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Ab initio Studies on the Hetero Diels-Alder Cycloaddition

Bon-Su Lee*, Chan Kyung Kim, Jung Wook Choi, and Ikchoon Lee

Department of Chemistry, Inha University, Incheon 402-751, Korea

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Hetero Diels-Alder reactions containing phosphorus atom at various positions of diene and dienophile as well as standard Diels-Alder reaction between ethylene and *cis*-1,3-butadiene have been studied using ab initio method. Activation energy showed a good linear relationship with the FMO energy gap between diene and dienophile, which can be normally used to explain Diels-Alder reactivity. Since π -bond cleavage and σ -bonds formation occur concertedly at the TS, geometrical distortion of diene and dienophile from the reactant to the transition state is the source of barrier. Based on the linear correlations between activation barrier and deformation energy, and between deformation energy and π -bond order change, it was concluded that the activation barrier arises mainly from the breakage of π -bonds in diene and dienophile. Stabilization due to favorable orbital interaction is relatively small. The geometrical distortions raise MO levels of the TS, which is the origin of the activation energy. The lower barrier for the reactions of phosphorus containing dienophile (reactions C, D, and E) can be explained by the electronegativity effect of the phosphorus atom.

Introduction

Diels-Alder (DA) reaction is one of the widely used chemical reactions in organic synthesis to form a six membered cyclic compound by the reaction of a diene and a dienophile. DA reaction is believed to proceed through a concerted [4+2] mechanism¹ or two step mechanism² involving diradical intermediate. It is generally accepted that the reaction proceeds through a concerted but not synchronous transition state.³

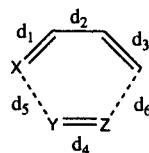
Reactivity of the DA reactions has been interpreted from the orbital interaction⁴ between frontier molecular orbitals (FMO) of reacting molecules. The primary interaction is the one between HOMO (or LUMO) of a diene and LUMO (or HOMO) of a dienophile. The regioselectivity of the DA reaction is well understood from the variation of the FMO energy level caused by the change in the reaction system, such as hetero atom substitution and/or attachment of substituents and, *inter alia*, secondary orbital interaction⁵ is the most important factor.

Hetero DA reaction is an important tool in synthesizing hetero cyclic compounds. After discovery of the existence of substituted phosphoethylene,⁶ experimental and theoretical works using this molecule as a dienophile have been actively studied.⁷ In an early study, the reactivity of the hetero DA reaction was explained based on the FMO levels,⁸ and thus information on the transition structures was not available

from the literature. In this work, we wish to study the reactivity and regioselectivity of DA reactions by the substitution of phosphorus atom at various positions of a diene and a dienophile shown in Scheme 1.

Calculation

Structures of reactants, transition states (TS), and products were minimized by the *ab initio* method using Gaussian 92 program.⁹ The 3-21G* basis set¹⁰ was used in the reaction of phosphorus containing compounds and 3-21G basis set¹¹ was used in the reaction between ethylene and *cis*-1,3-butadiene and this reaction is referred to a standard DA reaction. In all cases, *s-cis* conformer of a diene was used as a starting structure. Two isomers were possible in the case of *cis*-1,3-phosphabutadiene depending on the location of H atom attached to the phosphorus atom. Only the trans structure was used in the calculations.¹² Approximate TS's were located



A: X, Y, Z = CH₂

B: X = PH; Y, Z = CH₂

C: X, Z = CH₂; Y = PH

D: X, Y = PH; Z = CH₂

E: X, Z = PH; Y = CH₂

Scheme 1.

*To whom correspondence should be addressed.

Table 1. 3-21G* optimized bond lengths (in Å) and total energy (in a.u.) of the transition state and product for the reactions shown in Scheme 1^a

Reaction	Transition state							Product							
	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	E	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	E	
A ^b	1.370	1.394	1.370	1.376	2.210	2.210	-231.60321	1.515	1.318	1.515	1.540	1.541	1.541	-231.72915	
B	1.701	1.399	1.369	1.370	2.538	2.261	-532.46798	1.820	1.322	1.515	1.543	1.849	1.539	-532.58390	
C	endo	1.366	1.406	1.360	1.693	2.493	2.337	-532.47563	1.516	1.318	1.515	1.849	1.851	1.543	-532.58204
	exo	1.363	1.404	1.363	1.700	2.568	2.280	-532.47128	1.512	1.318	1.512	1.868	1.867	1.561	-532.57817
D	endo	1.695	1.415	1.354	1.684	2.862	2.457	-833.33436	1.819	1.321	1.516	1.853	2.187	1.544	-833.43880
	exo	1.695	1.411	1.357	1.689	2.856	2.444	-833.33422	1.831	1.323	1.516	1.856	2.194	1.547	-833.43405
E	endo	1.687	1.418	1.357	1.687	2.730	2.619	-833.33761	1.818	1.321	1.516	1.851	1.852	1.850	-833.43798
	exo	1.689	1.415	1.357	1.688	2.668	2.666	-833.33368	1.822	1.323	1.520	1.852	1.856	1.856	-833.43632

^aBond lengths (in Å) and total energy (in a.u.) of the reactants are as follows; (*cis*-1,3-butadiene(3-21G): d₁=d₃=1.319, d₂=1.477, E=-154.05515), (*cis*-1,3-phosphabutadiene: d₁=1.660, d₂=1.472, d₃=1.322, E=-454.90130), (ethylene(3-21G): d₁=1.315, E=-77.60099), (phosphaethylene: d₁=1.645, E=-378.44631). ^b3-21G calculation.

using the combined distances of the two terminal atoms between a diene and a dienophile with the reaction coordinate method¹³ and final structure was refined using OPT=CALL option from a preoptimized structure which has the highest energy before sudden drop in energy. Two TS's, endo and exo, were obtained depending on the orientation of P-H bond of phosphaethylene. TS's were verified by the only one negative imaginary frequency and other stationary points by all positive frequencies. MP2/6-31G*¹⁴ single point calculations have been done at the 3-21G* optimized structures in order to include electron correlation qualitatively.

Results and Discussion

3-21G* (3-21G in reaction A) optimized geometries and absolute energy of the reactants, TS's and products are summarized in Table 1. Bond lengths of the terminal atoms at TS are 2.21-2.48 Å between carbon atoms, 2.49-2.73 Å between carbon and phosphorus atoms, and 2.86 Å between two phosphorus atoms. Two TS's are possible depending on the orientation of P-H group of phosphaethylene, and the endo TS has lower energy than the *exo* TS due to reduced repulsion between P lone pair and π -MO's of a diene in the former, and this effect is usually known as endo lone pair effect.¹⁵ Since the TS structures involving phosphorus atom have similar orientation as that of reaction A, σ -lone pair of P atom could not participate in the reaction.

Activation energies, FMO energy differences in reactants are summarized in Table 2. From the data shown in Table 2, it is reasonable to assume that the reactivity of the DA reactions can be predicted from HOMO, LUMO energy gaps because the decrease in activation energy is proportional to the decrease in FMO energy gap. This explanation cannot be applied in the case of reactions D, E because of neglect in other stereoelectronic effects. The FMO energy gaps can be divided into two components depending on the MO's involved, that is, the energy difference between LUMO of dienophile and HOMO of diene, $\Delta E^{\text{FMO}}(1)$, and between HOMO of dienophile and LUMO of diene, $\Delta E^{\text{FMO}}(2)$. If $\Delta E^{\text{FMO}}(1) > \Delta E^{\text{FMO}}(2)$, it could be considered as normal electron flow and if $\Delta E^{\text{FMO}}(1) < \Delta E^{\text{FMO}}(2)$, it could be as inverse electron

Table 2. Summary of the activation energies (ΔE^{\ddagger} , in kcal/mol), and differences^a in FMO energy levels ($\Delta E^{\text{FMO}}(1)$, $\Delta E^{\text{FMO}}(2)$, in a.u.) for the hetero Diels-Alder reactions shown in Scheme 1

Reaction	$\Delta E^{\ddagger b}$	$\Delta E^{\text{FMO}}(1)$	$\Delta E^{\text{FMO}}(2)$
A	33.21 (14.38)	0.521	0.518
B	21.53 (5.66)	0.508	0.444
C	endo 16.20 (1.07)	0.416	0.501
	exo 18.93 (3.50)	0.416	0.501
D	endo 8.31 (-3.62)	0.404	0.427
	exo 8.40 (-4.02)	0.404	0.427
E	endo 6.28 (-4.87)	0.404	0.427
	exo 8.74 (-2.72)	0.404	0.427

^a $\Delta E^{\text{FMO}}(1) = E(\text{LUMO, dienophile}) - E(\text{HOMO, diene})$ and $\Delta E^{\text{FMO}}(2) = E(\text{LUMO, diene}) - E(\text{HOMO, dienophile})$. ^bActivation energies calculated at MP2/6-31G*/3-21G* (or 3-21G) are shown in parentheses.

flow.¹⁶ From Table 2, we can easily find that there is a good correlation between activation energy and the electron flow, that is, reactions with normal electron flow (reactions C, D, E) have a lower activation energy than the reactions (reactions A, B) with inverse electron flow.

The MP2/6-31G* single point calculation lowers the activation energy too much due to the overestimation of the electron correlation in the transition state.^{4b} But the relative reactivity does not change by the inclusion of electron correlation effect.

Using FMO energy gap differences alone, it is not easy to predict the height as well as existence of the activation barrier of DA reactions-this reaction should not have any barrier because the FMO correlation diagram favors orbital interactions between HOMO and LUMO. This simple idea could be in error because the MO's involved in the reaction do change energy levels as the reaction proceeds. Since the major component of a DA reaction is the transformation of three π -bonds into one π -bond and two σ -bonds, weakening of π -bonds could affect the magnitude of the activation barrier. Stabilizing effect from forming σ -bonds would be small

Table 3. Summary of deformation energies of diene ($\Delta E^{\text{def}}(\text{D})$), dienophile ($\Delta E^{\text{def}}(\text{P})$), total ($\Delta E^{\text{def}}(\text{T})$), and bond order changes of diene ($\Delta n_{\pi}(\text{D})$), dienophile ($\Delta n_{\pi}(\text{P})$), and total ($\Delta n_{\pi}(\text{T})$) for the hetero Diels-Alder reactions shown in Scheme 1^a

Reaction	$\Delta E^{\text{def}}(\text{D})$	$\Delta E^{\text{def}}(\text{P})$	$\Delta E^{\text{def}}(\text{T})$	$\Delta n_{\pi}(\text{D})$	$\Delta n_{\pi}(\text{P})$	$\Delta n_{\pi}(\text{T})$
A	22.61	10.76	33.37	-0.219	-0.341	-0.560
B	13.83	8.88	22.71	-0.210	-0.310	-0.520
C endo	14.51	3.62	18.13	-0.203	-0.272	-0.475
C exo	15.06	4.51	19.57	-0.195	-0.314	-0.509
D endo	7.17	2.21	9.38	-0.168	-0.218	-0.386
D exo	7.41	2.34	9.75	-0.167	-0.248	-0.415
E endo	6.60	1.96	8.56	-0.151	-0.236	-0.387
E exo	7.37	2.76	10.13	-0.149	-0.242	-0.391

^aEnergies in kcal/mol.

because of distances between two interacting fragments. In order to find the degree of geometrical distortion in the DA reaction, deformation energies¹⁷ of a diene and a dienophile were calculated and these are shown in Table 3. Deformation energy is defined as the energy required to transform reactant from its ground state to TS and it can be thought as the energy change caused by orbital rotation to achieve maximum overlap between MO's involved. In this work, we can define two deformation energies; deformation energy of a diene, $\Delta E^{\text{def}}(\text{D})$, and deformation energy of a dienophile, $\Delta E^{\text{def}}(\text{P})$. Sum of the deformation energies is defined as total deformation energy, $\Delta E^{\text{def}}(\text{T})$. Deformation energy has been successfully applied to S_N2 reactions to correlate activation energy and geometrical change,¹⁸ and it might be interesting to check if this correlation exists for the DA reaction. Plots of ΔE^{\ddagger} vs. deformation energies were displayed in Figure 1 using the data shown in Table 3. From the plot, we can find linear correlations between ΔE^{\ddagger} and three deformation energies ($\Delta E^{\text{def}}(\text{D})$, $\Delta E^{\text{def}}(\text{P})$, and $\Delta E^{\text{def}}(\text{T})$), which indicates that the major contribution to the activation energy came from the deformation of diene and dienophile*. Especially, unit slope in the correlation between ΔE^{\ddagger} and $\Delta E^{\text{def}}(\text{T})$ could be a direct indication that the molecular deformation is the source of the activation energy. On the other hand, there is a slight stabilizing effects originating from the favorable interaction of HOMO and LUMO of the reactant, and the magnitude of this stabilizing interaction might be obtained from the intercept of a plot of ΔE^{\ddagger} vs. $\Delta E^{\text{def}}(\text{T})$ shown in Figure 1 (-2.2 kcal/mol).

At the TS, π -bonds of diene and dienophile is breaking and new σ -bonds are forming between terminal atoms of a diene and a dienophile. In order to see the correlation between activation energy and degree of π -bond breaking, Pauling bond order¹⁹ of each π -bond was calculated using eq. (1), where $R(1)$ and $R(n)$ refer to bond with bond order

$$n = \exp \{ [R(1) - R(n)] / \alpha \} \quad (1)$$

1 and n , respectively, and α is a variable constant. The α values were calculated from the optimized structures of reactants and products in order to incorporate difference in bond lengths between second and third row elements: The $\alpha(\text{C-C})$ was 0.326 using $R(1)$ as d_5 bond of cyclohexene and R

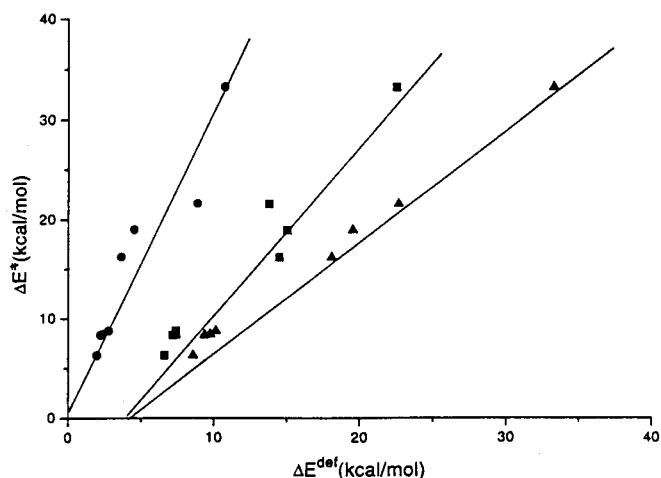


Figure 1. Plots of ΔE^{\ddagger} vs. $\Delta E^{\text{def}}(\text{D})$ ($r=0.945$), $\Delta E^{\text{def}}(\text{P})$ ($r=0.979$), and $\Delta E^{\text{def}}(\text{T})$ ($r=0.999$). Data symbols refer to the following: ■, $\Delta E^{\text{def}}(\text{D})$; ●, $\Delta E^{\text{def}}(\text{P})$; ▲, $\Delta E^{\text{def}}(\text{T})$. A best linear regression equation between ΔE^{\ddagger} and $\Delta E^{\text{def}}(\text{T})$ is $\Delta E^{\ddagger} = 1.06 \Delta E^{\text{def}}(\text{T}) - 2.16$.

($n, n=2$) as d_4 bond of ethylene. The $\alpha(\text{C-P})$ was 0.289 using $R(1)$ as d_5 bond of endo product of reaction C and $R(n, n=2)$ as d_4 bond of phosphoethylene. The π -bond order, n_{π} , could be $n-1$ assuming that the bond order from eq. (1) is sum of σ - and π -bond and σ bond order didn't change throughout the reaction. Difference in π -bond order, Δn_{π} , of each double bond in reactant can be obtained by the difference in bond orders between TS and reactant shown in eq. (2), where

$$\Delta n_{\pi} = n_{\pi}^{\text{TS}} - n_{\pi}^{\text{R}} \quad (2)$$

n_{π}^{TS} and n_{π}^{R} refer to the bond order at TS and reactant, respectively. Bond order change of a diene, $\Delta n_{\pi}(\text{D})$ and of dienophile, $\Delta n_{\pi}(\text{P})$ and total bond order change, $\Delta n_{\pi}(\text{T})$ were also tabulated in Table 3. Reference to Table 3 reveals that when the reaction involves phosphoethylene dienophile (as in reactions C, D, and E), the decrease in Δn_{π} , especially in $\Delta n_{\pi}(\text{P})$, is relatively large. This suggests facile cleavage of the π bond in the phosphorus containing dienophile since a $d_{\pi}(\text{P})-p_{\pi}(\text{C})$ bond should be weaker than a $p_{\pi}-p_{\pi}$ bond as the longer bond length ($d_4=1.645 \text{ \AA}$ for $\text{P}=\text{C}$ vs 1.315 \AA for $\text{C}=\text{C}$) in Table 1 and lower deformation energies, $\Delta E^{\text{def}}(\text{P})$ and $\Delta E^{\text{def}}(\text{T})$, in Table 3 indicate. Plots of activation energy vs. bond order changes shown in Figure 2, exhibits a good linear correlation in all cases. This might be an indirect indication that the activation energy of DA reaction comes from the destabilization caused by the cleavage of π -bonds in diene and dienophile.

From the linear relationships found in Figures 1 and 2, we could safely predict similar linear relationships between deformation energies and bond order changes, and these are displayed in Figure 3. From the linear correlations found in Figures 1, 2 and 3, the reactivity of DA reactions will depend on the changes in the molecular structure and this could be directly related to the change in π -bond lengths.

R. D. Bach, *et al.*, reported²⁰ that the origin of the barrier in the DA reaction comes from the closed-shell repulsion of π electrons. In order to check the FMO level changes, MO's of diene and dienophile and TS are shown in Figure

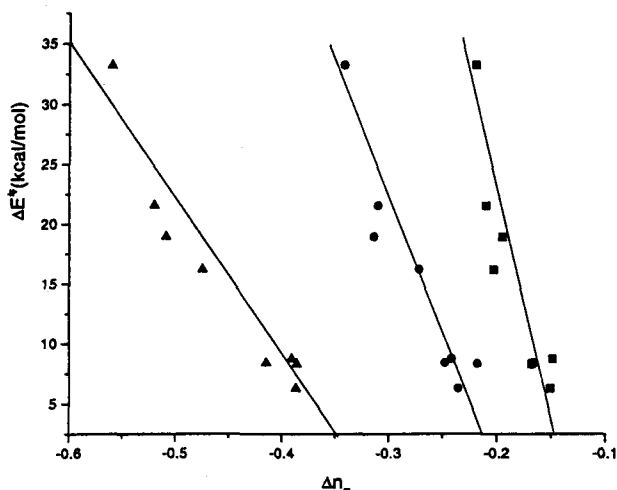


Figure 2. Plots of ΔE^* vs. $\Delta n_n(D)$ ($r=0.908$), $\Delta n_n(P)$ ($r=0.944$), and $\Delta n_n(T)$ ($r=0.960$). Data symbols refer to the following: ■, $\Delta n_n(D)$; ●, $\Delta n_n(P)$; ▲, $\Delta n_n(T)$.

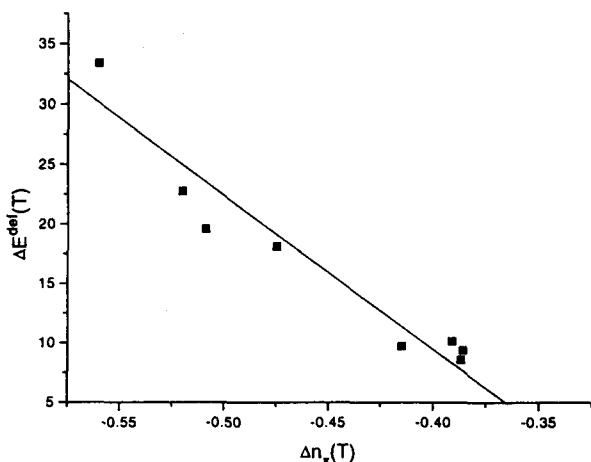


Figure 3. A plot of $\Delta E^{\text{def}}(T)$ vs. $\Delta n_n(T)$. Correlation coefficient of the plot is 0.962.

4. In this Figure, MO's of diene, dienophile, and TS are labelled as $\phi_1 \sim \phi_4$, π and π^* , and $\Psi_1 \sim \Psi_6$, respectively. From the correlation of MO's in reactant and TS, it can be seen that ψ_1 is stabilized while ψ_2 and ψ_3 are destabilized and thus results in the net destabiliation (Destabilization energy was 39.8 and 36.6 kcal/mol at HF/6-31G* and 3-21G calculation, respectively). Introduction of phosphorus atom into the reaction system did not change orbital interaction pattern shown in Figure 4 considerably. But in the case of phosphae-ethylene dienophile, there should be an energy change in π and π^* orbitals due to the difference in the electronegativity between carbon and phosphorus. The energy level shift will change energy gaps between interacting MO's and thus increases stabilizing effect and decreases destabilizing effects, which is the main cause of the lower activation energy of DA reactions involving phosphaeethylene dienophile with respect to ethylene dienophile. Works on the hetero DA reactions are in progress in our laboratory to study hetero atom effect systematically.

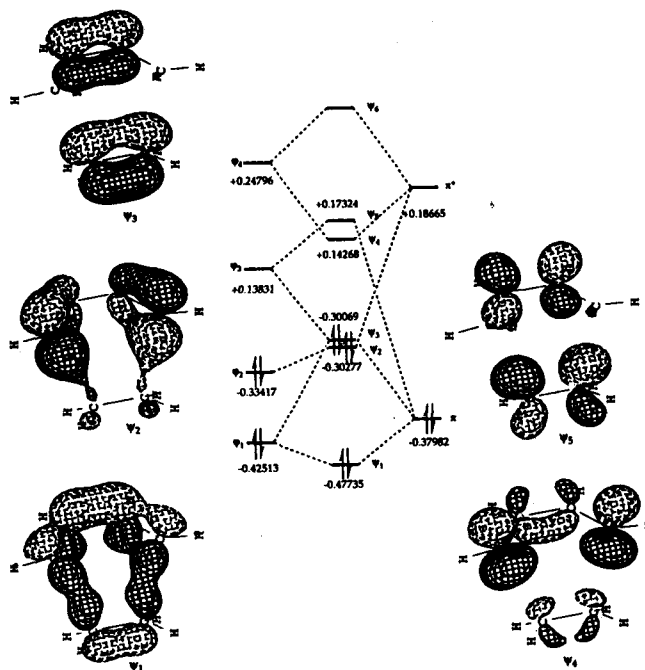


Figure 4. MO interaction diagram in the DA reaction between ethylene (π , π^*) and butadiene ($\phi_1 \sim \phi_4$) to form MO's at TS ($\psi_1 \sim \psi_6$). Numbers indicate orbital energies in a.u. calculated at 3-21G.

Conclusion

We can conclude that π -bond breaking is the main source of the activation barrier of DA reactions and the magnitude of the barrier could be estimated from the total deformation energy. Reactions with normal electron flow have lower energy barrier than the reactions with inverse electron flow, and this is caused by the MO energy change upon substitution of carbon by phosphorus atom in the dienophile.

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Inclusion of the deformation energies calculated from the TSs for the reactions D' and E' do not change the results obtained in Figure 1. The results are as follows; correlation coefficients (ΔE^ vs $\Delta E^{\text{def}}(D)$: $r=0.972$), (ΔE^* vs $\Delta E^{\text{def}}(P)$: $r=0.948$), (ΔE^* vs $\Delta E^{\text{def}}(T)$: $r=0.992$), (linear regression between ΔE^* and $\Delta E^{\text{def}}(T)$: $\Delta E^* = 1.10 \Delta E^{\text{def}}(T) - 3.39$).

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 - A referee pointed out the the energy difference between two isomers is too small ($E(\text{trans}) = -454.90131$ H, $E(\text{cis}) = -454.90119$ H). Calculations on the DA reactions between *cis*-phosphabutadiene and phosphoethylene have been carried out and the reactions are labelled as reaction D' and E' analogous to the reactions D and E, respectively. Final optimized energies are as follows; $E(\text{D}'\text{-endo-TS}) = -833.33501$ H, $E(\text{D}'\text{-endo-product}) = -833.33084$ H, $E(\text{D}'\text{-exo-TS}) = -833.43535$ H, $E(\text{D}'\text{-exo-product}) = -833.43207$ H, $E(\text{E}'\text{-endo-TS}) = -833.33798$ H, $E(\text{E}'\text{-endo-product}) = -833.43678$ H, $E(\text{E}'\text{-exo-TS}) = -833.33429$ H, $E(\text{E}'\text{-exo-product}) = -833.43449$ H.
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