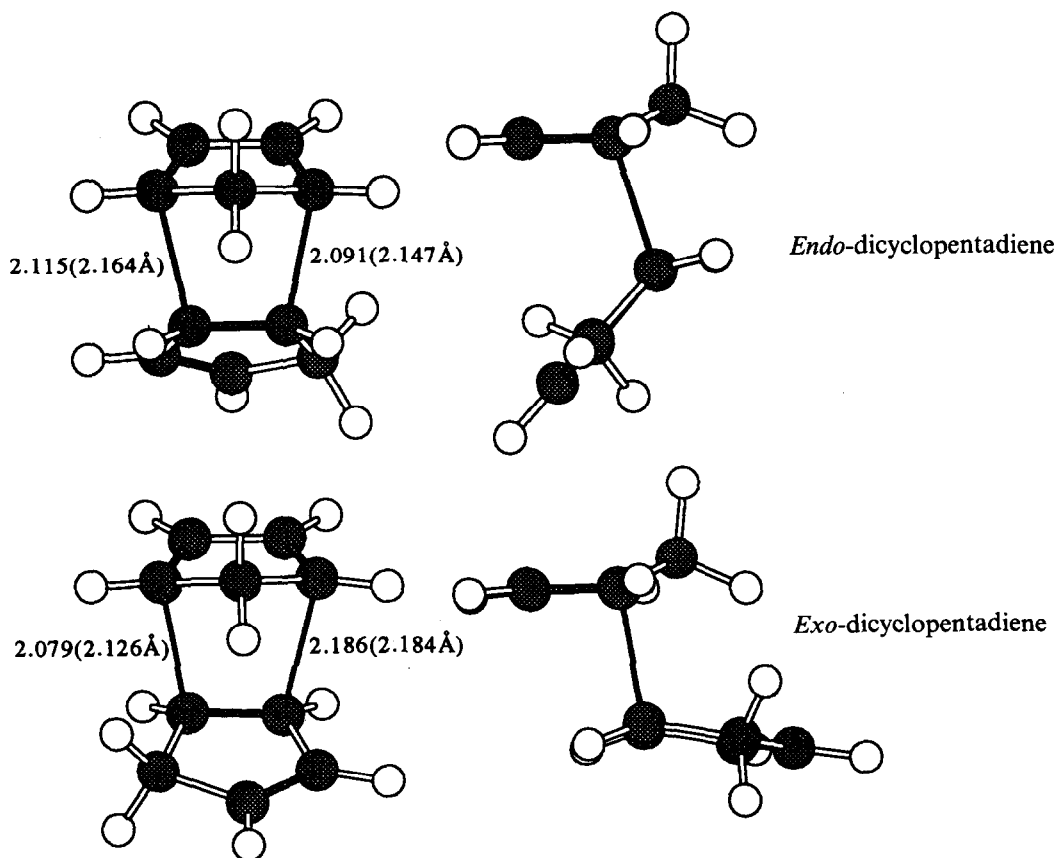


Fig. 2. (For figure caption see opposite page.)

reactions of the series presented in Table 6 in the order of their experimentally determined reactivity is 0.0, 2.4, 2.0, 3.7, 2.3, 0.7. The same relative activation energy calculated by the AM1 method is 0.0, 1.3, 2.0, 2.6, 2.4 and 1.3. The prediction of the

selectivity with the AM1 and PM3 methods is again incorrect, favoring in all cases the exo isomer. Similar results are obtained with low level ab initio calculations like RHF/STO-3G and RHF/3-21G.

Table 6

Calculated activation energies of the synchronous Diels–Alder reaction between cyclopentadiene and cyanoethylenes

Adduct	AM1	PM3	6-31G*	MP3/6-31G*//6-31G*	Exp.
Cyclopentadiene–ethylene	28.0	32.1	39.6 <sup>a</sup>	22.34 <sup>a</sup>	22.5 <sup>b</sup>
endo-Cyclopentadiene–acrylonitrile	30.4	33.4	35.88 <sup>a</sup>	18.53 <sup>a</sup>	14.0 <sup>c</sup>
exo-Cyclopentadiene–acrylonitrile	29.9	33.0	35.85 <sup>a</sup>	18.49 <sup>a</sup>	
Cyclopentadiene–fumaronitrile	30.0	34.1			12.6 <sup>d,e</sup>
endo-Cyclopentadiene–maleonitrile	31.7	34.7			11.4 <sup>e</sup>
exo-Cyclopentadiene–maleonitrile	30.3	34.5			
Cyclopentadiene–1,1-dicyanoethylene	28.7	33.4			8 <sup>f</sup>

<sup>a</sup> Ref. 3. <sup>b</sup> Ref. 16. <sup>c</sup> Ref. 17. <sup>d</sup> Ref. 18. <sup>e</sup> Ref. 5. <sup>f</sup> Ref. 19.

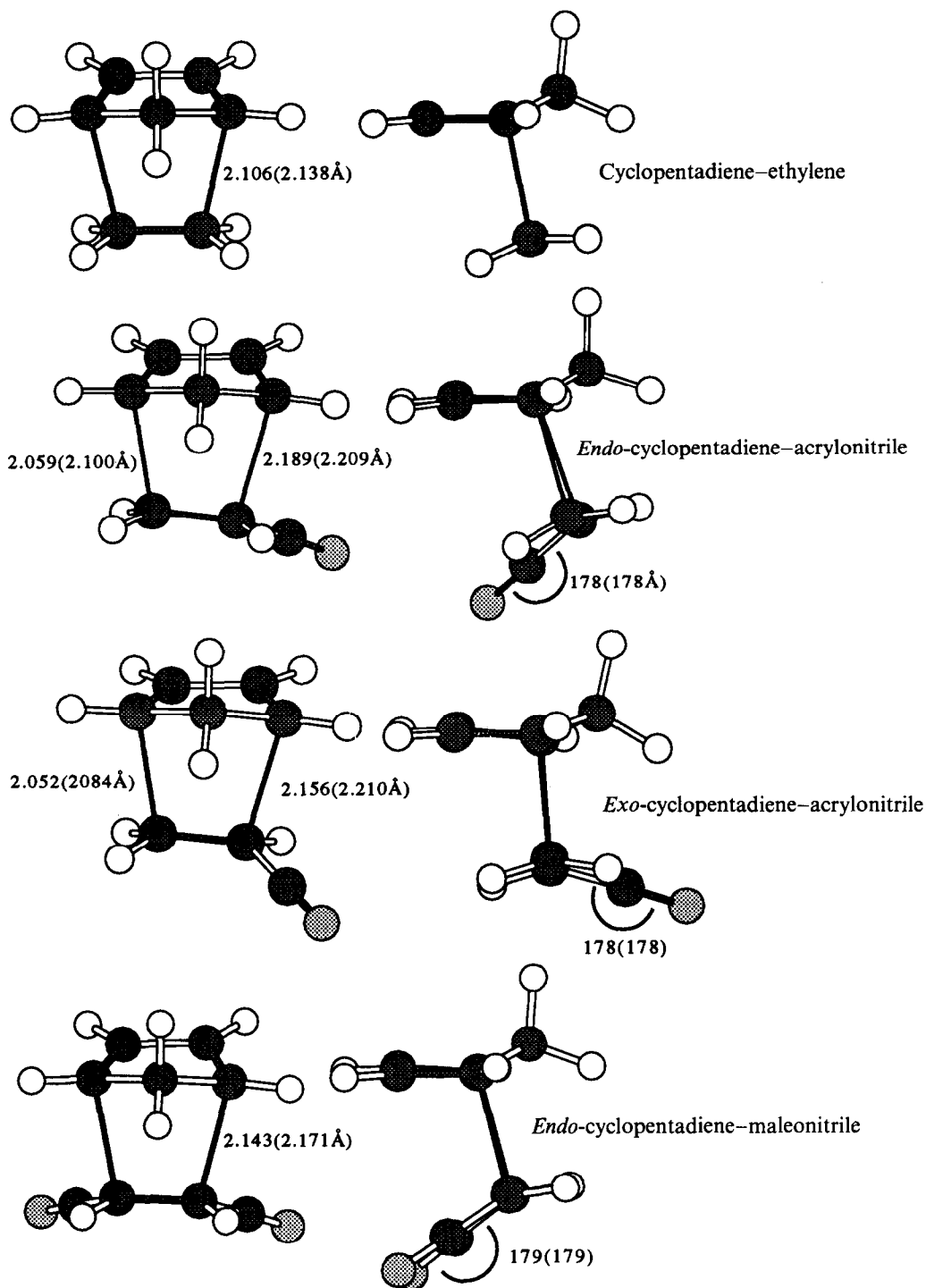


Fig. 2. AM1 and PM3 (values in parentheses) generated endo and exo transition states of cyclopentadiene dimerization.

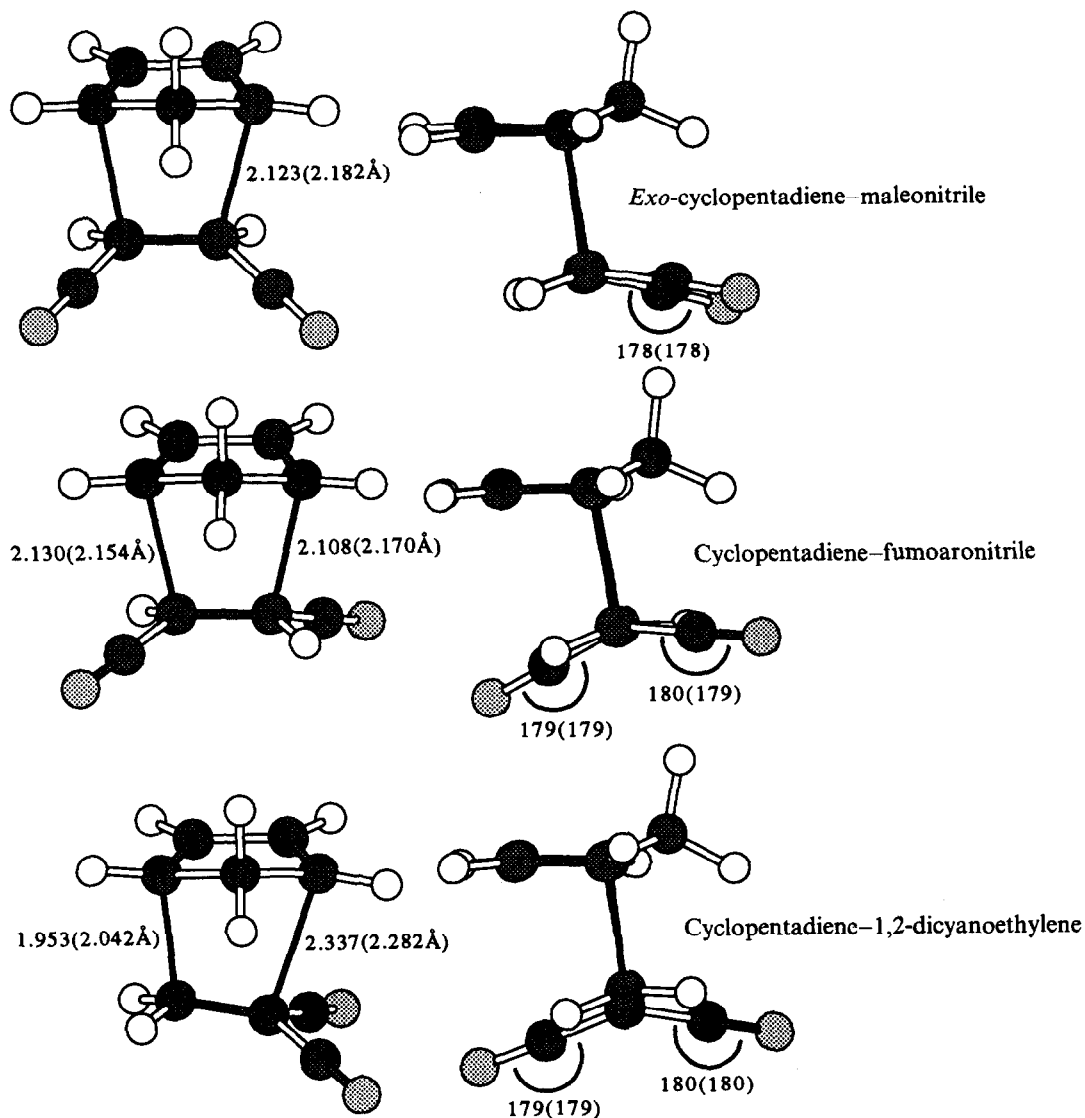


Fig. 3. AM1 and PM3 (values in parentheses) generated synchronous transition state structures of cyclopentadiene-cyanoethylene Diels-Alder adducts.

#### 4. Conclusion

The presented calculation results of the Diels-Alder transition states are based on the assumption that the mechanism of the reaction has only one transition state with formation of two C-C bonds simultaneously. The MOPAC AM1 and PM3 generated transition states are similar to the ones obtained by high level Gaussian calculations regarding the newly formed C-C bond distances

which are only 2–6% shorter. The prediction of the activation energies, however, as a more reliable physical property of the reaction since it can be determined experimentally, was a failure. The calculated order of reactivity is almost contrary to experimental data. The prediction of selectivity of the reaction for all studied cases was always wrong.

There are two possible explanations for these results: either both semiempirical AM1 and PM3 methods cannot handle the synchronous Diels-



Alder mechanism or the mechanism of this Diels–Alder reaction is not synchronous at all [20].

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