Assignment of the Major Geometrical Isomer of the Synthesized Stable Phosphorus Ylide: Crystallography and Theoretical Approaches

NILOUFAR AKBARZADEH-TORBATI* and MEHDI SHAHRAKI

Department of Chemistry, University of Sistan and Baluchestan, P.O. Box 98135-674, Zahedan, Iran
*Corresponding author E-mail: n.akbarzadeh@chem.usb.ac.ir

ABSTRACT

The crystal structure of di-t-butyl-(N-2-indolinone-1-yl)-3- (triphenylphosphoranylidene) succinate has been determined by X-ray crystallography. This ylide was crystallized in the monoclinic system with space group *P21/n* and cell parameters a=15.0375(6) Å, b = 11.5130(5) Å, c = 19.1325(8) Å, β = 101.577(4)°, V = 3245.0(2) Å^3, D$_{calc}$= 1.273 g.cm^{-3} and Z = 4. The final R value is 0.0435 for 44084 reflections. This stable ylide existed as a mixture of two geometrical isomers in solution as a result of restricted rotation around the carbon-carbon partial double bond. The X-ray study showed that adjacent carbonyl group in the ylide moiety of compound had a resonance with bond of C=P and also, intermolecular C-H…O hydrogen bonds were effective on stability of the crystal structure. In addition, the stability of the two Z- and E- isomers and the most important geometrical parameters have been elucidated by natural population analysis (NPA) and atoms in molecules (AIM) methods.

Key words: Ylide; X-ray Crystallography; Isomer; AIM; NBO

INTRODUCTION

Organophosphorus compounds have emerged as important reagents and intermediates in organic synthesis[1]. An important group of this class is phosphorus ylides, which are used in many reactions and synthesis of organic compounds[2-8]. The prominent role of these compounds is to convert the carbonyl groups to carbon-carbon double bonds[9]. Michael addition of phosphorus (III) compounds such as triphenylphosphine to acetylenic esters leads to reactive 1, 3-dipolar intermediate betaines which are not detected even at low temperature[10]. These unstable species can be trapped by a protic reagent, ZH, such as methanol, amide, imide, etc. to produce various compounds e.g. ylides[11, 12]. In the present work, we reported the synthesis of the stable phosphorus ylides obtained by the reaction between triphenylphosphine and di-t-butyl acetylenedicarboxylate in the presence of indoline-2-one[8] (Fig. 1). These ylides usually exist as a mixture of the two geometrical isomers, although some ylides exhibit one geometrical isomer. Assignment of the two Z- and E- isomers are possible by some experimental methods such as ^{1}H, ^{13}C NMR, IR spectroscopy, mass spectrometry and elemental analysis data [13-16]. In order to gain a better understanding of the major isomer, the crystal structure of di-t-butyl-(N-2-indolinone-1-yl)-3-(triphenylphosphoranylidene) succinate was determined by X-ray crystallography. In addition, some theoretical methods have been performed for calculating the most important geometrical parameters and also relative energies of the both geometrical isomers.

EXPERIMENTAL

Material and Methods

Di-tert-butyl acetylenedicarboxylate, triphenylphosphine and indoline-2-on were purchased from Fluka (Buchs, Switzerland) and used without further purification. All extra pure solvents including dichloromethane, 1, 2-dichloroethane and THF obtained from Merck (Darmstadt, Germany).

Melting points and IR spectra was measured on an Electrothermal 9100 apparatus and a Shimadzu IR-470 spectrometer, respectively. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker DRX-500 AVANCE instrument with CDCl$_3$ as a solvent at 500.1, 125.8, and 202.4 MHz, respectively. The X-ray diffraction measurements of ylide **4** were made on an Oxford Diffraction Gemini diffractometer 100K (Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å). The crystal of ylide **4** was solved by SHELXL-97 [17]. Absorption correction, data collection, cell refinement and data reduction have been carried out by using Oxford Diffraction Ltd [18-19], ORTEP (molecular graphics) [20], and WinGX (publication material)[21]. CCDC 760457 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center.

Preparation of di-tert-butyl2-(N-2-indolinone-1-yl)3(triphenylphosphoranylidene) succinate 4

To a magnetically stirred solution of 2-indolinone (0.15 g, 1 mmol) and triphenylphosphine (0.26 g, 1 mmol) in 10 mL of ethyl acetate was added, dropwise, a mixture di-t-butyl acetylenedicarboxylate (0.23 g, 1 mmol) in 4 mL of ethyl acetate at -5°C over 10 min. After approximately 10 h stirring at room temperature, product was filtered and recrystallized from ethyl acetate.

Di-tert-butyl 2-(N-2-indolinone-1-yl)-3-(triphenylphosphoranylidene) succinate **4**: White powder, yield 0.60 g (95%), m.p. 197-200°C, IR (KBr) (v_{max}, cm^{-1}): 1736, 1710 and 1638 (C=O). Analysis: Calc: for C$_{38}$H$_{40}$NO$_5$P (621.26) : C,73.4; H, 6.4; N, 2.25%; Found: C,73.3; H, 6.5; N, 2.1%. Major isomer (Z): ^{1}H NMR (500.1 MHz, CDCl3): δH 0.97 and 1.57 (18H, 2s, 2OCMe$_3$), 3.10 (^{1}H, 2d, ^{2}J$_{HH}$= 21.9 Hz, CH2), 5.47 (1H, d, ^{3}J$_{PH}$= 18.2 Hz, P=C-CH), 6.98 (1H, t, J=7.4 Hz, CH$_{arom}$), 7.11 (1H, d, J=7.2 Hz, CH$_{arom}$), 7.31 (1H, t, J=7.7 Hz, CHarom), 7.95 (1H, d, J=7.9 Hz, CH$_{arom}$), 7.37 -7.67 (15 H, m, 3C6H5). ^{13}C NMR (125.8 MHz, CDCl3): äC 28.2 and 28.4 (2CMe$_3$), 35.45 (CH$_2$), 37.7 (d, ^{1}J$_{PC}$ =122.5 Hz, P=C), 54.5 (d, ^{2}J$_{PC}$= 16.2 Hz, CH), 77.3 and 80.6 (2OCMe$_3$), 113.3-127.8 (6C, C$_6$H$_4$), 126.9 (d, ^{1}J$_{PC}$= 91.1 Hz, C$_{ipso}$), 128.5 (d, ^{3}J$_{PC}$= 12.2 Hz, C$_{meta}$), 131.9 (d, ^{4}J$_{PC}$= 1.9 Hz, C$_{para}$), 133.7 (d, ^{2}J$_{PC}$= 9.6 Hz, C$_{ortho}$), 168.7 (d, ^{3}J$_{PC}$= 11.8 Hz, C=O), 169.6 (d, ^{2}J$_{PC}$= 14.8 Hz, P-C=C), 173.7 (NC=O). ^{31}P NMR (202.4 MHz, CDCl$_3$): δ_P 22.5 (Ph$_3$P$^+$–C).

Table 1: Crystal data and structure refinement for C$_{38}$H$_{40}$NO$_5$P 4

C$_{38}$H$_{40}$NO$_5$P 4	Formula
621.68	Formula weight
100(2)	Temperature(K)
0.71073	Wavelenght (Å)
Monoclinic	Crystal system
*P*2$_1$/*n*	Space group
0.4×0.13×0.12	Crystal size/mm³
a = 15.0375(6) Å	Unit cell dimentions
b = 11.5130(5) Å	
c = 19.1325(8) Å	
β= 101.577(4)°	
3245.0(2) Å3	Volume
4	Z
1.273	Density(calculated) g cm^{-3}
3.6161- 32.5621°	Theta ranges for data collection
1320	F(000)
0.13 mm^{-1}	Absorption coefficient
-20 ≤ h ≤ 22	Index ranges
-16 ≤ k ≤ 16	
-25 ≤ l ≤ 28	
44084	Data collected
0.0772	Unique data (R_{int})
412/ 0	parameters / restraints
0.0435, 0.071	Final R_1, wR_2[a] (Obs. data)
0.107, 0.0788	Final R_1, wR_2[a] (all data)
412	Absolute structure parameter
0.794	Goodness of fit on F^2 (S)
0.393, -0.417	Largest diff peak and hole /e.Å^{-3}
760457	CCDC

[a]R_1 = S||F$_o$|-|F$_c$||/S|F$_o$|, wR2 = [S[w(F$_o$²-F$_c$²)²]/S[w(F$_o$²)²

RESULTS AND DISCUSSIONS

X-ray Crystallography

For establishing the major conformer, X-ray analysis of the ylide **4** is preceded. The single crystals were grown from a mixture of $CHCl_3/Et_2O$ solution. A summary of the crystal data for ylide **4**, experimental details and refinement results is given in **Table 1**. The molecular structure of ylide **4**, showing the atom numbering scheme is illustrated in **Fig. 2**. Also, the molecular packing of ylide **4** is drawn in **Fig. 3**.

Table 2: Hydrogen bond geometries of $C_{38}H_{40}NO_5P$ in the crystal packing (Å). Symmetry codes: (i) 1-X,1-Y,1-Z, (ii) 1/2-X,-1/2+Y,3/2-Z

D -H···A	D -H	H···A	D···A	D - H···A
C3%H3A…O2[i]	0.99[a](1.09)[b]	2.47[a](2.74)[b]	3.3535[a](17)(2.4236)[b]	149[a] (60)[b]
C31%H31…O2	1.00(1.08)	2.42(2.34)	2.7890(15)(2.7715)	101(102)
C313%H31C…O311	0.98(1.08)	2.45(2.46)	3.0131(17)(3.0304)	116(111)
C314%H31D…O311	0.98(1.09)	2.50(2.48)	3.0938(16)(3.0312)	118(110)
C323%H32A…O321	0.98(1.07)	2.43(2.42)	3.0098(18)(2.9970)	118(112)
C324%H32F…O321	0.98(1.08)	2.48(2.42)	3.0407(17)(2.9904)	116(111)
C114%H114…O2[ii]	0.95(1.07)	2.39(2.49)	3.2702(17)(3.1807)	154(121)
C116%H116…O312	0.95(1.07)	2.55(2.46)	3.4452(16)(3.5107)	156(164)

[a]: The experimental data obtained from X-ray.   [b]: The theoretical data for the **Z**-isomer obtained at HF/6-31G(d,p) level.

Table 3. The selected Bond Lengths (Å), Bond Angles (°) and Torsion Angles for $C_{38}H_{40}NO_5$

Bond Lengths	(Å)	Bond Angles	(°)	Torsion Angles	(°)
O(321) - C(321)	1.2295[a](16) [1.2060][b] [1.2180][c]	O(322) - C(321) - C(32)	110.15[a](10) [112.95][b] [116.60][c]	C(31) C(32) C(321) O(321)	14.7[a](2) [5.24][b]
O(322) - C(321)	1.3721(16) [1.3466] [1.3341]	O(321) - C(321) - O(322)	122.98(11) [122.04] [121.81]	P(1) C(32) C(321) O(321)	179.62(11) [168.13]
P(1) - C(32)	1.7208(13) [1.7268] [1.7386]	O(321) - C(321) - C(32)	126.87(12) [125.00] [121.60]	P(1) C(32) C(321) O(322)	-0.45(14) [-12.96]
C(32) - C(321)	1.4179(17) [1.4292] [1.4257]	P(1) - C(32) - C(321)	117.35(9) [119.93] [111.71]	C(31) C(32) C(321) O(322)	-165.33(10) [-173.64]
C(31) - C(32)	1.5094(18) [1.5075] [1.5036]	P(1) - C(32) - C(31)	120.99(9) [121.31] [121.03]	N(1) C(31) C(311) O(312)	-163.78(10) [-162.35]
N(1) - C(31)	1.4687(15) [1.4684] [1.4697]	C(31) - C(32) - C(321)	119.86(11) [118.42] [127.15]	N(1) C(31) C(32) C(321)	-105.00(13) [-72.13]
C(31) - C(311)	1.5315(18) [1.5340] [1.5354]	N(1) - C(31) - C(311)	110.12(10) [112.63] [112.01][c]	C(311) C(31) C(32) C(321)	24.16(16) [38.50]
O(311) - C(311)	1.1992(16) [1.1904] [1.1896]	O(311) - C(311) - C(31)	125.80(12) [123.66] [124.55][c]	N(1) C(31) C(32) P(1)	90.68(12) [124.65]
O(312) - C(311)	1.3463(15) [1.3175] [1.3196]	O(312) - C(311) - C(31)	107.27(10) [111.10] [110.27][c]	C(311) C(31) C(32) P(1)	-140.16(9) [-101.16]
				C(32) C(31) C(311) O(312)	63.82(13) [174.18]
				C(32) C(31) C(311) O(311)	-120.58(14) [116.52]

[a]: The experimental data obtained from X-ray for ylide **4** compound.
[b]: The theoretical data for the **Z-4** isomer obtained at HF/6-31G(d,p) level.
[c]: The theoretical data for the hypothetical **E-4** isomer obtained at HF/6-31G(d,p) level.

The X-ray study of ylide **4** shoewd some weak intermolecular C-H...O hydrogen bonds (**Table 2**) which are effective on stability of the crystal structure. Selected bond lengths, bond angles, and torsion angles of C38H40NO5P **4** are listed in **Table 3**. As can be seen in **Tables 2 and 3**, there is a good agreement between the obtained results emerged from these methods for crystal structure of ylide **4**, **E-4** (hypothetical) and **Z-4**.

On the basis of X-ray crystallography data, it is obvious that adjacent carbonyl group in the ylide moiety of ylide **4** ($C_{321}=O_{321}$, **Fig. 2**) has a resonance with bond of $C_{32}=P_1$. In the present work, single crystal X-ray diffraction of stable phosphorus ylide **4** was prepared from a solution involving 95% of major isomer (**Z** isomer, in accordance with ^{1}H-NMR data). Herein X-ray analysis exhibited the **Z**-structure for this compound, the tert-butoxy and triphenylphosphine groups are placed in the same

Table 4: Most important rotation parameters corresponding to H-bonds (bond lengths and their relevant bond angles) for the two E- and Z- isomers in ylide 4. Bond lengths in angstroms and bond angles in degrees

H-Bonding	E-4	Z-4
C_{82}-H_{85}...O_{58}	2.18[a]	2.47[a]
	(114.3)[b]	(111.3)[b]
C_4-H_7...O_{58}	2.53	2.46
	-164.8	-164.2
C_{26}-H_{29}...O_{56}	2.46	2.34
	-128.6	-120.6
C_{78}-H_{80}...O_{58}	2.32	2.48
	-102.1	-110.3

[a]Bond lengths on the basis of theoretical calculation
[b] Bond angles on the basis of theoretical calculation

Table 5: The values of r ´10³, ∇² × 10³ and Hamiltonian –H(r) ×10⁴ for the two Z-4 and E-4 isomers of ylide 4 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	6.192	20.50	-10.11	1	3.441	11.68	-6.857
2	3.754	12.69	-7.236	2	13.03	52.77	-16.11
3	7.593	34.52	-20.30	3	13.12	49.71	-11.88
4	6.316	25.63	-10.77	4	13.09	49.85	-12.31
5	14.25	54.31	-12.45	5	11.84	45.87	-12.86
6	14.96	56.92	-12.63	6	11.60	45.20	-13.22
7	11.26	43.46	-11.01	7	8.985	32.38	-6.484
8	11.64	45.15	-12.84	8	8.047	33.12	-12.21
9	11.40	44.62	-13.40	9	2.644	8.139	-4.577
10	7.234	27.32	-8.087	10	2.790	8.974	-4.899
11	12.20	43.84	-16.42	11	9.166	36.60	-12.41
12	9.653	37.96	-11.53	12	9.543	34.40	-16.45
13	9.918	36.09	-16.97	13	9.518	32.86	-14.50
14	9.191	31.61	-14.71				

Table 6: The most important geometrical parameters involving the value of -H_{tot}/au, dipole moment/D and the number of hydrogen bonds for the two Z- and E- isomers of ylide 4

Geometrical isomer	-H_{tot}/au	dipole moment/D	number of hydrogen bond
E-**4**	171.2	3.17	14
Z-**4**	144.8	4.35	13

**Table 7: The charges on different atoms for both Z- and
E- isomers in ylide 4 calculated at HF/6-31G(d,p) level**

Number of atom	Z-4a	E-4a	Z-4c	E-4c
P1	3.25 [a]	3.24	3.24	3.25
	(3.22×10^{-1})[b]	(2.65×10^{-1})	(3.81×10^{-1})	(2.58×10^{-1})
	(1.87)[c]	(1.87)	(1.87)	(1.87)
C2	-7.63×10^{-1}	-7.81×10^{-1}	$-7.37 \times 10^{-}$	-7.6×10^{-1}
	(-7.06×10^{-1})	(-6.82×10^{-1})	$(-7.49 10^{-1})$	(-7.79×10^{-1})
	(-8.93×10^{-1})	(-8.80×10^{-1})	(-8.90×10^{-1})	(-8.69×10^{-1})
C36	7.48×10^{-1}	7.48×10^{-1}	7.52×10^{-1}	7.66×10^{-1}
	(4.83×10^{-1})	(4.49×10^{-1})	(5.17×10^{-1})	(6.09×10^{-1})
	(-1.06×10^{-1})	(-1.03×10^{-1})	(-9.91×10^{-2})	(-1.03×10^{-1})
C38	1.85	1.85	1.85	1.86
	(9.11×10^{-1})	(9.07×10^{-1})	(9.25×10^{-1})	(1.02)
	(9.68×10^{-1})	(9.63×10^{-1})	(9.76×10^{-1})	(9.68×10^{-1})
O39	-1.40	-1.40	-1.40	-1.42
	(-7.09×10^{-1})	(-7.14×10^{-1})	(-7.16×10^{-1})	(-7.12×10^{-1})
	(-7.79×10^{-1})	(-8.03×10^{-1})	(-7.90×10^{-1})	(-8.18×10^{-1})
O40	-1.28	-1.27	-1.31	-1.27
	(-4.54×10^{-1})	(-4.13×10^{-1})	(-5.77×10^{-1})	(-7.31×10^{-1})
	(-6.68×10^{-1})	(-6.52×10^{-1})	(-6.93×10^{-1})	(-6.70×10^{-1})

a) Calculated by AIM method.b) Calculated by CHelpG keyword.c) Calculated by NPA method.

side of carbon-carbon double bond (**Fig. 1.**). On the other hand, the structural assignments of the **Z**-isomer as a major form have previously been reported for other phosphorus ylides[22, 15]. Herein the ^{1}H NMR spectrum of ylide **4** exhibited two singlets at 0.97 and 1.57 ppm arising from the two tert-butoxy groups; this only occurs for the **Z**-isomer of ylide **4** because of the tert-butoxy group (at 0.97 ppm) is shielded due to the anisotropic effect of a phenyl group of triphenylphosphine. This phenomenon for the two tert-butoxy groups in the **E**-isomer could not be observed in the ^{1}H NMR spectroscopy and chemical shifts for the two tert-butoxy groups in this isomer should be appeared near to each other, this imply that on other demonstration for confirmation of the **Z**-isomer in comparison with the **E**-isomer. On the basis of this information the results of previous works [8] should be corrected, and the major form should be reported for the **Z**-isomer of ylide **4** or other ylides.
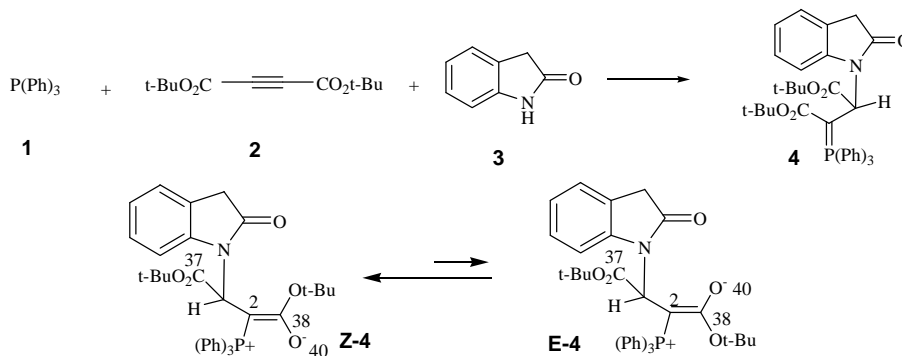

**Fig. 1: The reaction between triphenylphosphine 1, di-tert-butyl acetylenedicarboxylate
2 and indoline-2-one 3 for generation of stable phosphorus ylide 4, two
rotational isomers Z-4 and E-4 (major and minor, respectively) for ylide 4**

Table 8: The selected ^{13}C NMR chemical shift (d in ppm) and coupling constants (J in Hz) for some functional groups in the Z-4 and E-4 isomers as a major and minor

groups	d^C/ppm	J_{PC}/Hz
2s 2OMe*	49.0[a] (45.2)[b] , 52.5[a] (47.0)[b] *	
2s 2OMe**	49.0[a] (47.0)[b] , 50.4[a] (47.0)[b]**	
d C_{ipso}	127.0 (126.5)	92.3[a] (92.5)[b]
d C_{ipso}	124.5 (125.6)	91.2[a] (90.7)[b]
d C=O[39]	169.1 (167.3)	
d C=O[40]	169.1 (164.5)	
d C_{para}	133.6 (132.7)	
d C_{para}	133.1 (133.0)	
d C_{meta}	128.8 (126.3)	
d C_{meta}	128.5 (126.6)	
d C_{ortho}	133.6 (133.7)	9.2 (10.7)
d C_{ortho}	133.7 (132.7)	8.9 (10.1)
6C, C_6H_4	122.85 (121.3) , 133.5 (137.7)	
6C, C_6H_4	122.85 (123.2) , 133.4 (127.8)	
NC=O	167.5 (173.3)	
NC=O	167.5 (174.2)	
d, P=C[2]	38.9 (33.40)	
d, P=C[2]	37.2 (31.9)	
d, P-C=C[38]	171.4 (173.3)	13.2 (13.0)
d, P-C=C[38]	170.9 (174.2)	13.2 (12.8)
d, P-C-C[36]H	55.3 (52.7)	15.6 (15.53)
d, P-C-C[36]H	54.2 (51.9)	15.6 (13.9)

[a] Experimental data in accordance with the results reported in the literature [8].   [b] Theoretical data**.**

* Is relevant to the **Z** isomer

Is relevant to the **E isomer

Table 9: The selected ^1H NMR chemical shift (d in ppm) for some functional groups in the Z-4 and E-4 isomers as a major and minor

groups	d^H/ppm		
6H 2s 2CO$_2$Me*	3.78[a] (3.40)[b] , 3.80[a] (3.90)[b] *	3.71[a] (2.94)[b] 3.79[a]	
6H 2s 2CO$_2$Me**	(2.49)[b]**		
1H, d, P=C-C-H[37]	7.26 (7.07)*	7.26(7.08)	
1H, d, P=C-C-H[37]	7.33 (7.25)	7.33(7.35)	

[a] Experimental data in accordance with the results reported in the literature [8][b] Theoretical data.* Is relevant to the Z isomer **Is relevant to the E isomer

Theoretical studies

For assignment of the two **Z** and **E** isomers as a minor or major form in phosphorus ylide **4** containing an indoline-2-one, first the **Z**- and the **E**-isomers were optimized for all ylide structures at HF/6-31G(d,p) level of theory [14, 23] by Gaussian 03 package program[24]. The relative stabilization energies in both the geometrical isomers have been calculated at HF/6-31G (d,p) and B3LYP/6-311++G** levels. Atoms in molecules (AIM) [25], natural population analysis (NPA) methods and CHelpG keyword at HF/6-31G(d,p) level of theory have been employed in order to gain a better understanding of most geometrical parameters of both the **E-4** and the **Z-4** of phosphorus ylides. The numbers of critical points and intramolecular hydrogen bonds as well as the charge of atoms that constructed on the **Z**- and **E**- isomers have been
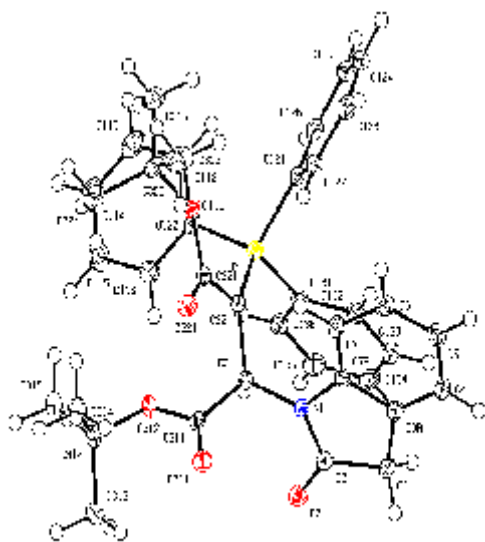
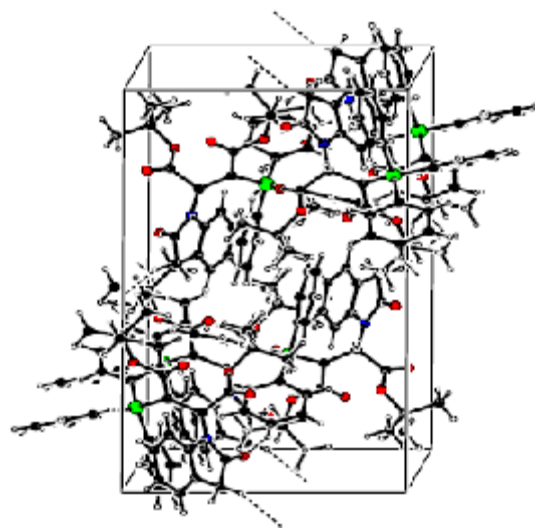**Fig. 2: ORTEP view of the molecular geometry of ylide 4**

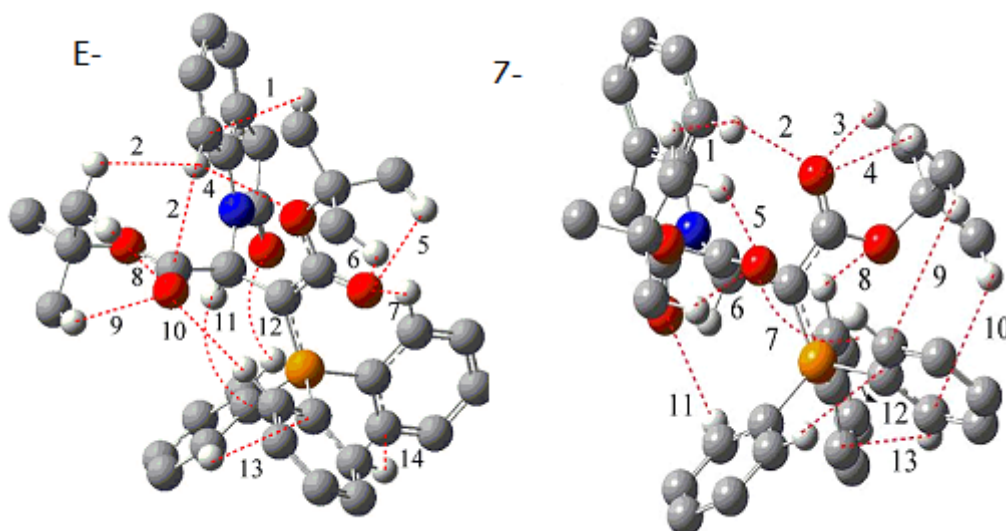**Fig. 3: The molecular packing diagram of ylide 4**

Fig. 4: Intramolecular hydrogen bonds (dotted lines) in the two E-4 and Z-4 geometrical isomers of stable ylide 4

recognized. In addition, J_{x-y}, the values of proton and carbon coupling constants and also chemical shifts (δ^H_{iso}, δ^C_{iso}) have been calculated at mentioned level using SPINSPIN keyword. The relative stabilization energies for the two isomers (**Fig. 4**) are compared and it is concluded that **Z-4** isomer is more stable than **E-4** form (2.55 kJ/mol) at HF level.

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 at HF/6-31G (d,p) level of theory by the AIM2000 program package [26]. 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 $\nabla\rho(r)$ 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 [$\nabla^2\rho(r) < 0$] [27]. 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[28]. The ranges of r(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[29]. The AIM calculation indicates intramolecular hydrogen bond critical points (H-BCP) for the two **Z-4** and **E-4** isomers. Intramolecular H-BCPs along with a part of molecular graphs for the two rotational isomers are shown in **Fig. 4** (dotted line). Most important geometrical parameters involving some H-bonds (bond length and their relevant bond angle) are reported in **Table 4**. The electron density (ρ)×10³, Laplacian of electron density $\nabla^2 \rho(r)$×10³, and energy density -H(r)×10⁴ are also reported in **Table 5**

A negative total energy density at the BCP reflects a dominance of potential energy density, which is the consequence of accumulated stabilizing electronic charge[30]. Herein, the number of hydrogen bonds in **E-4** and **Z-4** are 8 and 7, respectively. The values of (ρ and ∇^2(r))×10³ for those are in the ranges 0.028-0.042 and 0.031-0.051 e/a_0^5, and 0.012-0.056 and 0.08-0.052 e/a_0^5, respectively. In addition, the Hamiltonian [-H(r) ×104] are in the ranges 8.08-20.3 and 4.5-16.11 au, respectively (**Table 6**). These HBs show $\nabla^2\rho(r)$ > 0 and H(r) < 0, which according to classification of Rozas et al. [29] are medium-strength hydrogen bonds. In ylide **4** the dipole moment for the **E-4** isomer (3.17 D) is smaller than the **Z-4** isomer (4.35 D), and the value of -H_{tot} (=$\sum$-H(r) ×104) for the **Z-4** isomer (144.68 au) is smaller than the **E-4** isomer (163.80 au). Although, dipole moment, number of hydrogen bonds and -Htot in both of the **E-4**, taken altogether, appear as two factors on stability of the **E-4**, but these values are not able to provide a power full effect as a dominance of potential energy. It seems that other factors i.e. other intramolecular exception of H-BCPS and anisotropic effect of phenyl group in ylide **4** containing triphenylphosphine within the structure of the **Z-4** isomer could be accounted against mentioned factors for changing the order of relative energy between the **Z-** and **E-** isomers. As a result, the **Z-4** has a considerable stability with respect to the **E-4** (**Table 4**). As expected, according to theoretical calculations the relative energy at HF/6-31G (d,p) level, are compatible with experimental results from the X-ray crystallography, ¹H , ¹³C and ¹³P NMR spectroscopy which indicate the **Z-4** is more abundance isomer (**Table 4**).

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 7** for the two **Z-** and **E-** isomers of ylide **4**. There is a good agreement between the results in three methods. The differences between the charge on P_1 atom in relation to **Z-4** and **E-4** are very close to each other in three methods.

Furthermore the individual chemical shifts have been characterized by NMR calculations at the mentioned level for the **E-4** and **Z-4** geometrical isomers. The total spin–spin coupling constant is the sum of two isomers. The paramagnetic spin-orbit (PSO) diamagnetic spin-orbit (DSO) Fermi-contact (FC) and spin-dipole (SD) terms and the value of chemical shifts (d) and coupling constants (Jx-y) are reported in **Tables 8 and 9**. As can be seen there is a good agreement between both the experimental [8] and theoretical chemical shifts (d) and coupling constants (J_{x-y}). In the present work molecular structures of ylide **4** involving three large

atoms such as sulfur, phosphorus and nitrogen are huge with the large numbers of other atoms, for this reason, employment of basis set higher than HF/6-31G(d,p) is impossible for performance of more accurate calculations. This limitation causes a small difference between both the experimental and theoretical coupling constants in some functional groups.

CONCLUSIONS

On the basis of X-ray crystallography data, adjacent carbonyl group in the ylide moiety of synthesized ylide had a resonance with bond of C=P. Also, X-ray study of synthesized ylide exhibited some weak intermolecular C-H…O hydrogen bonds which are effective on stability of the crystal structure. Thus, the results of previous works should be corrected, and the major form should be reported for the **Z**-isomer of this ylide. Although, dipole moment, number of hydrogen bonds and -Htot in both of the **E-4**, taken altogether, appeared as two factors on stability of the **E-4**, but these values are not able to provide a power full effect as a dominance of potential energy. It showed that other factors i.e. other intramolecular exception of H-BCPS and anisotropic effect of phenyl group in ylide **4** containing triphenylphosphine within the structure of the **Z-4** isomer could be accounted against mentioned factors for changing the order of relative energy between the **Z-** and **E-** isomers. As a result, the **Z-4** had a considerable stability with respect to the **E-4.** As expected, according to theoretical calculations the relative energy at HF/6-31G (d,p) level, were compatible with experimental results from the X-ray crystallography, ^{1}H , ^{13}C and [13]P NMR spectroscopy which indicate the **Z-4** was more abundance isomer.

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