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Understanding the stability of two different geometrical isomers in stable phosphorus ylides derived from benzotriazole: A quantum mechanical study

Hojjat Ghasempour[1]*, Mohammad Zakarianejad[2], Sayyed Mostafa Habibi-Khorassani[3], Batoul Makiabadi[4], Simin Norozpour[5]

[1]Department of Chemistry, Kerman Branch, Islamic Azad University, Kerman, (I.R.IRAN)
[2]Department of Chemistry, Payam Noor University, Tehran, (I.R.IRAN)
[3]Department of Chemistry, The University of Sistan and Baluchestan, Zahedan, (I.R.IRAN)
[4]Department of Chemical Engineering, Sirjan University of Technology, Sirjan, (I.R.IRAN)
[5]Department of Chemistry, Bardsir Branch, Islamic Azad University, Bardsir, (I.R.IRAN)
E-mail : hojjat_ghasempour@yahoo.com

ABSTRACT

Stable crystalline phosphorus ylides were obtained in excellent yields from the 1:1:1 addition reactions between triphenylphosphine and dialkylacetylenedicarboxylates, in the presence of NH-heterocyclic compound, such as benzotriazole. These stable ylides usually exist in solution as a mixture of 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, stability of the *Z*- and the *E*- isomers were undertaken for the two rotamers of phosphorus ylides involving benzotriazoleby natural population analysis (NPA) and atoms in molecules (AIM) methods.

KEYWORDS

Stable phosphorus ylides;
Triphenylphosphine;
Z- and *E*-rotamers;
Benzotriazole.

INTRODUCTION

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[1-17]. Several methods have been developed for preparation of phosphorus ylides[10,11]. These ylides are usually prepared by treatment of a phosphonium salt with a base, and phosphonium salts are usually prepared from the phosphine and alkyl halide[2,3]. Phosphonium salts are also prepared by Michael addition of phosphorus to activated olefines[1]. The phosphonium salts are most often converted to the ylides by treatment with a strong base, though weaker bases can be used if the salt is acidic enough. Michael addition of phosphorus (ø) compounds such as triphenylphosphine to acetylenic esters leads to reactive 1, 3-dipolar intermediate betaines which are not detected even at low temperature. These unstable species can be trapped by a protic reagent, ZH, such as methanol, amide, imide, etc. to produce various compounds e.g. ylides[4-17].

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 spectroscopy, mass spectrometry and elemental analysis data. For this reason quantum mechanical calculation has been performed in order to gain a better understanding of the most important geometrical parameters and also relative energies of both the geometrical isomers.

RESULTS AND DISCUSSION

Theoreticalstudy

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 ^{1}H and ^{13}C NMR and IR spectroscopes, mass spectrometry and elemental analysis data. For this reason quantum mechanical calculation has 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

A facile synthesis of the reaction between triphenylphosphine1, dialkylacetylendicarboxylates2 and benzotriazole3 (as a NH- heterocyclic compound) for generation of phosphorus ylides4a-c involving the two geometrical isomers such as *Z*- and *E*- isomers have been earlier reported[18]. The reaction is shown in Figure 1. For assignment of the two *Z* and *E* isomers as a minor or major form in phosphorus ylides4a-c containing a benzotriazole, first the *Z*- and the *E*- isomers were optimized for all ylide structures at HF/6-31G(d,p) level of theory[19] by Gaussian98 package program[20]. 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)[21], natural population analysis (NPA) methods and CHelpG keywordat 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(a, c) and the *Z*-4(a, c) 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 recognized. 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 Figures 2 and 3) are reported in TABLE 1.As can be seen, isomers *E*-4a and *E*-4c are more stable than*Z*-4a and *Z*-4c (0.15 and 1.95 kcal/mol, respectively) at B3LYP/6-311++G**level.

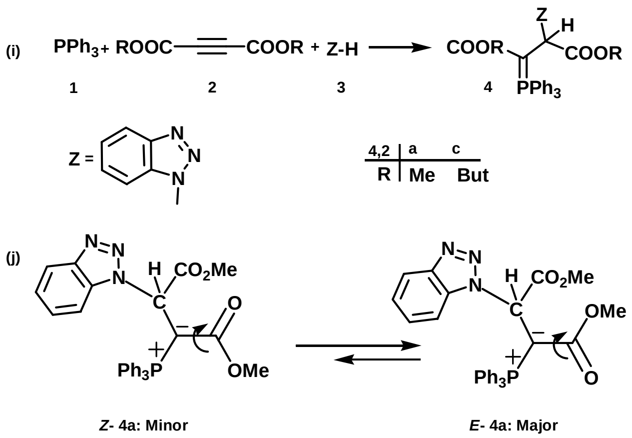

Figure 1 : (i)The reaction between triphenylphosphine 1, dialkyl acetylenedicarboxylate 2 (2a or2c) and benzotriazole3 for generation of stable phosphorus ylides 4 (4a or4c). (j)The two isomers *Z*-4a and *E*-4a (minor and major, respectively) of ylide 4a.

TABLE 1 : The relative energy (kcal/mol) for the two *Z* and *E* isomers of ylides4a and 4c, obtained at HF/6-31G(d,p) and B3LYP/6-311++G(d,p) levels.

Conformer	HF	B3LYP
Z-4a	1.00	0.15
E-4a	0.00	0.00
Z-4c	1.97	1.95
E-4c	0.00	0.00

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[22]. 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, $^2\rho(r)$, identifies regions of space wherein the electronic charge is locally depleted $[\nabla^2\rho(r) > 0]$ or built up $[\nabla^2\rho(r) < 0]$[21]. 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[22]. 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[23]. The AIM calculation indicates intramolecular hydrogen bond critical points (H-BCP) for the two *Z*-4(a, c) and *E*-4(a, c) isomers. Intramolecular H-BCPs along with a part of molecular graphs for the two rotational isomers are shown in Figures. 2 and 3 (dotted line). Most important geometrical parameters involving some H-bonds (bond length and their relevant bond angle) are reported in TABLE 2. The electron densities $(\rho)\times10^3$, Laplacian of electron density $\nabla^2\rho(r)\times10^3$, and energy density $-H(r)\times10^4$ 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[24]. Herein, the number of hydrogen bonds in both categories (*E*-4a and *Z*-4a) and (*E*-4c and *Z*-4c) are (7 and 6) and also (13 and 9), respectively. The values of ρ and $\nabla^2\rho(r)\times10^3$ for those are in the ranges (0.003 – 0.016 and 0.002 – 0.015 e/a_0^3) and (0.003 – 0.017 and 0.002 – 0.014 e/a_0^3) and also (6.00 – 44.40 and 5.21 – 42.41 e/a_0^5) and (7.87 – 46.19 and 5.72 – 40.57 e/a_0^5), respectively. In addition, the Hamiltonian $[-H(r)\times10^4]$ are in the ranges (6.60 – 16.80 and 5.58 – 15.85 au) and (6.58 – 19.21 and 6.44 – 16.75 au), respectively (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.[25] are medium-strength hydrogen bonds. In both ylides the dipole moment for the two *E*-4a and *E*-4c isomers (5.95 and 5.01 D, respectively) are smaller than the two *Z*-4a and *Z*-4cisomers (6.02 and 6.80 D, respectively) and the value of $-H_{tot}$ $(=\sum -H(r)\times10^4)$ for the two *E*-4a and *E*-4cisomers (79.43 and 166.05 au, respectively) are larger than the two *Z*-4a and *Z*-4c isomers (69.41 and 109.16 au, respectively).These differences, containing a fairly difference in number of hydrogen bonds, in dipole moment for ylide4a (TABLE 5) and in $-H_{tot}$, altogether, make a slight stability of *E*-4a in comparison with *Z*-4a isomer. Also, these parameters in ylide4c make a favorable and considerable stability on *E*-4c in comparison with *Z*-4c. Also, the charge on different atoms which

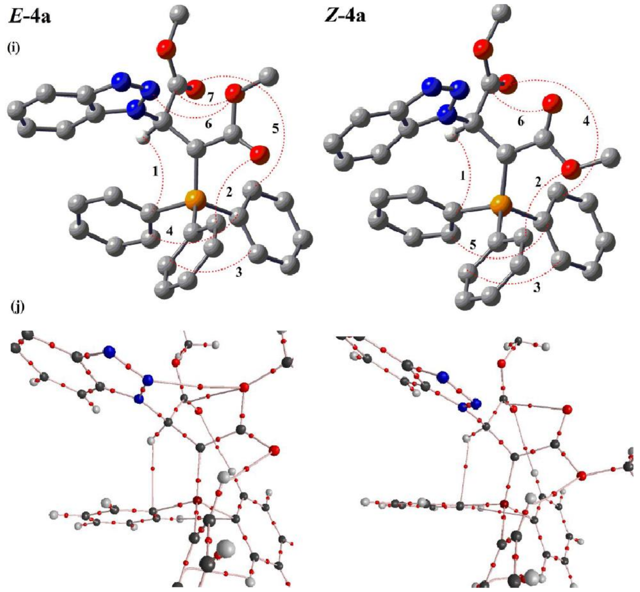

Figure 2 : (i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-4a and *Z*-4a geometrical isomers of stable ylide 4a, (j) Part of molecular graphs, including intramolecular hydrogen bond critical points (BCPS) for the two rotational isomers such as *E*-4a and *Z*-4a. Small red spheres, and lines corresponding to BCPS bond paths, respectively

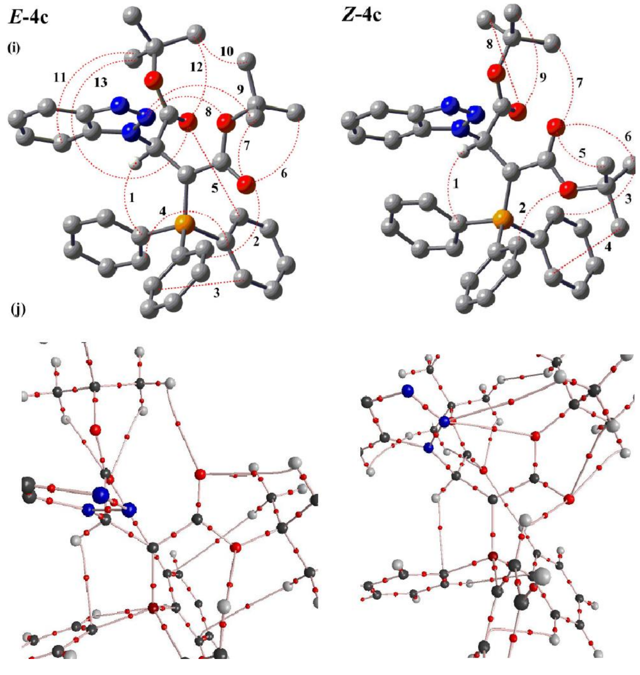

Figure 3 : (i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-4cand *Z*-4cgeometrical isomers of stable ylide 4c, (j) Part of molecular graphs, including intramolecular hydrogen bond critical points (BCPS) for the two rotational isomers such as *E*-4cand *Z*-4c.Small red spheres, and lines corresponding to BCPS bond paths, respectively.

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 ylides4a and 4c. There is good agreement between the results in three methods.

TABLE 2 : Most important geometrical parameters corresponding to H-bonds (bond lengths and their relevant angles) for the two *Z* and *E* isomers in both ylides4a and 4c. Bond lengths in Angstroms and bond angles in degrees, respectively

	***E*-4a**	***Z*-4a**	***E*-4c**	***Z*-4c**
$C_{10}H_{13}....O_{3(4)^*}$	2.40[a](121.02)[b]	2.51(101.10)	2.42(104.44)	2.81(105.45)
$C_3H_{42}.....C_{31}$	2.60(122.62)	2.56(117.97)	2.54(117.67)	2.65(116.56)
$C_{21}H_{24}....O_{51}$	3.15(124.05)		3.48(124.89)	
$C_{32}H_{35}....C_{20}$		2.66(107.23)		2.45(111.18)

[a] bond length; [b] bond angle; * Is relevant to the*Z* isomer

TABLE 3 : The values of a=ρ(r) ×10³, b=∇²ρ×10³ and c=-H(r) ×10⁴ for the two *Z*-4a and *E*-4a isomers of ylide4a calculated at the hydrogen bond critical points. All quantities are in atomic units.

E	a	b	c	*Z*	a	b	-c
1	03.29	06.00	06.60	1	08.23	10.10	07.35
2	11.77	44.40	10.52	2	09.84	29.14	10.35
3	08.14	29.14	07.08	3	02.12	05.21	05.58
4	08.74	10.49	08.73	4	09.01	31.02	15.12
5	15.62	41.98	16.80	5	15.74	42.41	15.16
6	14.54	42.43	15.52	6	10.29	33.28	15.85
7	13.32	37.12	14.18				

TABLE 4 : The values of a=ρ(r) ×10³, b=∇²ρ×10³ and c=–H(r) ×10⁴ for the two *Z*-4cand *E*-4cisomers of ylide4ccalculated at the hydrogen bond critical points. All quantities are in atomic units.

E	a	b	c	*Z*	a	b	-c
1	04.24	14.14	07.45	1	08.10	17.21	08.54
2	10.25	42.54	14.41	2	09.28	30.24	12.35
3	04.42	15.12	09.43	3	07.77	11.04	10.01
4	09.14	19.12	10.03	4	02.89	05.72	06.44
5	11.12	38.65	15.02	5	11.11	37.00	14.54
6	10.81	33.21	14.14	6	12.14	40.57	13.03
7	17.56	46.19	19.21	7	13.15	39.29	15.47
8	13.14	34.12	16.03	8	10.80	40.20	12.03
9	13.55	38.29	14.58	9	14.57	38.55	16.75
10	03.99	07.87	06.58				
11	04.85	13.99	09.88				
12	12.99	30.87	13.58				
13	16.85	38.99	15.71				

According to the theoretical calculations in gas phase (TABLE 1), isomers *E*-4a and *Z*-4a have a little difference in stability (0.15 kcal/mol), and difference in stability of two isomers *E*-4c and *Z*-4c is fairly high (1.97 kcal/mol). This result is completely consistent with the obtained results on the basis of AIM calculation for determination of the most geometrical parameters. In synthesis of ylids4a and 4c[18], the ^1H, ^{13}C, ^{31}P NMR data demonstrate more production of *E*-4a (52%) and *E*-4c (100%) as a major isomers. These results are compatible with those obtained in theoretical calculations.

TABLE 5 : 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 ylides4a and 4c.

Geometrical isomer	$-H_{tot}$/au	Dipole moment/D	number of hydrogen bond
E-4a	79.43	5.95	7
Z-4a	69.41	6.02	6
E-4c	166.05	5.01	13
Z-4c	109.16	6.80	9

TABLE 6 : The charges on different atoms for the two *Z* and *E* isomers in both ylides4a and 4c, calculated at HF/6-31G(d,p) theoretical level.

Number of atom	*Z*-4a	*E*-4a	*Z*-4c	*E*-4c
C1	-0.68[a](-0.37)[b] (-0.89)[c]	-0.66(-0.49) (-0.87)	-0.65(-0.29) (-0.85)	-0.66(-0.48) (-0.85)
C2	1.76(0.93) (0.94)	1.77(0.93) (0.93)	1.74(0.88) (0.94)	1.75(0.91) (0.93)
C7	0.29(0.06) (-0.48)	0.26(0.08) (-0.49)	0.27(0.15) (-0.48)	0.30(0.12) (-0.49)
O5	-1.32(-0.62) (-0.75)	-1.38(-0.68) (-0.79)	-1.36(-0.60) (-0.77)	-1.37(-0.69) (-0.79)
O6	-1.33(-0.51) (-0.67)	-1.31(-0.48) (-0.69)	-1.34(-0.55) (-0.68)	-1.30(-0.52) (-0.69)
P11	3.20(0.11) (1.86)	3.20(0.12) (1.85)	3.22(0.10) (1.84)	3.21(0.11) (1.85)

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

CONCLUSION

The assignment of the *Z*- and *E*- isomers as a minor or major form in both the ylides 4a and 4c were undertaken by AIM and NPA methods and also CHelpG keyword. Quantum mechanical calculations show that ylide4a exists in two different forms (*E*-4a and *Z*-4a) with different values in solution but, in ylide4c, with presence of bulky alkyl groups (di-*tert*-butyl instead of dimethyl groups), much differenceinstability of *E*-4c and *Z*-4carisesand bulky alkyl groups preventthe conversion of *E*-4c to *Z*-4c. So, leading to the formation of high efficient product in single isomer form (*E*-4c). These results are in agreement with those obtained in synthesis of the ylides4a and 4c.

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REFERENCES

[1] H.R.Hudson; Primary, Secondary and Tertiary Phosphines, Plyphosphines and Heterocyclic Organophosphorus (ø) Compounds, in the Chemistry of Organophosphorus Compounds. F.R.Hantley, Wiley (Ed); New York, **1**, 386-472 **(1990)**.

[2] R.Engel; Synthesis of Carbon-phosphorus Bonds, CRC Press: Boca Rotan, FL., **(1988)**.

[3] J.I.G.Cadogan; Organophosphorus Reagent in Organic Synthesis, Academic press: New York, **(1979)**.

[4] A.Ramazani, N.Noshiranzadeh, A.Ghamkhari, K.Slepokura, T.Lis; Helv.Chim.Acta., **91**, 2252 **(2008)**.

[5] A.Ramazani, A.R.Kazemizadeh, E.Ahmadi, N.Noshiranzadeh, A.Souldozi; Current Org. Chem., **12**, 59 **(2001)**.

[6] B.E.Maryanoff, A.B.Reitz; Chem. Rev., **89**, 863 **(1989)**.

[7] M.T.Maghsoodlou, N.Hazeri, S.M.Habibi-Khorassani, Z.Moeeni, G.Marandi, M.Lashkari, M.Ghasemzadeh, H.R.Bijanzadeh; J. Chem. Res., 566 **(2007)**.

[8] M.Anary-Abbasinejad, H.Anaraki-Ardakani, H.Hosseini-Mehdiabad; Phosphorus Sulfur and Silicon Relat. Elem., **183**, 1440 **(2008)**.

[9] A.Hassanabadi, M.Anary-Abbasinejad, A.Dehghan; Synth. Commun., **39**, 132 **(2009)**.

[10] H.Anaraki-Ardakani, S.Sadeghian, F.Rastegari, A.Hassanabadi, M.Anary-Abbasinejad; Synth. Commun., **38**, 1990 **(2008)**.

[11] M.Adib, M.Mostofi, K.Ghanbary, H.R.Bijanzadeh; Synthesis., **10**, 1663 **(2005)**.

[12] S.M.Habibi-Khorassani, M.T.Maghsoodlou, M.Nassiri, M.Zakarianejad, M.Fattahi; Arkivoc., **16**, 168 **(2006)**.

[13] M.T.Maghsoodlou, N.Hazeri, S.M.Habibi-Khorassani, A.Ghulame-Shahzadeh, M.Nassiri; Phosphorus Sulfur and Silicon Relat. Elem., **181**, 913 **(2006)**.

[14] M.Kalantari, M.R.Islami, Z.Hassani, K.Saidi; Arkivoc., **10**, 55 **(2006)**.

[15] M.R.Islami, F.Mollazehi, A.Badiei, H.Sheibani, Arkivoc., **15**, 25 **(2005)**.

[16] M.T.Maghsoodlou, S.M.Habibi-Khorassani, M.K.Rofouei, S.R.Adhamdoust, M.Nassiri; Arkivoc., **12**, 145 **(2006)**.

[17] A.A.Esmaili, M.Ghereghloo, M.R.Islami, H.R.Bijanzadeh; Tetrahedron., **59**, 4785 **(2003)**.

[18] M.T.Maghsoodlou, N.Hazeri, S.M.Habibi-Khorassani, R.Heydari, M.Nassiri, Gh.Marandi, Z.Moeeni, U.Niromand, Z.Eskandari-Torbaghan; J. Phosphorus, Sulfur, and Silicon., **181**, 865 **(2006)**.

[19] A.E.Reed, R.B.Weinstock, F.J.Weinhold; J. Chem. Phys., **83**, 735 **(1985)**.

[20] M.J.Frisch et al.; Gaussian 98, Revision A. 7, Gaussian, Inc., Pittsburg h, PA, **(1998)**.

[21] R.F.W.Bader; Atoms in molecules A Quantum Theory, Oxford University, New York, **(1990)**.

[22] F.W.Biegler König, J.Schönbohm, D.Bayles; J. Comput. Chem., **22**, 545 **(2001)**.

[23] S.J.Grabowski; J.Mol. Struct., **562**, 137 **(2001)**.

[24] W.D.Arnold, E.Oldfield; J.Am.Chem.Soc., **122**, 12835 **(2000)**.

[25] I.Rozas, I.Alkorta, J.Elguero; J. Am. Chem. Soc., **122**, 11154 **(2000)**.