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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 particle 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 using AIM method.

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 organophosrhorus 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 have 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]. 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.

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 also obtained from Merk (Darmstadt, Germany).

RESULTS AND DISCUSSION

Calculations

A facile synthesis of the reaction between triphenylphosphine 1, dialkyl acetylendicarboxylates 2 and 2-thiazoline-2-thiol 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-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[32]. 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 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 fac-

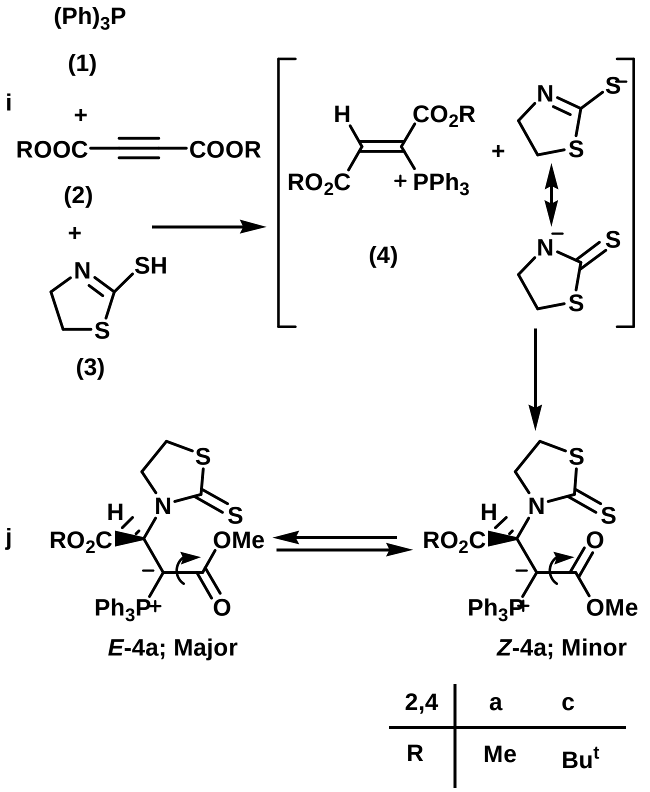

Figure 1 : i) The reaction between triphenylphosphine 1, dialkyl acetylenedicarboxylate 2 (2a or 2c) and 2-thiazoline-2-thiol 3 for generation of stable phosphorus ylides 4 (4a or 4c). j) The two *Z*-4a and *E*-4a rotational isomers (Minor and Major, respectively) of ylide 4a.

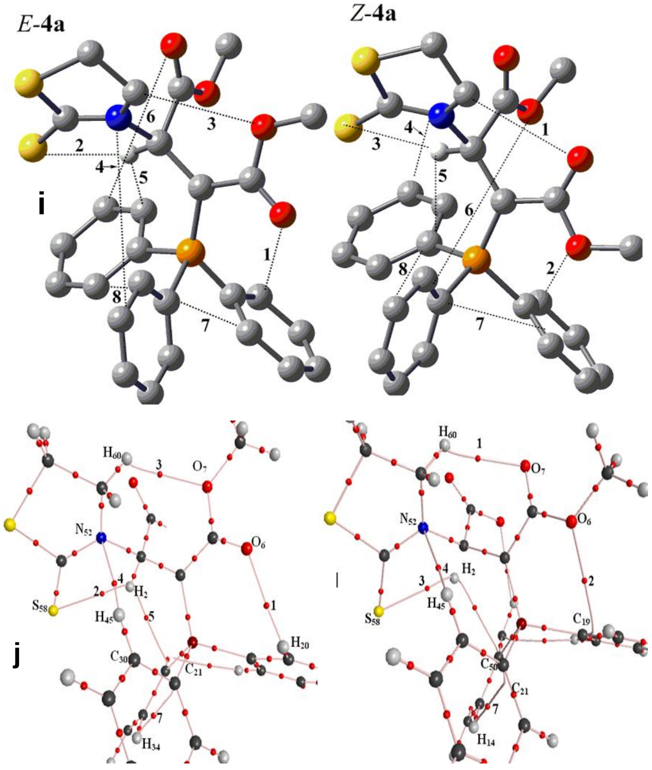

Figure 2 : i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-4a and *Z*-4a geometrical isomers of stable ylide 4a. j) Part of molecular graphs, including intermolecular hydrogen bond critical points (BCPs) for the two *E*-4a and *Z*-4a geometrical isomers of stable ylide 4a.

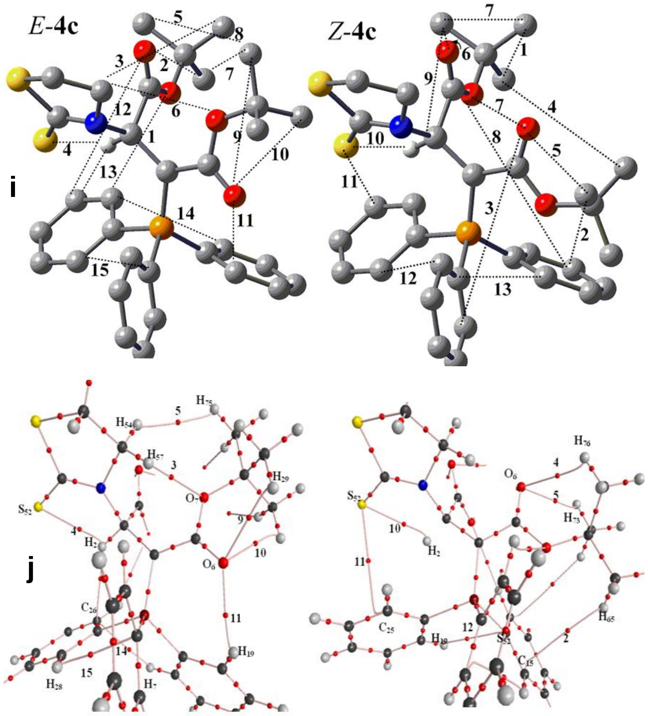

Figure 3 : i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-4c and *Z*-4c geometrical isomers of stable ylide 4c. j) Part of molecular graphs, including intermolecular hydrogen bond critical points (BCPs) for the two *E*-4c and *Z*-4c geometrical isomers of stable ylide 4c.

tors 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 Figures 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.

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
Z-4a	0.00	0.00
E-4a	0.09	0.33
Z-4c	0.00	0.00
E-4c	3.76	1.82

Further investigation was undertaken in order to determine more effective factors on stability of the two *Z*- and *E*- isomers, on the basis of AIM calculations[34] at HF/6-31G(d,p) level of theory by the AIM2000 program package[35]. In recent years, AIM theory has often 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 $\rho(r)$ and on the Laplacian of the electron density $\nabla^2\rho(r)$. The Laplacian of the electron density, $\nabla^2\rho(r)$, identifies regions of space wherein the electronic charge is locally depleted $[\nabla^2\rho(r) > 0]$ or built up $[\nabla^2\rho(r) < 0]$[34].

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[36]. 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 Figures 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 $\rho(r)$, Laplacian of electron density $^2\rho(r)$, and energy density -H(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 charge[37]. 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-

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

[a] Bond lengths; [b] Bond angles

0.017 and 0.002-0.015 e/a_0^3), (0.021-0.058 and 0.023-0.058 e/a_0^3) and (0.007-0.062 and 0.008-0.057 e/a_0^3), 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).

TABLE 3 : The values of $\rho \times 10^3$, $\nabla 2\rho$ 10^3 and hamiltonian [-H(r)] $\times 10^4$ 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	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H(r) \times 10^4$	*Z*	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H(r) \times 10^4$
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 $\rho \times 10^3$, $\nabla 2\rho$ 10^3 and hamiltonian [-H(r)] $\times 10^4$ 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	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H(r) \times 10^4$	*Z*	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H(r) \times 10^4$
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				

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 (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 $-H_{tot}$ ($=\sum H(r)$) 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 fairly 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).

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

On the basis of theoretical calculations (TABLE 1), both the *Z*-4a and *Z*-4c have a slightly 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 oxygen 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 deference in total Hamiltonian ($-H_{tot}$) and a fairly deference in dipole moment, taken altogether as dominate two 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 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 dimethy groups the structures in both the *E*-4a and *Z*-4a, Figures 2 and 3) within (*E*-4c and *Z*-4c forms) make 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 a 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 pass through a considerably low energy barrier, this leads to a plausible observation of the two *E*-4a and *Z*-4a (See Figure 1, j).

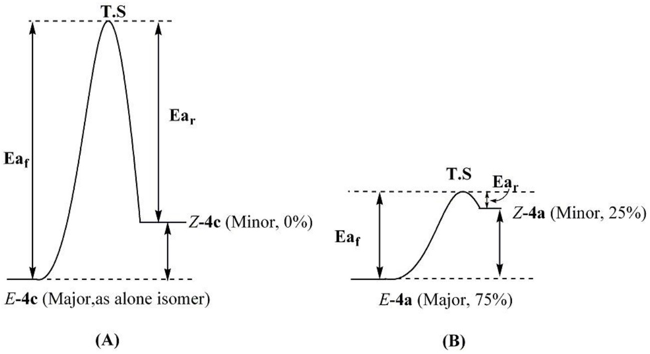

Figure 4 : Interchangeable process of geometrical isomers for ylides 4a and 4c. A) A very high restricted barrier energy for introversion process between the two *E*-4c and *Z*-4c isomers. B) A low restricted barrier energy for introversion process between the two *E*-4a and *Z*-4a isomers.

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.

Furthermore, the individual chemical shifts have been characterized by NMR calculations at 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 ($J_{x\text{-}y}$) are reported in TABLES 7-10. As can be seen there is good agreement between both the experimental[31] and theoretical chemical shifts (δ) and coupling constants ($J_{x\text{-}y}$). In the present work, molecular structures of ylides 4(a, c) involving four large atoms such as two sulfur atoms, one phosphorus,

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

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

TABLE 7 : Selected ^{13}C NMR chemical shift (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, Cortho	133.47 (135.09)	
d, P-C-C^1H	61.37 (55.21)	

[a] Experimental data in accord with the results reported in the literature[31]; [b] Theoretical data.

TABLE 8 : Selected ^{1}H NMR chemical shift (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[31]; [b] Theoretical data.

TABLE 9 : Selected ^{13}C NMR chemical shift (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.[31]; [b] Theoretical data.

TABLE 10 : Selected ^{1}H NMR chemical shift (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.[31]; [b] Theoretical data.

one nitrogen and four oxygen are huge molecules with the very large number of other atoms (C, H), this point make a limitation for employment of basis set higher than B3LYP/6-311++G(d,p) in a higher performance for more accurate calculations. This causes difference between both the experimental and theoretical coupling constants in some functional groups.

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 determination of chemical shifts and coupling constants of the two major *E*-4a and minor *Z*-4a geometrical isomers. Both former and later theoretical results are compatible with the experimental data from the ^{1}H, ^{13}C and ^{13}P NMR spectroscopy.

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