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ORIGINAL ARTICLE

NMR study and AIM analysis for assignment of the two *Z*- and *E*-isomers in phosphorane containing a 2-thiazoline-2-thiol

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Abstract Triphenylphosphine reacts with dialkyl acetylenedicarboxylates in the presence of a SH-heterocyclic compound such as 2-thiazoline-2-thiol 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 partial 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 were investigated by using natural population analysis (NPA).

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1. 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 (Nakamura et al., 2000; Yasui et al., 2005). In recent years there has been an increasing interest in the synthesis of organophosphorus compounds, that is, those bearing a carbon atom bound directly to a phosphorus atom (Corbridge, 1995; Engel, 1988; Johnson, 1966; Cadogan, 1979; Hudson, 1990; Shen, 1998; Yavari and Feiz-Javadian, 2006; Yavari et al., 2006). This interest has resulted from the recognition of the value of such compounds in a variety of biological, industrial and chemical synthetic uses (Corbridge, 1995; Engel, 1988; Johnson, 1966; Cadogan, 1979; Hudson, 1990). A large number of methods have appeared describing novel synthesis of organophosphorus compounds (Cadogan, 1979; Hudson, 1990). There are many studies on the reaction between trivalent phosphorus nucleophiles and unsaturated carbonyl compounds in the presence of a proton source such as alcohol or phenol (Hudson, 1990). Ylides are important reagents in synthetic organic chemistry, especially in the synthesis of naturally occurring products and compounds with biological and pharmacological activity (Adib et al., 2005). The synthesis of phosphorus ylides

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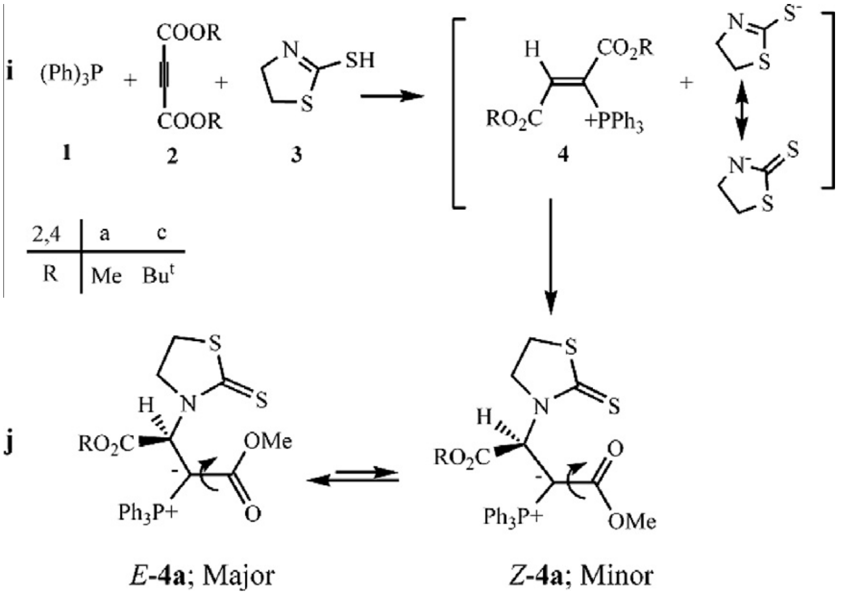

Figure 1 (i) The reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxylate **2** (**2a** or **2c**) and **2**-thiazoline-**2**-thiol **3** for generation of stable phosphorus ylides **4** (**4a** or **4c**). (j) The two *Z*-**4a** and *E*-**4a** rotational isomers (minor and major, respectively) of ylide **4a**.

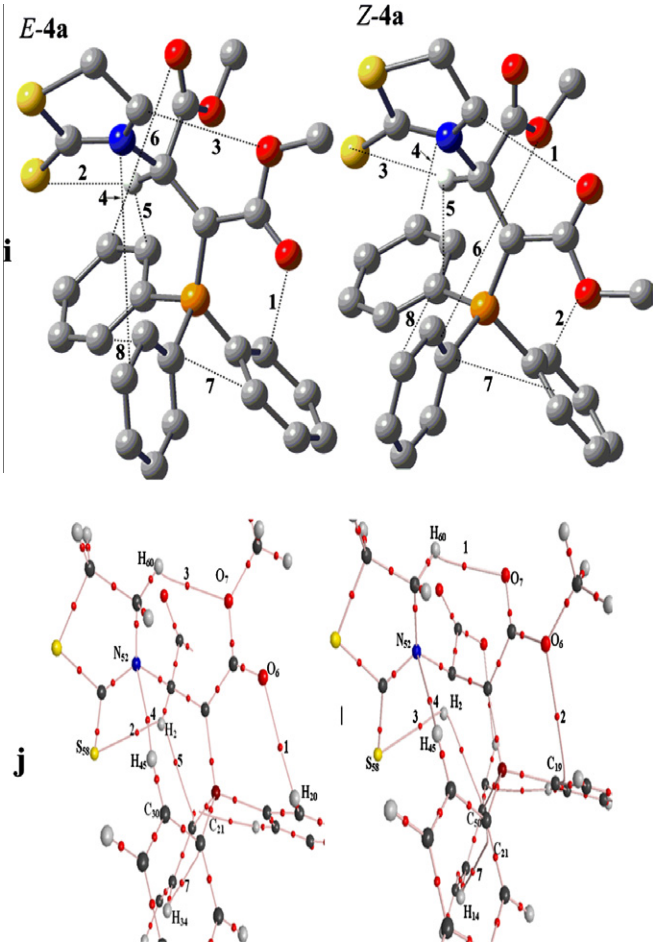

Figure 2 (i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-**4a** and *Z*-**4a** geometrical isomers of stable ylide **4a**. (j) A part of molecular graphs, including intermolecular hydrogen bond at critical points (BCPs) for the two *E*-**4a** and *Z*-**4a** geometrical isomers of stable ylide **4a**.

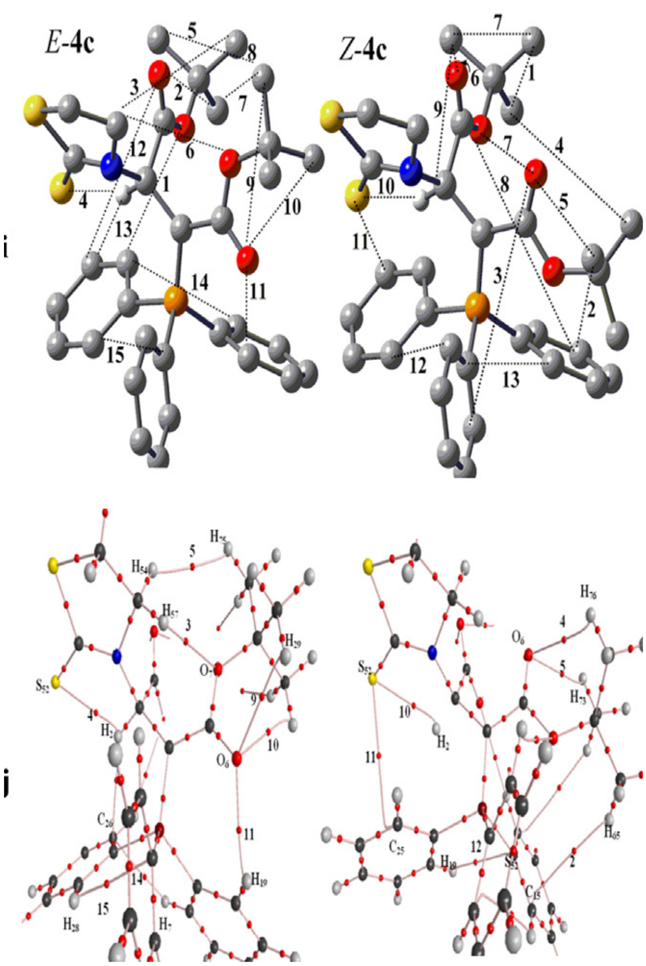

Figure 3 (i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-**4c** and *Z*-**4c** geometrical isomers of stable ylide **4c**. (j) **A** part of molecular graphs, including intermolecular hydrogen bond at critical points (BCPs) for the two *E*-**4c** and *Z*-**4c** geometrical isomers of stable ylide **4c**.

is an important reaction in organic chemistry because of the application of these compounds in the synthesis of organic products (Yavari et al., 2006; Adib et al., 2005; Ramazani et al., 2008; Maghsoodlou et al., 2006; Islami et al., 2005; Yavari et al., 2002; Hassani et al., 2006; Habibi-Khorassani et al., 2006; Maghsoodlou et al., 2009; Maghsoodlou et al., 2008; Hazeri et al., 2008; Habibi-Khorassani et al., 2008; Wittig, 1980; Adib et al., 2005; Habibi-khorassani et al., 2009, 2007; Maghsoodlou et al., 2006; Maryanoff and Rietz, 1989; Kazemian et al., 2008). Phosphorus ylides most often are prepared by the 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 (Kolodiazhnyi, 1994; Cherkasov and Pudovic, 1994; Corbridge, 1995; Engel, 1988; Johnson, 1966; Cadogan, 1979; Hudson, 1990), though they can be obtained by Michael addition of phosphorus nucleophiles to activated olefins (Cadogan, 1979; Hudson, 1990). 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 ^{1}H and ^{13}C NMR and IR spectroscopes, 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.

2. Material and methods

Quantum mechanical calculation has been performed by Gaussian98 program and using the AIM2000 program packages. Di-*tert*-butylacetylenedicarboxilate, triphenylphosphine and 2-thiazoline-2-thiol were purchased from Fulka (Buchs, Switzerland) and used without further purification. All extra pure solvents including 1,2-dichloroethane and THF were also obtained from Merk (Darmstadt, Germany).

3. Results and discussion

3.1. Calculations

A facile synthesis of the reaction between triphenylphosphine **1**, dialkyl acetylendicarboxylates **2** and 2-thiazoline-2-thiol **3** (as a SH-heterocyclic compound) has been earlier reported (Maghsoodlou et al., 2005) for the generation of phosphorus ylides **4(a, c)** involving two geometrical isomers such as *Z*- and *E*-isomers. The reaction is shown in Fig. 1. For the assignment of the two *Z*- and *E*-isomers as a minor or major form in phosphorus ylides **4(a, c)** containing a 2-thiazoline-2-thiol, 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 (Frisch et al., 1998). The relative stabilization energies for both the geometrical isomers have been calculated at HF/6-31G(d,p) and B3LYP/6-311++G(d,p) levels. Atoms in molecules (AIM) and natural population analysis (NPA) methods and also CHelpG keyword at HF/6-31G(d,p) level of theory have been employed in for the calculation of charge on the atoms order to gain a better understanding of 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 was constructed on the *Z*- and *E*-isomers. The results altogether reveal the effective factors on stability of *Z*- and *E*-ylide isomers. The relative stabilization energies for the two *Z*-**4(a**, **c)** and *E*-**4(a**, **c)** isomers (see Figs. 2 and 3) 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 (0.33 and 1.82 kcal/mol, respectively) at B3LYP level.

Further investigation was undertaken in order to determine more effective factors on the stability of the two *Z*- and *E*-iso-

Table 1 The relative energy (kcal/mol) for both the *Z*- and *E*-isomer of ylides **4a** and **4c**, obtained at HF/6-31G(d,p) and B3LYP/6-311++G(d,p) levels.

Conformer	HF	B3LYP
Z-**4a**	0.00	0.00
E-**4a**	0.09	0.33
Z-**4c**	0.00	0.00
E-**4c**	3.76	1.82

mers, on the basis of AIM calculations (Bader, 1990) at HF/6-31G(d,p) level of theory by the AIM2000 program package (Biegler König et al., 2001). In recent years, AIM theory has often been applied in the analysis of H-bonds. In this theory, the topological properties of the electron density distribution are derived from the gradient vector field of the electron density $\rho(\mathrm{r})$ and on the Laplacian of the electron density $\nabla^2\rho(\mathrm{r})$. The Laplacian of the electron density, $\nabla^2\rho(\mathrm{r})$, identifies regions of space wherein the electronic charge is locally depleted $[\nabla^2\rho(\mathrm{r}) > 0]$ or built up $[\nabla^2\rho(\mathrm{r}) < 0]$ Bader, 1990.

Two interacting atoms in a molecule form a critical point in the electron density, where $\nabla\rho(\mathrm{r}) = 0$ is 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 (Biegler König et al., 2001). The ranges of $\rho(\mathrm{r})$ and $\nabla^2\rho(\mathrm{r})$ are 0.002–0.035 $\mathrm{e/a_0^3}$ and 0.024–0.139 $\mathrm{e/a_0^5}$, respectively, if H-bonds exist (Grabowski, 2001). The AIM calculation indicates intramolecular hydrogen bonds and critical points (H-BCP) for the two *Z*-**4(a, c)** and *E*-**4(a, c)** isomers. Intramolecular H-BCPs with a part of molecular graphs for the two rotational isomers are shown in Figs. 2 and 3. Most important rotational parameters involving some H-bonds (bond lengths and their relevant bond angles) are reported in Table 2. The electron density $\rho(\mathrm{r})$, Laplacian of electron density $\nabla^2\rho(\mathrm{r})$, and energy density $-H(\mathrm{r})$ are also reported in Tables 3 and 4. A negative total energy density at the BCP reflects a dominance of potential energy density, which is the consequence of accumulated stabilizing electronic

Table 2 Most important geometrical parameters corresponding to H-bonds (bond lengths and their relevant bond angles) for the two *E*- and *Z*-isomers in both ylides **4a** and **4c**. Bond lengths in angstroms and bond angles in degrees, respectively.

	E-4a	*Z*-4a		*E*-4c	*Z*-4c
C_{53}–$H_{60}\cdots O_7$	2.41[a] (118.06)[b]	2.38 (119.49)	C_{76}–$H_{78(76)}\cdots O_6$	2.42 (111.28)	2.44 (110.87)
C_{21}–$H_{25}\cdots O_6$	2.41 (103.41)	2.72 (89.39)	C_{68}–$H_{69(73)}\cdots O_6$	2.40 (111.69)	2.42 (112.07)
C_1–$H_2\ldots S_{58}$	2.54 (116.38)	2.55 (115.79)	C_{56}–$H_{57(39)}\cdots O_7$	2.95 (87.31)	2.53 (117.52)
C_{42}–$H_{45}\cdots N_{52}$	2.80 (153.84)	2.76 (150.60)	C_1–$H_2\cdots S_{52}$	2.55 (112.58)	2.62 (109.18)

[a] Bond lengths.

[b] Bond angles.

Table 3 The values of $\rho\times10^3$, $\nabla^2\rho\times10^3$ and Hamiltonian $-H(\mathrm{r})\times10^4$ 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	$\rho\times10^3$	$\nabla^2\rho\times10^3$	$-H(\mathrm{r})\times10^4$	*Z*	$\rho\times10^3$	$\nabla^2\rho\times10^3$	$-H(\mathrm{r})\times10^4$
1	13.78	57.32	18.9	1	12.82	47.24	9.9
2	17.15	58.04	12.4	2	12.29	44.20	11.4
3	12.40	45.80	9.5	3	6.28	22.84	7.1
4	5.69	21.12	7.1	4	16.90	57.72	13.1
5	10.55	38.92	17.6	5	10.27	38.80	17.9
6	7.58	29.00	8.5	6	8.76	32.32	7.4
7	10.49	38.84	17.8	7	10.31	37.00	17.2
8	10.89	37.48	16.0	8	9.95	34.24	14.6

Table 4 The values of $\rho\times10^3$, $\nabla^2\rho\times10^3$ and Hamiltonian $-H(\mathrm{r})\times10^4$ 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	$\rho\times10^3$	$\nabla^2\rho\times10^3$	$-H(\mathrm{r})\times10^4$	*Z*	$\rho\times10^3$	$\nabla^2\rho\times10^3$	$H(\mathrm{r})\times10^4$
1	5.89	23.96	9.6	1	3.08	13.52	7.8
2	11.87	46.12	13.0	2	2.77	8.96	4.9
3	11.44	44.88	13.6	3	9.71	38.40	17.7
4	17.14	59.96	14.3	4	13.00	49.28	11.9
5	2.44	9.12	6.1	5	12.66	48.56	12.7
6	9.63	39.24	13.4	6	12.66	49.40	13.8
7	3.21	11.68	7.3	7	11.91	46.48	13.3
8	2.19	7.64	5.1	8	4.88	20.72	9.6
9	13.61	51.44	11.9	9	3.04	11.96	7.8
10	13.18	50.04	12.1	10	15.55	57.08	17.4
11	15.17	61.88	17.3	11	4.28	11.04	4.8
12	5.89	23.96	9.6	12	9.24	31.76	14.4
13	12.24	44.36	17.6	13	9.63	36.28	17.5
14	11.48	39.80	15.2				
15	11.11	41.04	18.2				

charge (Arnold and Oldfield, 2000). Herein, the number of hydrogen bonds in both categories (*E*-**4a** and *Z*-**4a**) and (*E*-**4c** and *Z*-**4c**) are 8 and 8 and also 15 and 13, respectively. The values of $\rho(r)$ and $\nabla^2\rho(r)$ are in the ranges 0.006–0.017 and 0.006–0.017 e/a_0^3, 0.002–0.017 and 0.002–0.015 e/a_0^3, 0.021–0.058 and 0.023–0.058 e/a_0^5 and 0.007–0.062 and 0.008–0.057 e/a_0^5, respectively. In addition the Hamiltonian $-H(r)$ is in the range 7.1–18.9 and 7.1–17.9 au and 5.1–18.2 and 4.8–17.7 au (see Tables 3 and 4).

These HBs show $\nabla^2\rho(r) > 0$ and $H(r) < 0$, which according to classification of Rozas et al. (2000) are medium—-strength hydrogen bonds. In both ylides the dipole moment for the two *E*-**4a** and *E*-**4c** isomers (5.14 and 6.13 D, respectively) are smaller than the two *Z*-**4a** and *Z*-**4c** isomers (7.92 and 9.86 D, respectively) and the value of $-H_{tot}$ $(=H(r))$ for the two *E*-**4a** and *E*-**4c** isomers (107.8 and 184.3 au, respectively) are larger than the two *Z*-**4a** and *Z*-**4c** isomers (98.6 and 153.6 au, respectively). These differences in the most important geometrical parameters of the *E*-**4(a**, **c)**, with respect to the *Z*-**4(a**, **c)**, involving a fair difference in dipole moment and a considerable difference in $-H(r)$ and also approximately same number of hydrogen bonds, taken altogether, make a stability on these isomers in comparison with the *Z*-**4(a, c)** forms (the results are summarized in Table 5).

On the basis of theoretical calculations (Table 1), both the *Z*-**4a** and *Z*-**4c** have a slight stability with respect to the two *E*-**4a** and *E*-**4c** (0.33 and 1.82 kcal/mol) isomers and seem to be different from the results of predictable properties of the most important geometrical parameters (Table 5). Perhaps, this slightly different behavior is relevant to the huge structures of the two ylides **4(a, c)** involving four large atoms such as the two sulfurs, one phosphorus, one nitrogen and four oxygens 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 are shown in Table 5 (involving a considerable difference in total Hamiltonian ($-H_{tot}$) and a fair difference in dipole moment, taken altogether as two dominant factors of stability on the two *E*-**4a** and *E*-**4c**) are compatible with the experimental results from the ^{1}H, ^{13}C and ^{31}P NMR spectroscopy which indicate the two isomers of *Z*-**4a** and *E*-**4a** with experimental abundance percentage of 75% for *E*-**4a** (as a major form) and also only a lone isomer of **4c** (*E*-**4c**). Moreover, the total number of hydrogen bonds in the two *Z*-**4c** and *E*-**4c** (13, 15) are more than two in the *Z*-**4a** and *E*-**4a** (8, 8). 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 accompanied by more steric factor of the bulky *tert*-buthyl groups (compare with dimethyl groups the structures in both the *E*-**4a** and *Z*-**4a**, Figs. 2 and 3) within the structures (*E*-**4c** and *Z*-**4c** forms) makes a good opportunity for enhancement of energy barrier and also explanation of abundance percentage of the these two isomers. Hence, interconversion process between the two *E*-**4c** and *Z*-**4c** isomers needs to pass through very high restricted barrier energy, particular in solution media. For this reason it is possible to see only a single isomer as a lone isomer of **4c** (*E*-**4c**). On the contrary, interconversion process for both the *E*-**4a** and *Z*-**4a** geometrical isomers passes through a considerably low energy barrier, which leads to a plausible observation of the two *E*-**4a** and *Z*-**4a** (see Fig. 1, j).

Also, the charge on different atoms which are calculated by AIM and NPA methods and also CHelpG keyword at HF/6-31G(d,p) level are reported in Table 6 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 most important geometrical parameters involving the value of $-H_{tot}$/au, dipole moment/D and number of hydrogen bonds for the two *Z*- and *E*-isomers of ylides **4a** and **4c**.

Isomer	$-H_{tot}$/au	Dipole moment/D	Number of hydrogen bonds
Z-**4a**	98.6	7.92	8
E-**4a**	107.8	5.14	8
Z-**4c**	153.6	9.86	13
E-**4c**	184.3	6.13	15

Table 6 The charges on different atoms for the two *Z*- and *E*-isomers in both ylides **4a** and **4c** at HF/6-31G(d,p) level.

Number of atom	*Z*-**4a**	*E*-**4a**	*Z*-**4c**	*E*-**4c**
C1	6.59×10^{-1}[a] (0.40)[b](−0.11)[c]	6.78×10^{-1} (0.39)(−0.11)	7.05×10^{-1} (0.54)(−0.11)	7.07×10^{-1} (0.46)(−0.11)
C3	-7.93×10^{-1} (−0.76)(−0.83)	-7.84×10^{-1} (−0.77)(−0.83)	-7.82×10^{-1} (−0.66)(−0.83)	-7.50×10^{-1} (−0.66)(−0.81)
C5	1.85 (0.79)(0.91)	1.83 (0.76)(0.90)	1.87 (0.85)(0.90)	1.84 (0.80)(0.91)
O6	−1.40 (−0.60)(−0.78)	−1.42 (−0.62)(−0.78)	−1.41 (−0.60)(−0.77)	−1.40 (−0.61)(−0.80)
O7	−1.28 (−0.34)(−0.45)	−1.28 (−0.28)(−0.44)	−1.29 (−0.53)(−0.48)	−1.29 (−0.54)(−0.47)
P4	3.21 (0.44)(1.74)	3.22 (0.42)(1.74)	3.24 (0.20)(1.75)	3.21 (0.25)(1.74)

[a] Calculated by AIM method.
[b] Calculated by CHelpG keyword.
[c] Calculated by NPA method.

Furthermore, the individual chemical shifts have been characterized by NMR calculations at the mentioned level for the two major *E*-**4(a, c)** and minor *Z*-**4(a, c)** geometrical isomers. The total spin–spin coupling constant is the sum of four components: the paramagnetic spin–orbit (PSO), diamagnetic spin–orbit (DSO), Fermi-contact (FC), and spin-dipole (SD) terms. The value of chemical shifts (δ) and coupling constants (J_{x-y}) is reported in Tables 7–10. As can be seen there is a good agreement between both the experimental (Maghsoodlou et al., 2005) and theoretical chemical shifts (δ) and coupling constants (J_{x-y}). In the present work, molecular structures of ylides **4(a, c)** involving four large atoms such as two sulfur, one phosphorus, one nitrogen and four oxygen atoms are huge molecules with the very large number of other atoms (C, H), this point makes a limitation for employment of basis set higher than B3LYP/6-311++G(d,p) in a higher performance for more accurate calculations. This limitation causes a small difference between both the experimental and theoretical coupling constants in some functional groups.

Table 7 Selected ^{13}C NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for some functional groups in the *E*-**4a** isomer as a major form.

Groups	δ^{C}/ppm	J_{PC}/Hz
2s, 2OMe	52.57[a] (50.61)[b]	
	54.01 (51.53)	
d, C_{ipso}	123.33 (125.39)	92.1[a] (90.8)[b]
d, $C^8{=}O$	169.82 (166.75)	13 (13.4)
d, $C^5{=}O$	171.07 (169.28)	12.3 (10.9)
d, C_{para}	132.36 (132.64)	
d, $P{=}C^3$	41.28 (39.93)	
d, C_{meta}	129.13 (126.98)	12.2 (8.9)
C^{55}–C–N	28.15 (22.43)	
C^{53}–C–S	49.24 (48.38)	
C=S	195.13 (204.68)	
d, C_{ortho}	133.47 (135.09)	
d, P–C–C^1H	61.37 (55.21)	

[a] Experimental data in accordance with the results reported in the literature (Maghsoodlou et al., 2005).
[b] Theoretical data.

Table 8 Selected ^{1}H NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for some functional groups in the *E*-**4a** isomer as a major form.

Groups	δ^{H}/ppm	J_{PH}/Hz
4H, 2s, $2CO_2Me$	3.13[a] (3.12)[b]	
	3.78 (3.72)	
15H, m, $3C_4H_5$	7.49–7.67	
	(7.42–7.97)	
1H, d, P–C–C–H^2	5.41 (5.33)	17.5[a] (14.9)[b]
2H, m, CH_2N	3.14 (3.42)	
2H, m, CH_2S	4.40 (3.14)	

[a] Experimental data in accord with the results reported in the literature (Maghsoodlou et al., 2005).
[b] Theoretical data.

Table 9 Selected ^{13}C NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for some functional groups in *Z*-**4a** isomer as a minor form.

Groups	δ^{C}/ppm	J_{PC}/Hz
2s, 2OMe	52.38[a] (49.03)[b]	
	53.78 (50.02)	
d, C_{ipso}	125.7 (126.50)	92.5[a] (92.5)[b]
d, C_{ortho}	133.50 (135.10)	
d, C_{meta}	129.1 (127.30)	12.2 (15.37)
d, C_{para}	132.4 (132.10)	
d, $C^5{=}O$	170.8 (168.30)	
d, $C^8{=}O$	170.3 (169.00)	17.9 (15.80)
C^{55}–C–N	27.98 (26.17)	
C^{53}–C–S	50.20 (49.79)	
d, P–C–C1–H^2	60.96 (56.28)	
d, P=C	42.34 (33.12)	
$C^{54}{=}S$	195.3 (205.0)	

[a] Experimental data in accord with the results reported in the literature (Maghsoodlou et al., 2005).
[b] Theoretical data.

Table 10 Selected ^{1}H NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for some functional groups in the *Z*-**4a** isomer as a minor form.

Groups	δ^{H}/ppm	J_{PH}/Hz
6H, 2s, $2CO_2Me$	3.53[a] (3.29)[b]	
	3.75 (3.77)	
15H, m, $3C_6H_5$	7.49–7.67	
	(7.52–7.95)	
1H, d, P–C–C–H^2	5.39 (5.22)	14.4[a] (18.8)[b]
2H, m, CH_2N	3.25 (3.53)	
2H, m, CH_2S	4.56 (4.20)	

[a] Experimental data in accord with the results reported in the literature (Maghsoodlou et al., 2005).
[b] Theoretical data.

4. Conclusion

The assignment of the *E*- and *Z*-isomers as a major or minor form in both the ylides **4a** and **4c** were undertaken by AIM and NPA methods and also CHelpG keyword. Quantum mechanical calculations were clarified how the ylides **4a** and **4c** exist in solution as a mixture of the two geometrical isomers (*E*-**4a** and *Z*-**4a**) or a lone isomer (*E*-**4c**), respectively. In addition NMR study on the basis of theoretical calculations were employed for the determination of chemical shifts and coupling constants of the two major *E*-**4a** and minor *Z*-**4a** geometrical isomers. Both the former and the latter theoretical results are compatible with the experimental data from the ^{1}H, ^{13}C and ^{13}P NMR spectroscopy.

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