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Theoretical investigation of an unusual substituent effect on the dienophilicity of >C═P— functionality present in 2-phosphaindolizines

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Effect of the number and positions of the methoxycarbonyl substituents in 2-phosphaindolizine on the feasibility of its Diels–Alder (DA) reaction with 1,3-butadiene has been investigated theoretically at the density functional theory (DFT) level. Among the series of four differently substituted 2-phosphaindolizines, 3-methoxycarbonyl-2-phosphaindolizine does not undergo the DA reaction due to the highest activation barrier (29.49 kcal mol^{-1}) and endothermicity, whereas the activation barrier of the corresponding reaction of 1,3-bis(methoxycarbonyl)-2-phosphaindolizine is lowest (22.43 kcal mol^{-1}) with exothermicity making it possible to occur. This reactivity trend is corroborated by FMO energy gaps as well as by global electrophilicity powers of the reactants. Copyright © 2008 John Wiley & Sons, Ltd.

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Keywords: DFT calculations; Diels–Alder reaction; 2-phosphaindolizines; substituent effect; NBO analysis; global electrophilicity

INTRODUCTION

The Diels–Alder (DA) reaction is an important tool in synthetic organic chemistry for the construction of six-membered rings.[1–5] The mechanism of the DA reaction has been the subject of an intensive investigation for sometime[6–13] and theoretical calculations have been frequently applied to analyze the substituent effect on the reactivity of diene and dienophile.[14–18] During the last couple of decades, the scope of the hetero-DA reaction has been extended to several classes of organophosphorus compounds, such as phosphaalkenes, phosphinines, and heterophospholes including azaphospholes incorporating a >C═P— functionality as the dienophile.[19–21] Our current interests center on the experimental and theoretical investigations of the DA reactions of a variety of anellated azaphospholes, including 2-phosphaindolizines, due to the stereo- and regioselectivities accompanying these reactions.[22–25] In the case of 2-phosphaindolizine, representatives obtained from the [4 + 1] cyclocondensation route[26–28] have an electron withdrawing group (EWG) only at the 3-position, that is, on the carbon of the dienophilic >C═P— moiety and do not undergo DA reaction with 2,3-dimethyl-1,3-butadiene. On the other hand, representatives obtained through 1,5-electrocyclization[29,30] have an additional EWG at 1-position also and undergo DA reaction easily (Scheme 1).[31,32]

In the present study, we attempt to analyze the unusual substituent effect on the dienophilicity of the >C═P— moiety in 2-phosphaindolizines quantitatively as well as qualitatively on the basis of thermodynamic parameters,[15–17] FMO approach,[14] natural bond orbital (NBO) interactions, Mulliken population analysis, and global electrophilicity scale.[33–36]

COMPUTATIONAL METHODS

In a number of investigations of the DA and hetero-DA reactions, the activation barriers calculated at the density functional theory (DFT)[37,38] level using B3LYP hybrid functional[39,40] have been found to be in good agreement with the experimental results. In the present study, therefore, geometries for all the reactants, cycloadducts, and the corresponding transition structures have been optimized in the gas phase at the B3LYP/6-31G** level of theory. In view of the endo-cycloadduct characterized by X-ray crystallography in one case,[32] only endo approach for the cycloaddition was examined. A concerted pathway was searched for the location of the transition state. Frequency calculations were done at the same level to determine zero-point energies and to characterize the transition structures by the presence of one and only one imaginary frequency corresponding to the movement in the direction of the reaction coordinate. The energies of activation (ΔE_a) and reaction (ΔE_{rxn}) have been computed by making zero point corrections to the single point energies calculated at the B3LYP/6-311++G** level. The intrinsic reaction coordinate (IRC)[41,42] calculations starting at the concerted transition structures were carried out at the B3LYP/6-31G** level to confirm its connection with the corresponding reactants and the cycloadducts. NBO analysis[43] was employed

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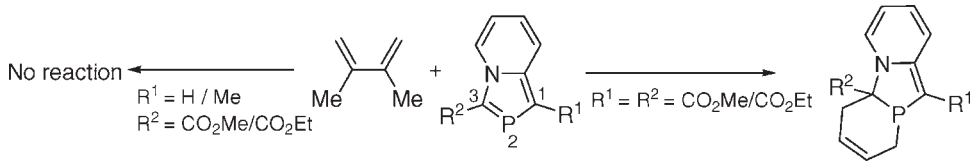


Scheme 1. Reactivities of mono- and disubstituated 2-phosphaindolizines in the DA reaction

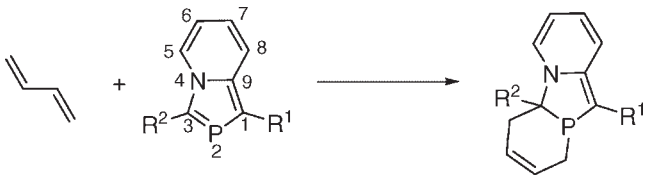
for the evaluation of the forming bonds. The charge transfer in the TS was determined by summing up the B3LYP/6-311++G** Mulliken charges in the two reactant units separately in the transition structure, and taking their difference.[14,34] The global electrophilicity index, ω, as defined by Parr *et al*. in terms of the electronic chemical potential μ and the chemical hardness η, was obtained from the expression: $\omega = \mu^2/2\eta$.[44] The electronic chemical potential (μ) and the chemical hardness (η) were evaluated in terms of the energies of the HOMO and LUMO, ε_H and ε_L, from the simple operational formulae $\mu \approx (\varepsilon_H + \varepsilon_L)/2$ and $\eta \approx \varepsilon_H - \varepsilon_L$, respectively.[37,45] All calculations have been done using Gaussian 03 package.[46]

RESULTS AND DISCUSSION

To understand the effect of the unsymmetrical substitution on the dienophilicity of the >C═P— moiety in 2-phosphaindolizines, the DA reactions of 1,3-butadiene (**1**) with unsubstituted 2-phosphaindolizine, **2a** as the reference dienophile along with three other representatives having methoxycarbonyl substituent at C3 (in **2b**), at C1 (in **2c**), and at both C1 and C3 (in **2d**) positions are examined (Scheme 2). Geometries of the transition structures (**TSa–TSd**), located on the concerted non-synchronous pathway, along with the corresponding reactants and cycloadducts showing relevant geometrical parameters optimized at B3LYP/6-31G** level are presented in Fig. 1. Activation energies (ΔE_a) and the energies of reaction (ΔE_{rxn}), with respect to the total energies of the reactants derived from the sum of the isolated reactant energies, calculated at B3LYP/6-311++G**//B3LYP/6-31G** level are given in Fig. 2.

Activation barriers and reaction energies

Calculated activation barrier for the DA reaction of the model unsubstituted 2-phosphaindolizine, **2a** is 27.52 kcal mol^{-1} and the reaction is endothermic by 0.76 kcal mol^{-1} (Fig. 2). In general, feasibility of the DA reaction is known to increase by the presence of EWG on the dienophile.[47–50] But in contrast, the introduction of the methoxycarbonyl group on the dienophilic unit, as in **2b**, results in raising both, the activation barrier (to 29.49 kcal mol^{-1}) and the endothermicity (to 8.17 kcal mol^{-1}). However, the presence of the methoxycarbonyl substituent at 1-position, as in **2c**, although not directly attached to the >C═P— moiety, lowers the activation barrier considerably and makes the reaction thermodynamically favorable. In the case of **2d**, which has been reported to undergo DA reaction experimentally,[32] the reaction is slightly exothermic and involves the lowest activation barrier (22.43 kcal mol^{-1}).



	R^1	R^2
a	H	H
b	H	CO_2Me
c	CO_2Me	H
d	CO_2Me	CO_2Me

Scheme 2. Theoretically investigated DA reactions

Asynchronicity and NBO analysis

The effect of the symmetrical and unsymmetrical substitution in the diene and dienophilic moieties on the extent of the asynchronicity in the transition state has been investigated earlier.[15,51,52] At the transition state, the bond formation was slower at the end having larger number of EW groups on the dienophile. Along the reaction pathway, measure of the bond formation is provided in a better way by the concept of the Wiberg bond indices (WBI)[53] computed from the NBO calculations (Fig. 1). All transition structures are found to be non-synchronous with a variation in the extent and direction of the asynchronicity. In **TSb**, having an EW methoxycarbonyl substituent on the dienophilic >C═P— moiety, the direction of the asynchronicity is in accordance with the earlier observations;[15,51,52] bond formation at the EWG bearing carbon-end is slower (WBI 0.36) than the phosphorus-end (WBI 0.52). The direction of the asynchronicity in the **TSa** corresponding to the unsubstituted 2-phosphaindolizine is opposite, the bond formation at the carbon-end is faster (WBI 0.44) than at the phosphorus end (WBI 0.32). Actually in the case of **2a**, the bridgehead nitrogen, owing to the donation of the electronic charge from lone pair to the >C═P— moiety, as characterized by $n_N \rightarrow \pi^*_{C-P}$ interaction (Fig. 3) having the NBO stabilization energy (E2) of 37.3 kcal mol^{-1}, acts as an electron-donating substituent. As a result, **2a** acts as an electron-rich dienophile, characterized by the inverse electron demand (IED) and the charge transfer of 0.08*e* from the dienophile to the diene component in the transition structure **TSa**. 1-Methoxycarbonyl substituent in **2c**, although not directly conjugated to the C═P double bond, stabilizes donation of the nitrogen electron pair to the antibonding C1–C9 π orbital, which overcomes the $n_N \rightarrow \pi^*_{C-P}$ interaction by 7.0 kcal mol^{-1} making the **TSc** only slightly asynchronous. On moving from **2a** to **2d**, the stabilization energy of $n_N \rightarrow \pi^*_{C-P}$ interaction decreases with a simultaneous increase in the stabilization energy of $n_N \rightarrow \pi^*_{C1-C9}$ interaction (Fig. 3) making the dienophilic moiety in **2d** sufficiently electron deficient and the **TSd** much asynchronous (WBI 0.31 and 0.56).

FMO approach versus charge transfer in TS

Application of the FMO approach reveals that the HOMO and the LUMO of **2a**, the dienophile with no EW substituent, are high lying (Table 1) making $LUMO_{diene}$–$HOMO_{dienophile}$ interaction

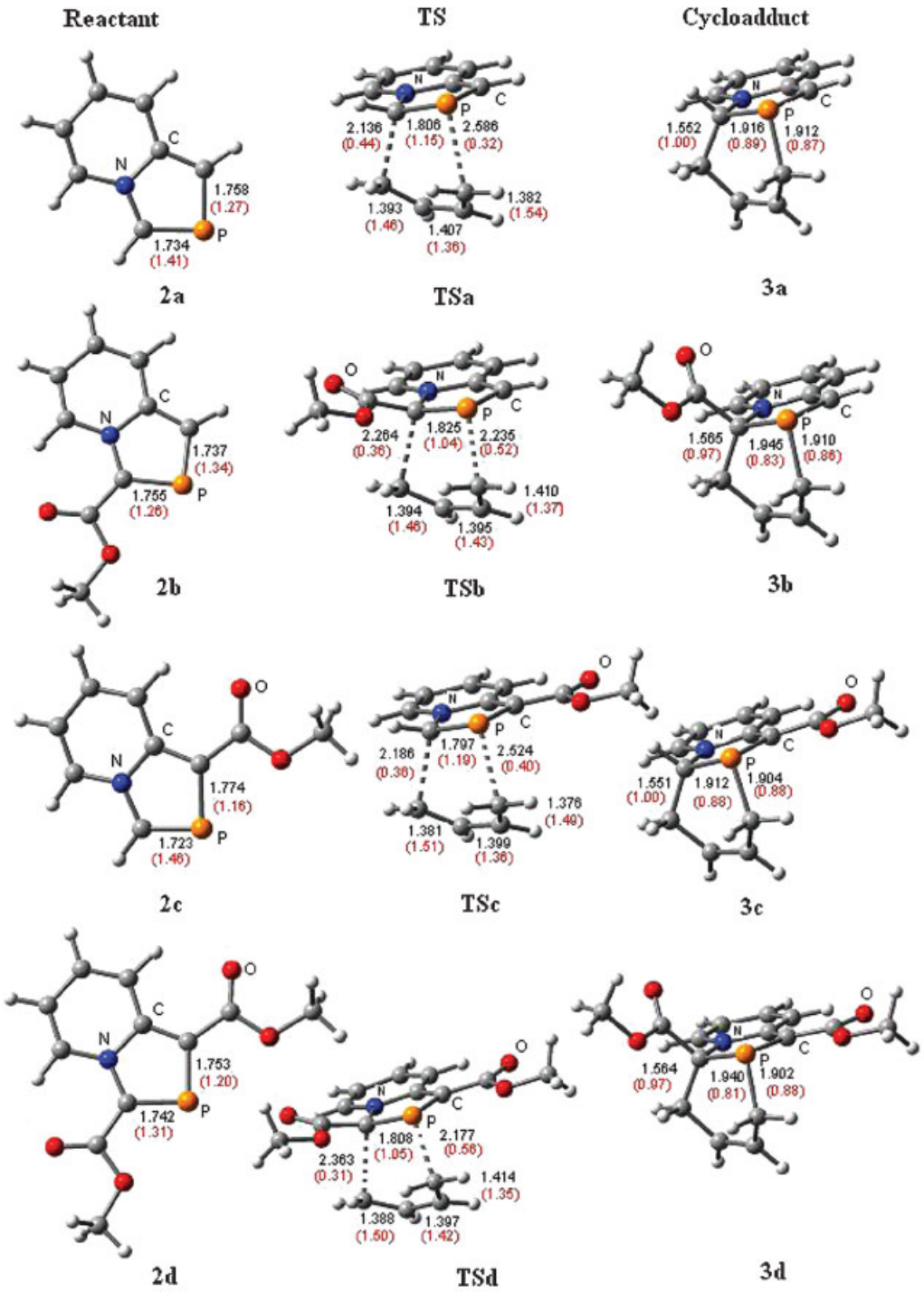


Figure 1. Optimized geometries (B3LYP/6-31G**) of **2a–2d**, **TSa–TSd**, and **3a–3d** with selected bond lengths (in Å) and Wiberg bond indices (in parenthesis)

(4.630 eV) more favorable than $LUMO_{dienophile}$–$HOMO_{diene}$ (5.098 eV) and hence, its DA reaction with butadiene is of Sustmann Type III ($LUMO_{diene}$–$HOMO_{dienophile}$ controlled)[18] with 'IED.' The IED is further supported by a charge transfer of 0.08*e* (as determined by the Mulliken population analysis) from the dienophile to the diene component in the **TSa**. Introduction of the methoxycarbonyl substituent in **2b** and **2c** stabilizes both the LUMO and the HOMO so that the $LUMO_{dienophile}$–$HOMO_{diene}$ interaction becomes slightly more favorable than the $LUMO_{diene}$–$HOMO_{dienophile}$. In the case of **2d**, the stabilization of both FMOs is to such an extent that the $LUMO_{dienophile}$–$HOMO_{diene}$ gap (4.299 eV) is smaller than the $LUMO_{diene}$–$HOMO_{dienophile}$ gap (5.129 eV) by 0.83 eV resulting in an appreciably favored interaction in accordance with the '*normal electron demand*' (NED) (Type I DA reaction[18]).

Recent studies reveal that substitutions stabilize the asynchronous transition structure by charge transfer between the diene and the dienophile components and hence favor an

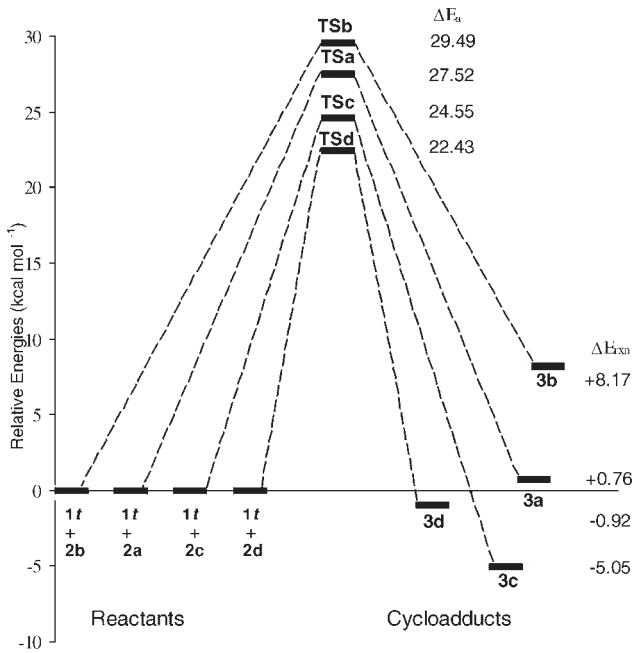


Figure 2. Reaction energies (ΔE_{rxn}) and activation barriers (ΔE_a) in kcal mol^{-1} calculated from the sum of the energies of isolated **1t** (*s-trans*-butadiene) and **2** at B3LYP/6-311++G** + ZPE at B3LYP/6-31G** level in gas phase for the DA reactions of **2a–2d**

asynchronous concerted mechanism by decreasing the activation barrier of the DA reaction.[51,52,54,55] For an NED-DA reaction, an increase in the electron-deficient character of the dienophile is expected to stabilize the transition state due to more effective charge transfer from the diene component causing lowering of the activation barrier. However, in the case of **2b** and **2c**, despite the introduction of EW methoxycarbonyl group in 2-phosphaindolizine and slightly more favorable LUMO$_{dienophile}$–HOMO$_{diene}$ interaction, transfer of small electronic charge (0.004 and 0.013*e* in the **TSb** and **TSc**, respectively) is found to occur in the reverse direction, that is, from butadiene to the dienophile making the transition state somewhat less stable and the activation barriers higher (Fig. 2). On the other hand, in **2d**, the TS is stabilized by a significant charge transfer of 0.08*e* from diene to dienophile in accordance with the NED, resulting in the lowering of the activation barrier (22.43 kcal mol^{-1}) and making the reaction feasible. The charge transfer value in **TSd** is almost of the same order as observed in the reaction of butadiene with acrolein (0.09*e*) and with acrylonitrile (0.11*e*).[56]

Global electrophilicity scale

In view of the recent application of the DFT-based global electrophilicity scale for describing the relative reactivities of differently substituted dienes and dienophiles,[33–36] global properties of **1c** (*s-cis*-butadiene) and **2a–2d** have been calculated (Table 1). In the present case, electron demand characterization of the investigated DA reactions is consistent with electronic chemical potential consideration. Lower value of the electronic chemical potential for **2d** ($\mu = -3.941$ eV) makes it act as an electron acceptor during interaction with 1,3-butadiene with relatively higher value of μ (-3.526 eV) characterizing the reaction to be NED controlled. On the other hand, higher chemical potential of **2a** (-3.292 eV) indicates it to act as an electron donor. The global electrophilicity index, ω, originally proposed by Parr *et al.*,[44] has been applied to characterize the substituent effect on the polarity and reactivity of the DA reactions. It has been found that with the increase in the $\Delta\omega$ values, obtained from the difference in the global electrophilicities of the diene and dienophile pair, polar character of the DA reaction increases leading to the lowering of the activation barrier.[36,52] It can be noted that the $\Delta\omega$ values of the DA reactions of 2-phosphaindolizines, **2a–2c** with **1** range from 0.080 to 0.418 eV ascribing them low to moderately low polar character,

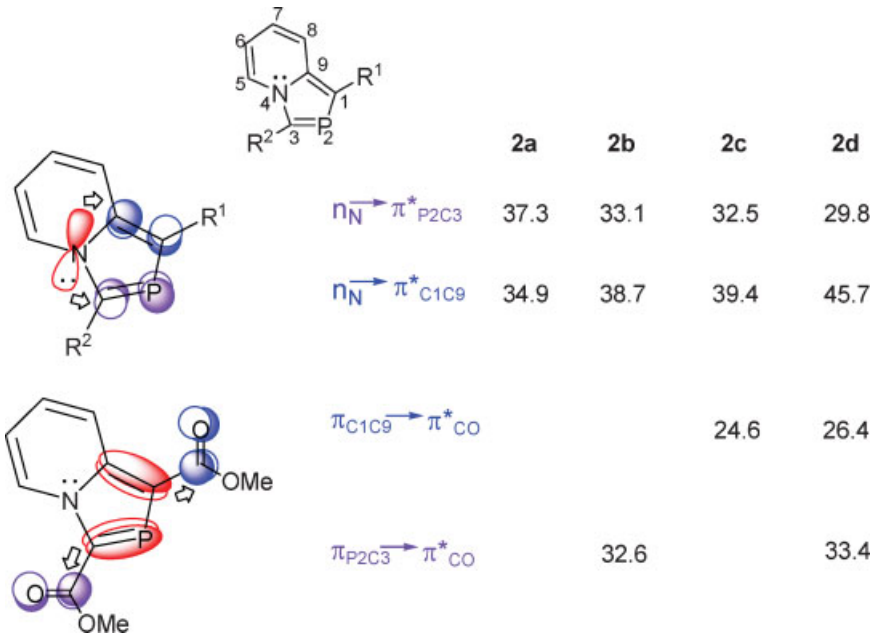


Figure 3. Second-order perturbative energy-lowering donor–acceptor interactions, E2 (in kcal mol^{-1}) obtained from NBO analysis of **2a–2d**

Table 1. Global properties (in eV) of substituted 2-phosphaindolizines and 1,3-butadiene

	HOMO	LUMO	μ	η	ω	$\Delta\omega^a$
1c[b]	−6.206	−0.846	−3.526	5.360	1.160	—
2a	−5.476	−1.108	−3.292	4.368	1.240	0.080
2b	−5.752	−1.540	−3.646	4.212	1.578	0.418
2c	−5.758	−1.536	−3.647	4.222	1.575	0.415
2d	−5.975	−1.907	−3.941	4.068	1.909	0.749

[a] $\Delta\omega = \omega_{phosphaindolizine} - \omega_{butadiene}$.
[b] s-*cis*-butadiene.

with the result that the activation barriers are too high for the reaction to take place. But $\Delta\omega$ value of 0.749 eV for the DA reaction of **2d** with **1** makes it sufficiently polar resulting in lowering of the activation barrier and the reaction feasible.

CONCLUSIONS

The bridgehead nitrogen in 2-phosphaindolizines acts as an electron-donating substituent to the >C═P— moiety, as characterized by the $n_N \rightarrow \pi^*_{C-P}$ NBO interaction. This interaction diminishes successively in the order **2a** > **2b** > **2c** > **2d** and only **2d** becomes sufficiently electrophilic, as revealed by its global electrophilicity power value (ω), to accept an efficient charge transfer from 1,3-butadiene thereby making the DA reaction polar to the optimum level of its occurrence.

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