Probing the Structural and Electronic Effects on the Origin of Π-Facial Stereoselectivity in 1-Methylphosphole 1-Oxide Cycloadditions and Cycldimerization

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Supporting Information

ABSTRACT: We have examined the Π-facial stereoselectivity in the Diels−Alder reactions of phosphole oxides computationally. The experimentally observed syn-cycloadditions have been rationalized with the Cieplak model and distortion−interaction model. The natural bond orbital analysis suggests that the hyperconjugative interactions are energetically preferred between the antiperiplanar methyl group present in the −P=O unit and the developing incipient (−C=C−) bond in syn-adducts in accordance with the Cieplak model. The distortion−interaction analysis carried out for syn and anti transition states of Diels−Alder reactions of 1-substituted phosphole 1-oxide with different dienophiles reveals that the syn selectivity is favored by distortions and interaction energies compared with the anti selectivity. The formation of a syn adduct is also stabilized by the \( \pi_C−\sigma_{PO} \) orbital interaction, and the repulsive \( n-\pi \) interaction destabilizes the anti adduct that leads to the 7.0 kcal/mol thermodynamic preference for the former adduct. Furthermore, the distortion−interaction model rationalizes the formation of stereospecific products in these Diels−Alder reactions, which however is not explicable with the much-debated Cieplak model.

INTRODUCTION

The Diels−Alder reactions of P(IV) derivatives of phosphole have attracted the attention of experimental and computational chemists because such reactions form a 7-phosphanorbornene moiety that holds unique properties of its P-center.1−5 The significance of the 7-phosphanorbornene derivatives was explained by Quin, Mathey et al., in fragmentation-related phosphorylation reactions,6,7 complexations,8−10 and in refuncionalization11−14 including deoxygenations.15−17 Westheimer first reported the preparation of P(IV) derivatives of phosphole, which was further explored for the synthesis of the dimers of phosphole derivatives including oxides, sulfoxides, and quaternary salts.18−20

The synthesized dimers of phosphole derivatives including oxides, sulfoxides, and quaternary salts are stereospecific, and no other products have been reported in such studies. Keglevich et al. also reported that the different substitutions at P(11)−O of phosphole oxides are regio- and stereospecific though such Diels−Alder reactions can give many isomers.21 No isomeric mixture has been reported till date. The product from the dimerization shows endo-fusion of the rings with bridged P−O located anti to the newly formed double bond in the adduct and both phosphoryl oxygens directed inward (Scheme 1). The [4 + 2] cycloaddition of phosphole 1-oxide with N-phenyl- or N-methylmaleimide was also reported.22

To explain these observed results, Keserü et al. performed semiempirical and ab initio calculations using PM3 and HF/3-21G* methods.23 All geometries and transition states (TSs) of 1-methylphosphole 1-oxide were performed by the PM3 method, and the preference led to the endo ring fusion from the enthalpy of activation (\( \Delta H^\# \)) data of all of the possible isomers in cycldimerization of 1-methylphosphole 1-oxide and P(11)−O is anti to the newly formed (−C=C−) double bond in the norbornene moiety. Furthermore, Kovács et al. have carried out experimental as well as theoretical studies on the 7-phosphanorbornene moiety to study the [4 + 2] cycloaddition reaction and later concluded that the formation of one of the endo isomers is energetically favored over the other isomers based on density functional theory (DFT).
calculations. The DFT results corroborate the experimental and single-crystal X-ray results. These studies primarily focused on rationalizing the formation of exo/endo products and regioselectivity of P(IV) derivatives of phospholes.

In this article, we have investigated the formation of syn and anti isomers of P(IV) derivatives of phosphole computationally. Therefore, this study was examined with the stable regio- and stereoisomers of phosphole with different dienophiles (Scheme 2). The formation of syn product can be rationalized with the hyperconjugative Cieplak model and also with the distortion–interaction strain model.

**RESULTS AND DISCUSSION**

The free energies of activation of the transition states and adducts were calculated using the B3LYP/6-31G(d) level of theory (Figure 1 and Table S1). A number of Diels–Alder reactions have been studied using the B3LYP DFT functional and reported in the literature. The calculated results were found to be in good agreement with the experimental observations, and other DFT functionals such as M06-2X also corroborated well with B3LYP results. We have computed the activation free energies for the syn and anti endo isomers of Diels–Alder reactions of 1-methylphosphole 1-oxide with different dienophiles like 1-methylphosphole 1-oxide and N-methylmaleimide, which were experimentally examined by Kovács et al. (Scheme 2). Ethylene has been chosen as a model dienophile to explore the Diels–Alder reaction with phosphole 1-oxide.

Initially, we have calculated the syn and anti transition structures and the adduct with ethylene as the diene molecule. The incipient bonds formed in the syn and anti isomers were synchronous in nature in the transition state geometries with distances of 2.28 and 2.30 Å, respectively (Figure 1).
formation of the syn adduct is both a kinetically and thermodynamically favored process. The activation free energies (Δ\(\text{G}\)) for the syn and the anti transition states (TS-1-syn, TS-1-anti) are 28.8 and 37.1 kcal/mol, respectively, at the B3LYP/6-31G(d) level of theory (Figure 1). To examine the relative preference for the formation of syn adduct using the B3LYP functional, we have also examined this reaction with the M06-2X/6-31G(d) level of theory. M06-2X describes the dispersion forces better than the B3LYP functional.27 The calculated results with M06-2X corroborate the formation of syn adduct for 1-methylphosphole 1-oxide as diene and ethylene as dienophile (Figure S1).

There are reports where Fallis et al. examined the syn/anti facial selectivity of thiophene 1-oxide adducts with many dienophiles, and the syn selectivity was attributed to the Cieplak effect.28−30 The Cieplak model was employed to rationalize many facial selectivity reactions. The Cieplak model is based on a hypothesis, in which the antiperiplanar donor orbital and the \(\sigma^*\) antibonding orbital of the incipient bonds overlap to stabilize the facial selective product formation. Therefore, hyperconjugative stabilization energy was examined using natural bond orbital (NBO) as implemented in Gaussian 09 (Figure 2).31−36 The better donor methyl group at the P(11)–O position of 1-methylphosphole 1-oxide is antiperiplanar to the incipient bonds (C2–C7 and C3–C8 bonds) in the syn adduct for the Diels–Alder reaction between 1-methylphosphole 1-oxide and ethylene. The second-order perturbation theory calculations, \(E(2)\), suggest that the hyperconjugative interactions are possible in the syn isomer (0.6 kcal/mol). On the other hand, the anti endo isomer yields a lower hyperconjugation interaction energy (0.3 kcal/mol). Therefore, it appears that the Cieplak model might operate during the formation of syn isomer in such Diels–Alder reactions. The effect of solvent on the syn/anti selectivity was also examined. These Diels–Alder reactions were carried out in triethylamine as a solvent; therefore, we have also performed single-point calculations using triethylamine as a solvent. The calculated results with polarizable continuum model (PCM)\(_{\text{triethylamine}}^\text{M062-X/6-31G(d)}\) showed lower activation barriers for the syn and anti transition states; however, they are in good agreement with the B3LYP/6-31G(d) gas-phase results (Table S2).

The distortion–interaction analysis was carried out with the syn and anti transition states of 1-methylphosphole 1-oxide and ethylene as a dienophile. Figure 3 shows that the 5.0 kcal/mol energy preference for the syn transition state is derived.
from the distortion energies of the diene. The distortion in the dienophile for syn and anti transition states is similar (∼0.3 kcal/mol); however, the interaction energy favors the formation of the syn transition state by 3.4 kcal/mol.

The study extended with the dimerization of 1-methylphosphole 1-oxide using the same level of theory. Initially, we have calculated the hyperconjugative interaction of the 1-methylphosphole 1-oxide dimer using NBO analysis by second-order perturbation theory, $E(2)$, calculations, where the methyl group is present on the bridge position P(11)−O, which is antiperiplanar to the incipient bonds. The hyperconjugative stabilizing interaction energy for the syn form of 1-methylphosphole 1-oxide is 0.6 kcal/mol, similar to that obtained with dienophiles like ethylene, whereas for the anti isomer, the hyperconjugative interaction energy is 0.3 kcal/mol between the donor P(11)−O bond and the newly formed incipient −C−C− bond (Figure 2).

The distortion−interaction energy was further considered for the formation of the dimer with 1-methylphosphole 1-oxide. The incipient bonds formed in the TS-2-syn endo and TS-2-anti endo isomers were asynchronous in nature in the transition state geometries with the distances of 2.05 and 2.96 Å in syn geometry and 2.12 and 3.24 Å in the anti geometry (Figure 4). Recently, Kovács et al. reported the similar asynchronicity in the transition state geometries of 1-methylphosphole 1-oxide dimerization using the HF/3-21G level of theory.\(^{22}\) The activation energies using B3LYP/6-31G(d) for the syn and anti transition states of the dimer of 1-methylphosphole 1-oxide are 7.7 and 15.7 kcal/mol, respectively. The calculated PCM_{triethylamine}-M06-2X/6-31G(d) level of theory showed lower activation barriers for syn and anti transition states compared with the anti transition state geometries with the distances of 2.05 and 2.96 Å in syn geometry and 2.12 and 3.24 Å in the anti geometry (Figure 4).

The [4 + 2] cycloadditions of 1-alkyl-3-methyl-2,5-dihydro-1H-phosphole with N-methylmaleimide and N-phenylmaleimide were also reported.\(^{22}\) The syn cyclo-adducts were also found in each case, and no anti products were reported. Therefore, we have examined the cycloaddition of 1-methylphosphole 1-oxide with the dienophile N-methylmaleimide computationally. Second-order perturbation energy, $E(2)$, calculations were performed, where the methyl group present on P(11)−O antiperiplanar to the newly formed incipient bond shows hyperconjugative interaction (0.5 kcal/mol) and the anti isomers show hyperconjugative interaction (0.3 kcal/mol), where the P(11)−O donor bond is antiperiplanar to the incipient (−C−C−) bond (Figure 2).\(^{31−36}\) These results corroborate the Cieplak model for the formation of syn adduct as observed in previous cases.

The transition state calculations performed for 1-methylphosphole 1-oxide and N-methylmaleimide showed that the bond formation is synchronous in nature (Figure 6).

The distortion−interaction energies for the Diels−Alder reaction between 1-methylphosphole 1-oxide and N-methylmaleimide are shown in Figure 7. The distortion energies in the dienophile for syn and anti transition states are similar in this case. Distortion−interaction strain model results show that the 5.0 kcal/mol energy preference for the syn transition state is derived from the distortion energies of the diene, and also
The experimental reports on these Diels–Alder studies showed very clearly with different dienophiles that the exo isomers are not formed in any of such cases. Therefore, to extend the study to examine the complete stereospecificity, exo isomers have also been computed. The activation free energies of syn and anti exo isomers calculated at B3LYP/6-31G(d) level of theory (Scheme 2). The calculated distortion energies for the syn endo and anti endo transition structures for the Diels–Alder reaction of 1-methylphosphole 1-oxide with N-methylmaleimide (brown, activation energy; green, distortion energy of the diene; and red, interaction energy; in kcal/mol). Bond lengths are reported in angstrom (Å).

The interaction energy favors the formation of the syn transition state by 3.4 kcal/mol.

The hyperconjugative interactions $E(2)$ calculated for the syn exo isomers suggest that the donation from the donor (−CH$_3$) group to the newly formed (−C−C−) bonds is larger or comparable to that from their corresponding syn endo isomers (Table S4). Therefore, it appears that the Cieplak effect can rationalize the formation of the syn adduct in all of the cases studied; however, the exclusive formation of the endo isomer cannot be explained. The distortion–interaction model performed for the exo isomers suggests that the diene distortion energy is much higher than that of their corresponding endo isomers and that interaction energies also prefer the formation of later isomers (Figures S3 and S4).

The examination of the syn and the anti transition states of 1-methylphosphole 1-oxide with ethylene, its dimer, and N-methylmaleimide suggests that the filled, filled and filled, and unfilled orbital interactions might occur in these cases. The NBO-calculated second-order perturbation energy results reveal that the $\pi_{CC}^\sigma$−$\sigma_{PO}^\pi$ interaction can contribute to stabilizing the syn isomers and the computed values are 2.3 kcal/mol for 1-syn, 2.2 kcal/mol for 2-syn endo, and 2.2 kcal/mol for 3-syn endo adducts (Figures 8a and S5, S6). On the other hand, the anti isomer shows a repulsive n−π interaction between the nonbonding oxygen lone pair of the phosphorus moiety and the $\pi_{C=C}$ bond (Figures 8b and S7).42 Therefore, secondary orbital interactions reveal that the $\pi_{CC}^\sigma$−$\sigma_{PO}^\pi$ interaction also contributes to the formation of the syn adduct and the repulsive n−π interaction in the anti adduct leads to the thermodynamic preference for the syn adduct.

Note that the syn isomers of these Diels–Alder adducts can experience attractive intramolecular C−H⋯π-type interactions between the C−H proton of the P−CH$_3$ unit and the olefinic π-unit of the norbornene ring (Figure S8). The calculated structures of the syn isomers of 1-syn, 2-syn endo, and 3-syn endo reveal that the intramolecular C−H⋯π distances are within the sum of the van der Waals radii (<2.9 Å). There are reports available in the literature to support the intramolecular C−H⋯π interactions in a variety of systems.45 The nuclear Overhauser enhancement effect substantiates the intramolecular C−H⋯π interactions in similar systems. However, such C−H⋯π interactions would be relatively weaker compared with intramolecular C−H⋯π interactions as in the latter case the −C−H donor unit can align to achieve a better direction for interaction with the π-system.46

**CONCLUSIONS**

The present study explores the Diels–Alder reactions of 1-methylphosphole 1-oxide with dienophiles like ethylene, 1-methylphosphole 1-oxide and N-methylmaleimide using the B3LYP/6-31G(d) level of theory (Scheme 2). The calculated results suggest that the syn endo isomers are energetically favored compared to the anti endo isomers. The Cieplak model rationalizes the formation of the syn adduct due to the

![Figure 6](image6.png)

**Figure 6.** Activation energy and activation free energy of TS-3-syn endo and TS-3-anti endo are labeled in bold and parentheses, respectively (reported in kcal/mol). Bond lengths are reported in angstrom (Å).

![Figure 7](image7.png)

**Figure 7.** B3LYP/6-31G(d) level of theory calculated distortion interaction energies for the syn endo and anti endo transition structures for the Diels–Alder reaction of 1-methylphosphole 1-oxide with N-methylmaleimide (brown, activation energy; green, distortion energy of the diene; and red, interaction energy; in kcal/mol).

![Figure 8](image8.png)

**Figure 8.** (a) Stabilizing $\pi_{CC}^\sigma$−$\sigma_{PO}^\pi$ interaction in the syn adduct (1-syn) and (b) destabilizing n$\pi$interaction in the norbornene unit of the 1-anti adduct.
stronger hyperconjugative interaction arising between the donor (−CH₃) group and the antiplanar incipient bond formed in Diels–Alder reactions between 1-methylphosphol-1-oxide (dieno) and ethylene, N-methylmaleimide, and its dimer. The Cieplak model fails to rationalize the formation of endo/exo isomers in such Diels–Alder reactions. The distortion–interaction model however quantitatively explains the stereospecific product formation for the Diels–Alder reactions of phosphene with dienophiles. The distortion–interaction model clearly showed that the distortion energies of diene contribute to the formation of syn products with all of the dienophiles studied here. Furthermore, the interaction energies have also contributed in the case of dimerization of 1-methylphosphol-1-oxide and the cycloaddition of 1-methylphosphol-1-oxide with N-methylmaleimide. The secondary orbital interactions in the π-σ* interaction bond in the syn isomer also contribute to the thermodynamic preference for the formation of this adduct. Nonetheless, the syn isomer can also experience the attractive intramolecular C–H–π type interaction. The orbital analysis suggests that the repulsive nπ-σ* interaction would be stronger compared with the stabilizing π-σ* interaction in the anti adduct. Importantly, the endo/exo isomers in such Diels–Alder reactions can also be accounted for using the distortion–interaction strain model.

**COMPUTATIONAL METHODS**

Full geometrical optimizations have been carried out using Becke’s three-parameter exchange–correlation functional of Lee, Yang, and Parr (B3LYP) level with the 6-31G(d) basis set.45–47 Harmonic vibrational frequency calculations were also performed at the B3LYP/6-31G(d) level of theory to confirm minima of optimized geometries with all positive frequencies, and transition state structures were characterized by one imaginary frequency. Moreover, we have performed geometry optimization and frequency calculation using the M06-2X/6-31G(d) level of theory. Furthermore, we have performed the intrinsic reaction coordinate (IRC) using the B3LYP/6-31G(d) level of theory.48 The IRC calculations reveal that the reactant and product are connected via the transition state on the potential energy surface of the examined Diels–Alder reaction (Figure S2). We have further performed single-point calculations at the M06-2X/6-31G(d) and B3LYP/6-31G(d) level of theory optimized geometries with the self-consistent reaction field method using the polarizable continuum model (PCM) solvation model in triethylamine (ε = 2.3832).49,50 Triethylamine was considered as a solvent because these Diels–Alder reactions were carried out experimentally using this solvent.52 We have calculated activation energy (ΔE) as

\[ ΔE = E_A - (E_R + E_C) \]  

where ΔE is the energy difference, E_A is the energy of the transition states or products, and E_R and E_C are the energies of the reactants.

Free energies are also calculated as

\[ ΔG = G_s - G_f \]  

where ΔG is the difference in free energy, G_s is the free energy of the transition states, and G_f is the free energy of the initial reactants.

Distortion–interaction energy calculations have also been performed on the same level of theory as in eq 3

\[ ΔE_{int} = ΔE^d_{(dieno)} + ΔE^d_{(dienophile)} - ΔE_{activation} \]  

where ΔE_{int} is the interaction energy, ΔE^d_{(dieno)} is the distortion energy of diene, ΔE^d_{(dienophile)} is the distortion energy of the dienophile, and ΔE_{activation} is the activation energy.

The NBO calculations have been carried out using the B3LYP/6-31G(d) level of theory. All of the calculations were performed using Gaussian 09 suite of the programme.51

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01165.

Adduct energies (ΔE), activation free energy (ΔG), hyperconjugative interactions energies, and distortion–interaction energies; single-point calculation using the M06-2X/6-31G(d) level of theory; B3LYP/6-31G(d) optimized Cartesian coordinates for all of these geometries (PDF)

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**Notes**

The authors declare no competing financial interest.

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