

AIM analysis for assignment of the two *Z*- and *E*-isomers in phosphorane containing a dimedon-1-yl

Nilofar Akbarzadeh,^a Alireza Rezvani,^a Sayyed Mostafa Habibi Khorassani,^{a*} Majid Moradian^b and Zahra Ghahghayi^a

^aDepartment of Chemistry, The University of Sistan and Baluchestan, P.O. Box 98135-674, Zahedan, Iran.

^bDepartment of Chemistry, Islamic Azad University, Qaemshahr Branch, Iran.

Abstract: Triphenylphosphine reacts with dialkyl acetylenedicarboxylates in the presence of a SH-heterocyclic compound such as dimedon-1-yl to generate stable phosphorus ylides. These stable ylides exist in solution as a mixture of the two geometrical isomers as a result of restricted rotation around the carbon-carbon double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group. In the recent work, NMR study and the assignment of more stable *Z*- or *E*- isomers as the major form was investigated using AIM theoretical calculations.

Keywords: Stable phosphorus ylides; Dialkyl acetylenedicarboxylates; AIM; SH-heterocyclic compounds; *Z*- or *E*- isomers.

Introduction

Trivalent phosphorus compound is known to be a nucleophile, whereas it behaves as an electron donor toward good electron acceptor either in the ground or excited state [1, 2]. In recent years there has been increasing interest in the synthesis of organophosphorus compounds, that is, those bearing a carbon atom bound directly to a phosphorus atom [5-12]. This interest has resulted from the recognition of the value of such compounds in variety of biological, industrial and chemical synthetic uses [5-9]. A large numbers of methods has appeared describing novel synthesis of organophosphorus compounds [8, 9]. There are many studies on the reaction between trivalent phosphorus nucleophiles and an unsaturated carbonyl compounds in the presence of a proton source such as alcohol or phenol [9]. Ylides are important reagents in synthetic organic chemistry, especially in the synthesis of naturally occurring products and compounds with biological and pharmacological activity [13]. The synthesis of phosphorus ylides is an important reaction in organic chemistry because of the application of these compounds in the synthesis of organic products [12-30]. Phosphorus ylides most often prepare by treatment of a phosphonium salt with a base. Most of the phosphonium salts are usually made from the reaction of phosphine and an alkyl halide [3-9], though they can

be obtained by Michael addition of phosphorus nucleophiles to activated olefins [8, 9].

A facile synthesis of the reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxylates **2** and dimedon-1-yl **3** (as a SH- heterocyclic compound) have been earlier reported [31] for generation of phosphorus ylides **4(a, c)** involving the two geometrical isomer such as *Z*- and *E*- isomers. The reaction is shown in Figure 1. For assignment of the two *Z*- and *E*- isomers as a minor or major form in phosphorus ylides **4(a, c)** containing a 2- dimedon-1-yl, first the *Z*- and *E*- isomers were optimized for all ylide structures at HF/6-31G (d,p) level of theory by Gaussian98 package program. The relative stabilization energies for both the geometrical isomers have been calculated at B3LYP/6-311++G** level. Atoms in molecules AIM, CHelpG and NBORead methods at HF/6-31G (d,p) level of theory have been performed in order to gain a better understanding of the most geometrical parameters in both the *E*-**4(a, c)** and the *Z*-**4(a, c)** of phosphorus ylides. The numbers of critical points and intramolecular hydrogen bonds have been recognized as well as the charge of atoms that constructed on the *Z*- and *E*- isomers. The results altogether reveal the effective factors on stability of *Z*- and *E*- ylide isomers.

*Corresponding author. Tel.: + (98) 5412446565; Fax: + (98) 5412446565; E-mail: smhabibius@yahoo.com

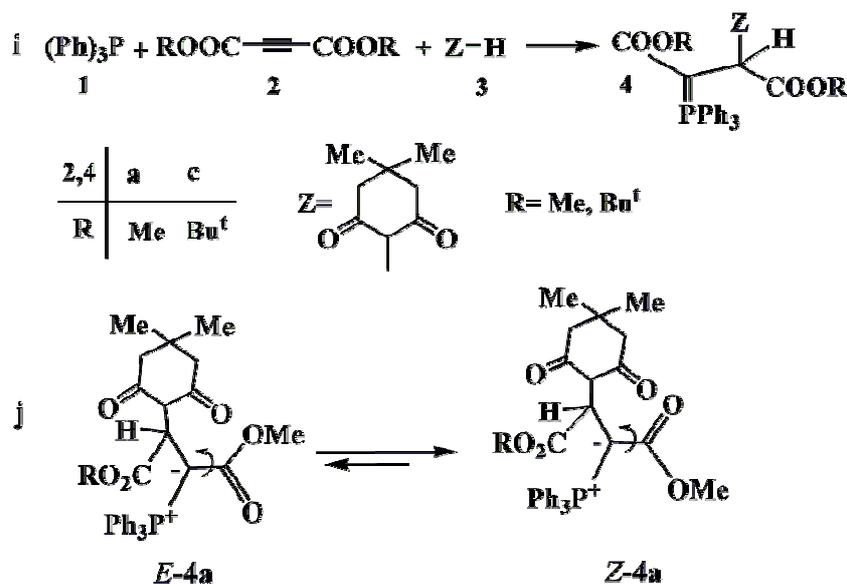


Fig. 1. i) The reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxylate **2** (**2a** or **2b**) and dimedon-1-yl **3** for generation of stable phosphorus ylides **4** (**4a** or **4c**). j) The two isomers *Z*-**4a** and *E*-**4a** (Major and Minor, respectively) of ylide **4a**.

Results and Discussion

Theoretical study

Recently, different reports have been published on the synthesis of stable phosphorus ylides from the reaction between triphenylphosphine and reactive acetylenic esters in the presence of N-H, C-H or S-H heterocyclic compounds. These ylides usually exist as a mixture of the two geometrical isomers, although some ylides exhibit one geometrical isomer. Assignment of the stability of the two *Z*- and *E*- isomers is impossible in phosphorus ylides by experimental methods such as ¹H and ¹³C NMR and IR spectroscopies, mass spectrometry and elemental analysis data. For this reason quantum mechanical calculations have been performed in order to gain a better understanding of the most important geometrical parameters and also relative energies of both the geometrical isomers.

Calculations

Structure and stabilities

In order to determine more stable form of both the geometrical isomers [*Z*-**4(a, c)** or *E*-**4(a, c)**] of ylides (**4a** or **4c**), first their structures were optimized at HF/6-31G (d,p) level of theory [32] by Gaussian98 program package.³³ Also relative stabilization energy of the two isomers has been calculated at HF/6-31G (d,p) and B3LYP/6-311++G (d,p) levels (See Figures 2 and 3). The relative stabilization energies for the two [*Z*-**4(a, c)** and *E*-**4(a, c)**] isomers are reported in Table 1, as can be seen, the *Z*-**4a** and the *Z*-**4c** isomers are more stable than the *E*-**4a** and the *E*-**4c** forms (3.30 and 4.40 kcal/mol, respectively) at B3LYP level.

Table 1. The relative energy (kcal/mol) for both the *Z*- and *E*- isomer of ylides, obtained at HF/6-31G (d,p) and B3LYP/6-311++G(d,p) levels.

Conformer	HF	B3LYP
<i>Z</i> -4a	0.00	0.00
<i>E</i> -4a	4.02	3.30
<i>Z</i> -4c	0.00	0.00
<i>E</i> -4c	5.41	4.40

Two interacting atoms in a molecule form a critical point in the electron density, where $\nabla\rho(r)=0$, called the bond critical point (BCP). The values of the charge density and its Laplacian at these critical points give useful information regarding the strength of the H-bonds [35]. The ranges of $\rho(r)$ and $\nabla^2\rho(r)$ are $(0.002-0.035)e/a_0^3$ and $(0.024-0.139)e/a_0^5$, respectively, if H-bonds exist.³⁶The AIM calculation indicates intramolecular hydrogen bond critical points (H-BCP) for the two **Z-4(a, b)** and **E-4(a, b)** isomers. Intramolecular H-BCPs are shown in Figures 2 and 3 (dotted line). The electron density (ρ), Laplacian of electron density $\nabla^2\rho(r)$, and energy density $H(r)$ are

also reported in Tables 2 and 3. A negative total energy density at the BCP reflects a dominance of potential energy density, which is the consequence of accumulated stabilizing electronic charge.³⁷ Herein, the number of hydrogen bonds in both categories (**E-4a** and **Z-4a**) and (**E-4c** and **Z-4c**) are (11 and 9) and also (21 and 17), respectively, the values of ρ and $\nabla^2\rho(r)$ are in the ranges $(0.001-0.014$ and $0.005-0.017) e/a_0^3$ and $(0.003-0.015$ and $0.003-0.018)$ also $(0.028-0.051$ and $0.019-0.069) e/a_0^5$ and $(0.014-0.056$ and $0.008-0.057) e/a_0^5$, respectively, in addition the Hamiltonian $[H(r)]$ is in the range $(0.40-1.86$ and $0.75-1.66$ au) and $(0.66-1.81$ and $0.43-1.59$ au)(See Tables 2 and 3).

Table 2. The values of $\rho \times 10^3$, $\nabla^2\rho \times 10^3$ and Hamiltonian $(-H) \times 10^4$ for the two **Z-4c** and **E-4c** isomers of ylide **4c** calculated at the hydrogen bond critical Points. All quantities are in atomic units

E	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$(-H) \times 10^4$	Z	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$(-H) \times 10^4$
1	6.13	25.90	11.47	1	13.19	50.36	12.46
2	4.81	17.72	10.30	2	13.15	49.76	11.65
3	4.64	17.94	10.90	3	17.92	70.17	11.67
4	9.03	36.78	12.44	4	12.88	50.21	13.95
5	4.65	19.07	9.22	5	12.32	47.09	12.10
6	3.12	13.86	7.73	6	14.01	56.77	13.46
7	1.37	4.88	3.44	7	7.31	29.95	11.17
8	4.18	15.28	9.44	8	7.61	29.48	15.91
9	13.52	52.73	14.17	9	4.02	17.06	9.31
10	12.84	49.57	13.11	10	3.96	15.05	9.66
11	9.81	37.67	9.81	11	4.10	12.58	6.48
12	12.51	44.62	16.74	12	9.37	38.11	12.78
13	0.71	2.67	1.84	13	3.41	10.67	5.68
14	4.99	20.94	9.56	14	2.58	8.02	4.56
15	3.58	14.13	9.34	15	10.58	36.72	4.28
16	14.69	56.09	12.99	16	10.10	34.92	15.34
17	13.34	50.54	11.71	17	9.18	32.01	15.31
18	13.84	49.60	6.58				
19	1.86	6.47	4.24				
20	10.35	38.77	18.07				
21	9.14	32.32	15.44				

Table 3. The values of $\rho \times 10^3$, $\nabla^2\rho \times 10^3$ and Hamiltonian $(-H) \times 10^4$ for both the *E-4a* and *Z-4a* isomers of ylide **4a** calculated at the hydrogen bond critical points. All quantities are in atomic units

E	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$(-H) \times 10^4$	Z	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$(-H) \times 10^4$
1	12.81	51.16	11.88	1	17.41	69.03	13.31
2	9.03	36.72	12.68	2	8.03	31.10	16.60
3	7.50	28.07	7.45	3	14.93	59.76	13.09
4	7.77	31.18	3.97	4	8.43	35.07	13.02
5	10.75	45.17	13.94	5	7.14	26.93	7.46
6	1.20	4.45	3.05	6	6.37	25.55	11.08
7	13.95	48.96	5.32	7	4.57	19.00	8.96
8	11.99	42.75	16.72	8	9.64	33.37	14.72
9	9.02	34.87	9.84	9	9.00	31.22	14.92
10	8.97	32.44	15.71				
11	10.38	39.63	18.60				

These HBs show $\nabla^2\rho(r) > 0$ and $H(r) < 0$, which according to classification of Rozas *et al* [38] are medium-strength hydrogen bonds. In both ylides the dipole moment for the two *E-4a* and *E-4c* isomers (3.73 and 3.32 D, respectively) are smaller than the two *Z-4a* and *Z-4c* isomers (5.74 and 5.50D, respectively) and the value of $H_{\text{tot}} (= \sum H(r))$ for the two *E-4a* and *E-4c* isomers (119.2 and 218.5 au, respectively) are larger than the two *Z-4a* and *Z-4c* isomers (113.1 and 185.8

au, respectively). These differences in the most important geometrical parameters of the *E-4(a, c)*, with respect to the *Z-4(a, c)*, respectively involving a fairly difference in dipole moment and a considerable difference in $H(r)$ and also approximately same number of hydrogen bonds, altogether, make a stability on these isomers in comparison with the *Z-4(a, c)* forms (The results are summarized in Table 4).

Table 4. The most important geometrical parameters involving the value of H_{tot} /au, dipolemoment/D and number of hydrogen bonds for the two *Z-* and *E-* isomers of ylides **4a** and **4c**

Isomer	$H(r)$ /au	Dipole moment /D	Number of hydrogen bond
Z-4a	113.1	5.74	9
E-4a	119.2	3.73	11
Z-4c	185.8	5.50	17
E-4c	218.5	3.32	21

Although, on the basis of theoretical calculations (Table 1), both the *Z-4a* and *Z-4c* have a stability with respect to the two *E-4a* and *E-4c* (3.30 and 4.40 kcal/mol) isomers and seem to be different from the results of predictable properties of the most important geometrical parameters (Table 4), perhaps, this different behavior is relevant to the huge structures of the two ylides **4(a, c)** involving four large atoms such as the two sulfurs, phosphorus and nitrogen and also the very large number of other atoms (C and H). This point, made a limitation in application of basis set higher than B3LYP/6-311++G (d,p) in a higher performance for more accurate calculations. Nevertheless, the results that were reported in Table 4, involving large $H_{\text{tot}}(r)$ and small dipole moment for the two *E-4a* and *E-4c*, are compatible with the experimental results from the ^1H , ^{13}C and ^{31}P NMR spectroscopies which indicate the two isomers of *Z-4a* and *E-4a* and also only a lone isomer of **4c**. Moreover, the total number of hydrogen bonds in the two *Z-4c* and *E-4c* (17, 21) are more than two the *Z-4a* and *E-4a*

(9, 11), this leads to a large rigidity in these geometrical isomers in comparison with the two *Z-4a* and *E-4a* forms. The rigidity of the two molecular structures by the very large intramolecular hydrogen bond critical points accompanied by more steric factor of the bulky tert-butyl groups (compare with dimethyl groups in both the *E-4a* and *Z-4a*, Figures 2 and 3) within the structures (*E-4c* and *Z-4c* forms) make a good opportunity for enhancement of energy barrier and also explanation the lone isomer of **4c**. Hence, interconversion process between the two *E-4c* and *Z-4c* isomers needs to pass through a very high restricted barrier energy (See Figure 4, A), particular in solution media, for this reason it is possible to see only a single isomer as a lone isomer of **4c**. On the contrary, interconversion process for both the *E-4a* and *Z-4a* geometrical isomers pass through a considerably low energy barrier (See Figure 4, B), this leads to a plausible observation of the two *E-4a* and *Z-4a* (See Figure 1, j).

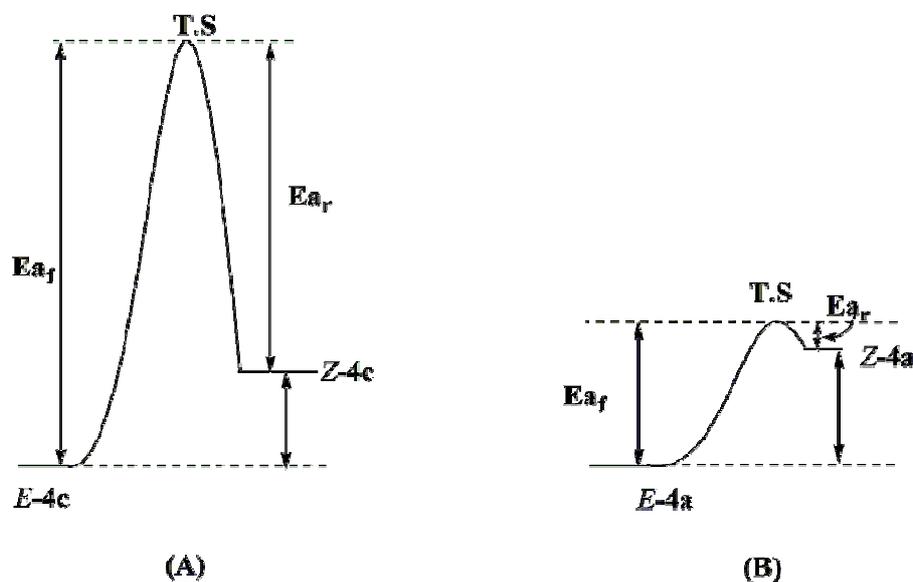


Fig. 4. Interchangeable process of geometrical isomers for ylides **4a** and **4c**. **A)** A very high restricted barrier energy for interconversion process between the two *E-4c* and *Z-4c* isomers. **B)** A Low restricted barrier energy for interconversion process between the two *E-4a* and *Z-4a* isomers.

Also, the charge on different atoms which are calculated by AIM, CHelpG, and NBOread methods at HF/6-31G (d,p) level are reported in Table 5 for the two *Z*- and *E*- isomers of

ylides **4a** and **4c**. There is a good agreement between the results in three methods.

Table 5. The charges on different atoms for both *Z* and *E* isomers in both ylides **4a** and **4c** calculated by AIM, CHelpG and NBORead respectively method at hf/4-31g(d,p)

number of atom	<i>Z</i> -4a	<i>E</i> -4a	<i>Z</i> -4c	<i>E</i> -4c
C1	3.76×10^{-1}	4.05×10^{-1}	4.15×10^{-1}	4.20×10^{-1}
	(0.30)	(0.55)	(0.52)	(0.61)
	(-0.31)	(-0.31)	(-0.31)	(-0.31)
C2	-7.82×10^{-1}	-7.85×10^{-1}	-7.18×10^{-1}	-7.39×10^{-1}
	(-0.70)	(-0.83)	(-0.73)	(-0.85)
	(-0.80)	(-0.82)	(-0.80)	(-0.80)
C4	1.81	1.84	1.82	1.84
	(0.87)	(0.90)	(0.81)	(0.99)
	(0.90)	(0.90)	(0.91)	(0.90)
O5	-1.43	-1.42	-1.42	-1.43
	(-0.68)	(-0.71)	(-0.63)	(-0.74)
	(-0.80)	(-0.80)	(-0.81)	(-0.81)
O6	-1.30	-1.28	-1.29	-1.27
	(-0.40)	(-0.37)	(-0.51)	(-0.71)
	(-0.66)	(-0.64)	(-0.69)	(-0.66)
P3	3.23	3.22	3.23	3.21
	(0.31)	(0.32)	(0.49)	(0.41)
	(1.74)	(1.74)	(1.75)	(1.74)

^aCalculated by AIM method^bCalculated by CHelpG method^cCalculated by NBORead method.

Conclusions

The assignment of the *Z*- and *E*- isomers as a major or minor form in both the ylides **4a** and **4c** were undertaken by AIM, CHelpG and NBORead methods. Quantum mechanical calculations were clarified how the ylides **4a** and **4c** exist in solution as a mixture of the two geometrical isomers or a lone isomer, respectively. This result was in good agreement with the experimental data.

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