THEORETICAL STUDY AND SYNTHESIS OF THE REACTION BETWEEN TRIPHENYLPHOSPHINE, DIALKYL ACETYLENEDICARBOXYLATES AND 2-AMINOBENZIMIDAZOLE, 2-HYDROXY-3-NITROPYRIDINE OR 1,2,3,4-TETRAHYDROCARBAZOLE

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Received October 8, 2009
Accepted March 26, 2010
Published online August 9, 2010

Triphenylphosphine reacts with dialkyl acetylenedicarboxylates in the presence of heterocyclic compounds, such as 2-aminobenzimidazole, 2-hydroxy-3-nitropyridine or 1,2,3,4-tetrahydrocarbazole to generate stable phosphorus ylides. Some ylides exist in solution as a mixture of two geometrical isomers as a result of restricted rotation around the carbon–carbon partical double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group, whereas others occur as a single isomer only. For this reason, the assignments of more stable *Z*- or *E*-isomers as the major or minor forms were investigated using theoretical calculations.

Keywords: Heterocyclic compounds; Stable phosphorus ylides; Theoretical calculations.

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, i.e., those bearing a carbon atom bound directly to a phosphorus atom[3–39]. This interest has resulted from the recognition of the value of such compounds in variety of biological, industrial and chemical synthetic use[3–7]. A large number of methods has appeared describing novel synthesis of organophosphorus compounds[6,7].

Collect. Czech. Chem. Commun. 2010, Vol. 75, No. 8, pp. 785–805

doi:10.1135/cccc2009523

There are many studies on the reaction between trivalent phosphorus nucleophiles and α,β-unsaturated carbonyl compounds in the presence of a proton source such as alcohol or phenol[7]. In the set of investigations that have been made on development of new routes in synthesis of stable phosphorus ylides[20–25], we now describe the reaction between triphenylphosphine **1** and dialkyl acetylenedicarboxylates **2** in the presence of heterocyclic compounds **3** for generating the corresponding stable phosphorus ylide **4** in fairly high yield. An "atoms in molecules" (AIM) analysis[40] at HF/6-31G level of theory has been performed in order to gain a better understanding of most geometrical parameters of both *E*-**4** (**a**, **c**, **d**, **e**, **f** and **h**) and *Z*-**4** (**a**, **c**, **d**, **e**, **f** and **h**) phosphorus ylides.

EXPERIMENTAL

Melting points and IR spectra (ν_{max}, cm^{-1}) of all compounds were measured on an Electrothermal 9100 apparatus and a Shimadzu IR-460 spectrometer, respectively. The ^1H, ^{13}C and ^{31}P NMR spectra (δ, ppm; *J*, Hz) were obtained on a BRUKER DRX-500 Avance instrument with $CDCl_3$ as a solvent at 500.1, 125.8 and 202.5 MHz, respectively. The mass spectra were recorded on a GCMS-QP5050A mass spectrometer operating at an ionization potential of 70 eV. Elemental analyses for C, H and N was performed using a Heraeus CHN-O-Rapid analyzer. Heterocyclic compounds **3**, dialkyl acetylenedicarboxylates and triphenylphosphine, purchased from Fluka, were used without further purifications.

Dimethyl 2-(*Z*-Aminobenzimidazol-1-yl)-3-(triphenylphosphanylidene)butanedioate (**4a**). General Synthetic Procedure

To a magnetically stirred solution of triphenylphosphine (0.26 g, 1 mmol) and 2-amino benzimidazole (0.13 g, 1 mmol) in 10 ml of acetone was added dropwise a mixture of dimethyl acetylenedicarboxylate (0.14 g, 1 mmol) in 3 ml of acetone at –5 °C over 10 min. After a few minutes stirring at room temperature the product was filtered, recrystallized and then washed with cold diethyl ether (3 × 5 ml). Colorless powder obtained as a final product, yield 0.52 g (96%), m.p. 208–210 °C. IR (KBr): 1725 and 1700 (C=O); 3100 (NH_2). MS (*m/z*, %): 537.22 (M^+, 3), 506.22 (M – OCH_3, 23), 262 (PPh_3, 38), 183 (PPh_2, 47), 108 (PPh, 23), 77 (Ph, 90). For $C_{31}H_{28}N_3O_4P$ (537.56) calculated: 69.27% C, 5.25% H, 7.82% N; found: 68.57% C, 5.31% H, 7.95% N.

Dimethyl 2-(2-aminobenzimidazol-1-yl)-3-(triphenylphosphanylidene)butanedioate (**4a**). Only isomer of **4a** (*Z*-**4a**): yield 96%. ^1H NMR (500.1 MHz, $CDCl_3$): 3.16 and 3.76 (6 H, 2 s, 2 OCH_3); 5.03 (1 H, d, $^3J_{PH}$ = 16.4, P=C-CH); 5.60 (1 H, d, $^3J_{HH}$ = 7.9, CH, $C_7H_6N_3$); 5.94 (2 H, bro, NH_2); 6.52 (1 H, t, $^3J_{HH}$ = 7.5, CH, $C_7H_6N_3$); 6.89 (1 H, t, $^3J_{HH}$ = 7.5, CH, $C_7H_6N_3$); 7.25 (1 H, d, $^3J_{HH}$ = 6.8, CH, $C_7H_6N_3$); 7.39–7.61 (15 H_{arom}, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): 42.6 (d, $^1J_{PC}$ = 126.3, P=C); 49.8 and 52.9 (2 s, 2 OCH_3); 56.8 (d, $^2J_{PC}$ = 15.3, P=C-**C**H); 106.3, 115.1, 118.0 and 120.6 (4 C, $C_7H_6N_3$); 125.6 (d, $^1J_{PC}$ = 92.3, C_{ipso}); 129.0, (d, $^3J_{PC}$ = 12.3, C_{meta}); 132.4 (C_{para}); 133.5 (d, $^2J_{PC}$ = 9.8, C_{ortho}); 134.3, 141.9 and 154.8 (3 C, $C_7H_6N_3$); 171.2 (d, $^3J_{PC}$ = 14.0, C=O ester); 171.5 (d, $^2J_{PC}$ = 12.3, P-C=**C**). ^{31}P NMR (202.5 MHz, $CDCl_3$): 23.31 (Ph_3P^+-C).

Diethyl 2-(2-aminobenzimidazol-1-yl)-3-(triphenylphosphanylidene)butanedioate (**4b**). Colorless powder, yield 0.53 g (95%), m.p. 151–153 °C. IR (KBr): 1700 and 1725 (C=O); 3150 (NH_2). MS (*m/z*, %): 565 (M^+, 3), 520 (M – OCH_2CH_3, 39), 475 (M – 2 OCH_2CH_3, 42), 262 (PPh_3, 68), 183 (PPh_2, 49), 108 (PPh, 26), 77 (Ph, 100). For $C_{33}H_{32}N_3O_4P$ (565.61) calculated: 70.08% C, 5.70% H, 7.43% N; found: 69.37% C, 5.65% H, 7.31% N.

Minor isomer of **4b** (*Z*-**4b**): yield 94%. ^{1}H NMR (500.1 Hz, $CDCl_3$): 0.45 and 1.27 (6 H, 2 t, $^3J_{HH}$ = 7.1, 2 $OCH_2C\mathbf{H}_3$); 3.73 and 4.23 (4 H, 2 m, 2 ABX_3 system, 2 $OC\mathbf{H}_2CH_3$); 5.02 (1 H, d, $^3J_{PH}$ = 16.8, P=C-CH); 5.59 (1 H, d, $^3J_{HH}$ = 7.9, CH, $C_7H_6N_3$); 5.98 (2 H, bro, NH_2); 6.51 (1 H, t, $^3J_{HH}$ = 7.5, CH, $C_7H_6N_3$); 6.88 (1 H, t, $^3J_{HH}$ = 7.5, CH, $C_7H_6N_3$); 7.25 (1 H, d, $^3J_{HH}$ = 7.7, CH, $C_7H_6N_3$); 7.38–7.71 (15 H_{arom}, m, 5 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): 13.9 and 14.2 (2 s, 2 $OCH_2\mathbf{C}H_3$); 42.4 (d, $^1J_{PC}$ = 124.6, P=C); 56.9 (d, $^2J_{PC}$ = 15.5, P=C-**C**H); 58.6 and 61.7 (2 s, 2 $O\mathbf{C}H_2CH_3$); 106.3, 115.0, 117.9 and 120.5 (4 C, $C_7H_6N_3$); 125.9 (d, $^1J_{PC}$ = 91.7, C_{ipso}); 128.9 (d, $^3J_{PC}$ = 12.3, C_{meta}); 132.3 (C_{para}); 133.6 (d, $^2J_{PC}$ = 9.8, C_{ortho}); 170.2 (d, $^3J_{PC}$ = 12.1, C=O); 170.6 (d, $^2J_{PC}$ = 14.3, P-C=**C**). ^{31}P NMR (202.5 MHz, $CDCl_3$): 23.35 (Ph_3P^+-C).

Di-tert-butyl 2-(2-aminobenzimidazol-1-yl)-3-(triphenylphosphanylidene)butanedioate (**4c**). Colorless powder, yield 0.60 g (97%), m.p. 103–105 °C. IR (KBr): 1744 and 1616 (C=O); 3145 (NH_2). MS (*m/z*, %): 621.31 (M^+, 4), 548 (M – OMe_3, 32), 262 (PPh_3, 66), 183 (PPh_2, 71), 108 (PPh, 56). For $C_{37}H_{40}N_3O_4P$ (621.72) calculated: 71.48% C, 6.49% H, 6.76% N; found: 71.51% C, 6.65 H, 6.71% N.

Only isomer of **4c** (*Z*-**4c**): yield 97%. ^{1}H NMR (500.1 MHz, $CDCl_3$): 0.96 and 1.54 (18 H, 2 s, 2 $OCMe_3$); 4.39 (1 H, d, $^3J_{PH}$ = 17.5, P=C-CH); 5.58 (1 H, d, $^3J_{HH}$ = 7.8, CH, $C_7H_6N_3$); 6.16 (2 H, bro, NH_2); 6.49 (1 H, t, $^3J_{HH}$ = 7.2, CH, $C_7H_6N_3$); 6.86 (1 H, t, $^3J_{HH}$ = 7.2, CH, $C_7H_6N_3$); 7.23 (1 H, d, $^3J_{HH}$ = 7.8, CH, $C_7H_6N_3$); 7.37–7.73 (15 H_{arom}, m, 3 C_6H_5). ^{13}C NMR (125.7 MHz, $CDCl_3$): 28.1 and 28.3 (2 $OC\mathbf{Me}_3$); 41.9 (d, $^1J_{PC}$ = 125.1, P=C); 57.7 (d, $^2J_{PC}$ = 15.6, P=C-**C**H); 78.4 and 81.5 (2 $O\mathbf{C}Me_3$); 106.2, 114.9, 117.9 and 120.4 (4 C, $C_7H_6N_3$); 126.4 (d, $^1J_{PC}$ = 91.5, C_{ipso}); 128.8 (d, $^3J_{PC}$ = 11.9, C_{meta}); 132.2 (C_{para}); 133.7 (d, $^2J_{PC}$ = 9.6, C_{ortho}); 134.6, 141.9 and 155.1 (3 C, $C_7H_6N_3$); 169.0 (d, $^3J_{PC}$ = 13.9, C=O); 170.9 (d, $^2J_{PC}$ = 11.7, P-C=**C**). ^{31}P NMR (202.5 MHz, $CDCl_3$): 23.06 (Ph_3P^+-C).

Dimethyl 2-(2-hydroxy-3-nitropyridine-2-carboxylate-2-yl)-3-(triphenylphosphanylidene)butanedioate (**4d**). Colorless powder, yield 0.51 g (94%), m.p. 156–158 °C. IR (KBr): 1723 and 1614 (C=O). MS (*m/z*, %): 544 (M^+, 3), 485 (M – CO_2Me, 41), 367 (M – 2 CO_2Me, 27), 262 (PPh_3, 60), 183 (PPh_2, 53), 108 (PPh, 26), 77 (Ph, 100). For $C_{29}H_{25}N_2O_7P$ (544.51) calculated: 63.97% C, 4.63% H, 5.14% N; found: 64.05% C; 4.71% H, 5.27% N.

Major isomer of **4d** (*Z*-**4d**): yield 77%. ^{1}H NMR (500.1 MHz, $CDCl_3$): 3.20 and 3.78 (6 H, 2 s, 2 OCH_3); 5.65 (1 H, d, $^3J_{PH}$ = 17.4, P=C-CH); 6.32–7.77 (18 H_{arom}, m, 3 C_6H_5, $C_5H_3N_2O_3$). ^{13}C NMR (125.8 MHz, $CDCl_3$): 42.9 (d, $^1J_{PC}$ = 128.7, P=C); 52.2 and 52.9 (2 OCH_3); 60.5 (d, $^2J_{PC}$ = 17.2, P=C-**C**H); 102.5 (1 C, $C_5H_3N_2O_3$); 125.5 (d, $^1J_{PC}$ = 90.3, C_{ipso}); 129.2 (d, $^3J_{PC}$ = 12.2, C_{meta}); 129.7 (d, $^4J_{PC}$ = 2.2, C_{para}); 132.7 (1 C, $C_5H_3N_2O_3$); 133.3 (d, $^2J_{PC}$ = 9.6, C_{ortho}); 138.2, 144.9 and 153.7 (3 C, $C_5H_3N_2O_3$); 165.2 (d, $^3J_{PC}$ = 12.8, C=O ester); 170.4 (d, $^2J_{PC}$ = 12.8, P-C=**C**). ^{31}P NMR (202.5 MHz, $CDCl_3$): 23.97 (Ph_3P^+-C).

Minor isomer of **4d** (*E*-**4d**): yield 23%. ^{1}H NMR (500.1 MHz, $CDCl_3$): 3.61 and 3.78 (6 H, 2 s, 2 OCH_3); 5.65 (1 H, d, $^3J_{PH}$ = 17.2, P=C-CH); 6.23–7.77 (18 H_{arom}, m, 3 C_6H_5, $C_5H_3N_2O_3$). ^{13}C NMR (125.8 MHz, $CDCl_3$): 43.1 (d, $^1J_{PC}$ = 128.7, P=C); 49.5 and 50.6 (2 OCH_3); 60.5 (d, $^2J_{PC}$ = 17.2, P=C-**C**H); 103.6 (1 C, $C_5H_3N_2O_3$); 125.5 (d, $^1J_{PC}$ = 90.3, C_{ipso}); 128.9 (d, $^3J_{PC}$ = 12.1, C_{meta}); 131.9 (d, $^4J_{PC}$ = 2.2, C_{para}); 132.1 (d, $^2J_{PC}$ = 9.8, C_{ortho}); 132.7,

137.2, 142.9 and 153.7 (4 C, $C_5H_3N_2O_3$); 165.2 (d, $^3J_{PC}$ = 12.8, C=O); 170.7 (d, $^2J_{PC}$ = 17.1, P-C=**C**). ^{31}P NMR (202.5 MHz, $CDCl_3$): 24.98 (Ph_3P^+-C).

Di-tert-butyl 2-(2-hydroxy-3-nitropyridine-2-carboxylate-2-yl)-3-(triphenylphosphanylidene)-butanedioate (**4e**). Colorless powder, yield 0.60 g (96%), m.p. 113–115 °C. IR (KBr): 1742 and 1678 (C=O). MS (*m/z*, %): 575 (M^+, 5), 474 (M – $CO_2C(Me)_3$, 47), 373 (M – 2 $CO_2C(Me)_3$, 20), 262 (PPh_3, 80), 183 (PPh_2, 73), 108 (PPh, 57). For $C_{35}H_{37}N_2O_7P$ (628.67) calculated: 66.87% C, 5.93% H, 4.46% N; found: 66.89% C, 6.05% H, 4.57% N.

Only isomer of **4e** (*Z*-**4e**). ^{1}H NMR (500.1 MHz, $CDCl_3$): 0.99 and 1.55 (18 H, 2 s, 2 $OCMe_3$); 5.53 (1 H, d, $^3J_{PH}$ = 18.3, P=C-CH); 6.33–8.69 (18 H_{arom}, m, 3 C_6H_5 and $C_5H_3N_2O_3$). ^{13}C NMR (125.8 MHz, $CDCl_3$): 28.1 and 28.1 (2 OC**Me**$_3$); 43.0 (d, $^1J_{PC}$ = 124.7, P=C); 60.9 (d, $^2J_{PC}$ = 18.4, P=C-**C**H); 78.7 and 81.8 (2 O**C**Me_3); 102.4 (1 C, $C_5H_3N_2O_3$); 126.2 (d, $^1J_{PC}$ = 91.7, C_{ipso}); 128.5 (d, $^3J_{PC}$ = 11.9, C_{meta}); 130.1 (1 C, $C_5H_3N_2O_3$); 131.9 (C_{para}); 132.1 (d, $^2J_{PC}$ = 9.7, C_{ortho}); 134.6, 153.5 and 164.4 (3 C, $C_5H_3N_2O_3$); 168.8 (d, $^3J_{PC}$ = 5.9, C=O); 169.3 (d, $^2J_{PC}$ = 5.9, P-C=**C**). ^{31}P NMR (202.5 MHz, $CDCl_3$): 23.50 (Ph_3P^+-C).

Dimethyl 2-(1,2,3,4-tetrahydrocarbazole-N-yl)-3-(triphenylphosphanylidene)butanedioate (**4f**). Colorless powder, yield 0.54 g (93%), m.p. 102–104 °C. IR (KBr): 1737 and 1616 (C=O). MS (*m/z*, %): 575 (M^+, 3), 544 (M – OMe, 44), 457 (M – 2 CO_2Me, 38), 262 (PPh_3, 60), 183 (PPh_2, 40), 108 (PPh, 27), 77 (Ph, 100). For $C_{36}H_{34}NO_4P$ (575.65) calculated: 75.12% C, 5.95% H, 2.43% N; found: 74.96% C, 6.03% H, 2.51% N.

Major isomer of **4f** (*Z*-**4f**): yield 61%. ^{1}H NMR (500.1 MHz, $CDCl_3$): 1.72 (4 H, m, 2 CH_2); 2.73 (4 H, m, 2 CH_2); 3.23 and 3.76 (6 H, 2 s, 2 OCH_3); 5.04 (1 H, d, $^3J_{PH}$ = 18.9, P=C-CH); 6.96–7.72 (19 H_{arom}, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.2, 22.2, 22.9 and 23.5 (4 CH_2, $C_{12}H_{12}N$); 41.9 (d, $^1J_{PC}$ = 123.21, P=C); 49.2 and 52.6 (2 OCH_3); 57.9 (d, $^2J_{PC}$ = 15.8, P=C-**C**H); 109.3, 110.4, 116.8, 118.2 and 120.2 (5 C, $C_{12}H_{12}N$); 126.1 (d, $^1J_{PC}$ = 91.4, C_{ipso}); 127.0 (1 C, $C_{12}H_{12}N$); 128.5 (d, $^3J_{PC}$ = 12.3, C_{meta}); 131.9 (C_{para}); 133.6 (d, $^2J_{PC}$ = 9.8, C_{ortho}); 135.9 and 136.0 (2 C, $C_{12}H_{12}N$); 169.7 (d, $^3J_{PC}$ = 18.1, C=O ester); 172.9 (d, $^2J_{PC}$ = 16.4, P-C=**C**). ^{31}P NMR (202.5 MHz, $CDCl_3$): 23.96 (Ph_3P^+-C).

Minor isomer of **4f** (*E*-**4f**): yield 39%. ^{1}H NMR (500.1 MHz, $CDCl_3$): 1.72 (4 H, m, 2 CH_2); 2.73 (4 H, m, 2 CH_2); 3.70 and 3.74 (6 H, 2 s, 2 OCH_3); 5.01 (1 H, d, $^3J_{PH}$ = 16.7, P=C-CH); 6.96–7.72 (19 H_{arom}, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.3, 22.2, 22.9 and 23.5 (4 CH_2, $C_{12}H_{12}N$); 43.8 (d, $^1J_{PC}$ = 135.7, P=C); 50.4 and 52.2 (2 OCH_3); 58.1 (d, $^2J_{PC}$ = 15.7, P=C-**C**H); 109.5, 110.2, 116.9, 118.2 and 120.1 (5 C, $C_{12}H_{12}N$); 127.5 (d, $^1J_{PC}$ = 91.1, C_{ipso}); 128.0 (1 C, $C_{12}H_{12}N$); 128.7 (d, $^3J_{PC}$ = 12.1, C_{meta}); 131.9 (C_{para}); 132.1 (d, $^2J_{PC}$ = 9.9, C_{ortho}); 135.9 and 136.2 (2 C, $C_{12}H_{12}N$); 169.0 (d, $^3J_{PC}$ = 12.5, C=O); 169.9 (d, $^2J_{PC}$ = 16.4, P-C=**C**). ^{31}P NMR (202.5 MHz, $CDCl_3$): 25.14 (Ph_3P^+-C).

Diethyl 2-(1,2,3,4-tetrahydrocarbazole-N-yl)-3-(triphenylphosphanylidene)butanedioate (**4g**). Yellow powder, yield 0.56 g (92%), m.p. 156–158 °C. IR (KBr): 1723 and 1614 (C=O). MS (*m/z*, %): 603 (M^+, 3), 530 (M – CO_2Et, 38), 457 (M – 2 CO_2Et, 31), 262 (PPh_3, 50), 183 (PPh_2, 73), 108 (PPh, 45), 77 (Ph, 100). For $C_{38}H_{38}NO_4P$ (603.70) calculated: 75.60% C, 6.34% H, 2.32% N; found: 75.62% C, 6.40% H, 2.39% N.

Major isomer of **4g** (*Z*-4g): yield 64%. ^{1}H NMR (500.1 Hz, $CDCl_3$): 0.54 and 1.26 (6 H, 2 t, $^3J_{HH}$ = 7.1, 2 OCH_2CH_3); 1.73 (4 H, m, 2 CH_2); 2.71 (4 H, m, 2 CH_2); 3.93 and 4.19 (4 H, 2 m, 2 ABX_3 system, 2 OCH_2CH_3); 5.05 (1 H, d, $^3J_{PH}$ = 17.1, P=C-CH); 6.99–7.60 (19 H_{arom}, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.8 MHz, $CDCl_3$): 14.18 and 14.33 (2 OCH_2CH_3), 21.33, 22.26, 23.02 and 23.57 (4 CH_2, $C_{12}H_{12}N$); 41.49 (d, $^1J_{PC}$ = 126.1, P=C); 57.91 (d, $^2J_{PC}$ = 14.6, P=C-**C**H); 58.68 and 61.12 (2 O**C**H_2CH_3); 109.18, 111.58, 116.73, 118.06 and 120.12 (5 C, $C_{12}H_{12}N$); 126.50 (d, $^1J_{PC}$ = 91.7, C_{ipso}); 127.94 (1 C, $C_{12}H_{12}N$); 128.63 (d, $^3J_{PC}$ = 12.2, C_{meta});

131.90 (C_{para}); 133.76 (d, $^2J_{PC}$ = 9.7, C_{ortho}); 136.03 and 136.22 (2 C, $C_{12}H_{12}N$); 169.92 (d, $^3J_{PC}$ = 12.6, C=O); 172.25 (d, $^2J_{PC}$ = 15.9, P-C=**C**). ^{31}P NMR (202.5 MHz, $CDCl_3$): 25.03 (Ph_3P^+-C).

Only isomer of **4g** (*E*-**4g**): yield 36%. ^{1}H NMR (500.1 MHz, $CDCl_3$): 1.25 and 1.30 (6 H, 2 t, $^3J_{HH}$ = 7.1, 2 OCH_2CH_3); 1.61 (4 H, m, 2 CH_2); 2.66 (4 H, m, 2 CH_2); 4.12 and 4.27 (4 H, 2 m, 2 ABX_3 system, 2 OCH_2CH_3); 4.97 (1 H, d, $^3J_{PH}$ = 18.3, P=C-CH); 6.99–7.60 (19 H_{arom}, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.8 MHz, $CDCl_3$): 14.3 and 14.9 (2 OCH_2CH_3); 21.3, 22.2, 22.9 and 23.5 (4 CH_2, $C_{12}H_{12}N$); 42.6 (d, $^1J_{PC}$ = 133.1, P=C); 58.1 (d, $^2J_{PC}$ = 15.2, P=C-**C**H); 60.9 and 61.1 (2 OCH_2CH_3); 109.2, 111.8, 116.9 118.09 and 119.9 (5 C, $C_{12}H_{12}N$); 127.2 (d, $^1J_{PC}$ = 91.4, C_{ipso}); 128.2 (1 C, $C_{12}H_{12}N$); 128.7 (d, $^3J_{PC}$ = 12.3, C_{meta}); 131.9 (C_{para}); 133.8 (d, $^2J_{PC}$ = 9.9, C_{ortho}); 136.0 and 136.4 (2 C, $C_{12}H_{12}N$); 170.3 (d, $^3J_{PC}$ = 17.7, C=O); 172.2 (d, $^2J_{PC}$ = 15.3, P-C=**C**). ^{31}P NMR (202.5 MHz, $CDCl_3$): 25.50 (Ph_3P^+-C).

Di-tert-butyl 2-(1,2,3,4-tetrahydrocarbazole-N-yl)-3-(triphenylphosphanylidene)butanedioate (**4h**). Colorless powder, yield 0.63 g (95%), m.p. 123–125 °C. IR (KBr): 1717 and 1616 (C=O). MS (*m/z*, %): 659 (M^+, 4), 558 (M – CO_2CMe_3, 44), 457 (M – 2 $OCMe_3$, 53), 262 (PPh_3, 72), 183 (PPh_2, 80), 108 (PPh, 69). For $C_{42}H_{46}NO_4P$ (659.81) calculated: 76.46% C, 7.03% H, 2.12% N; found: 76.51% C, 7.12% H, 2.01% N.

Only isomer of **4h** (*Z*-**4h**). ^{1}H NMR (500.1 MHz, $CDCl_3$): 1.04 and 1.58 (18 H, 2 s, 2 $OCMe_3$); 1.69 (4 H, m, 4 CH_2); 2.66 (4 H, m, 4 CH_2); 4.90 (1 H, d, $^3J_{PH}$ = 16.1, P=C-CH); 7.28–7.61 (19 H_{arom}, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.3, 22.0, 22.9 and 23.5 (4 CH_2, $C_{12}H_{12}N$); 28.3 and 28.6 (2 $OCMe_3$); 40.7 (d, $^1J_{PC}$ = 122.9, P=C); 58.5 (d, $^2J_{PC}$ = 15.9, P=C-**C**H); 77.4 and 80.2 (2 $OCMe_3$); 108.7, 110.1, 116.6, 117.8 and 120.1 (5 C, $C_{12}H_{12}N$); 127.7 (d, $^1J_{PC}$ = 91.1, C_{ipso}); 128.4 (d, $^3J_{PC}$ = 12.2, C_{meta}); 128.6 (1 C, $C_{12}H_{12}N$); 131.8 (C_{para}); 133.7 (d, $^2J_{PC}$ = 9.7, C_{ortho}); 135.9 and 136.2 (1 C, $C_{12}H_{12}N$); 168.3 (d, $^3J_{PC}$ = 10.9, C=O); 171.1 (d, $^2J_{PC}$ = 15.4, P-C=**C**). ^{31}P NMR (202.5 MHz, $CDCl_3$): 23.77 (Ph_3P^+-C).

RESULTS AND DISCUSSION

The reaction between triphenylphosphine **1** and dialkyl acetylenedicarboxylate **2** in the presence of heterocyclic compounds **3**, such as 2-aminobenzimidazole, 2-hydroxy-3-nitropyridine or 1,2,3,4-tetrahydrocarbazole led to stable phosphorous ylides **4** in fairly high yield (Fig. 1). These reactions were carried out in acetone at ambient temperature and were completed after a few minutes. The ^{1}H, ^{31}P and ^{13}C NMR spectra of the crude products clearly indicated the formation of compounds **4a–4h**. No products other than **4a–4h** could be detected by NMR spectroscopy. The structures of compounds **4a–4h** were deduced from the elemental analyses, mass, IR, ^{1}H, ^{13}C and ^{31}P NMR spectra. Although the presence of the ^{31}P nucleus has complicated both the ^{1}H and ^{13}C NMR spectra of **4d**, **4f** and **4g**, it helps in assignment of the signals by long-range spin–spin couplings with the ^{1}H and ^{13}C nuclei (see Experimental). The ^{1}H, ^{13}C and ^{31}P NMR spectra of ylides **4d**, **4f** and **4g** show the mixture of two isomers (see Fig. 1j). The ylides moieties of these compounds are strongly conjugated with the adjacent carbonyl group and rotation around the partial double bond in

(*E*)-**4** and (*Z*)-**4** geometrical isomers is slow on the NMR time scale at ambient temperature. As can be seen, only one geometrical isomer was observed for ylides **4a–4c**, **4e** and **4h**, presumably, because of both the more plausible intramolecular hydrogen bonds and the bulky *tert*-butyl groups (see Fig. 1k). The assignment of *E*-**4** (**d**, **f** and **g**) and *Z*-**4** (**d**, **f** and **g**) isomers as the major or minor in phosphorous ylides have been reported previously[35–39]. The ^{1}H NMR spectrum of **4d** exhibited two singlets at δ 3.20 and 3.78 ppm arising from methoxy group in the *Z*-isomer, and two singlets at δ 3.61 and 3.78 ppm from that in the *E*-isomer. The methyl group at δ 3.20 in the *Z*-isomer is shielded due to the anisotropic effect of a phenyl group of triphenylphosphine. This effect confirms why the *Z*-**4d** and *E*-**4d** isomers

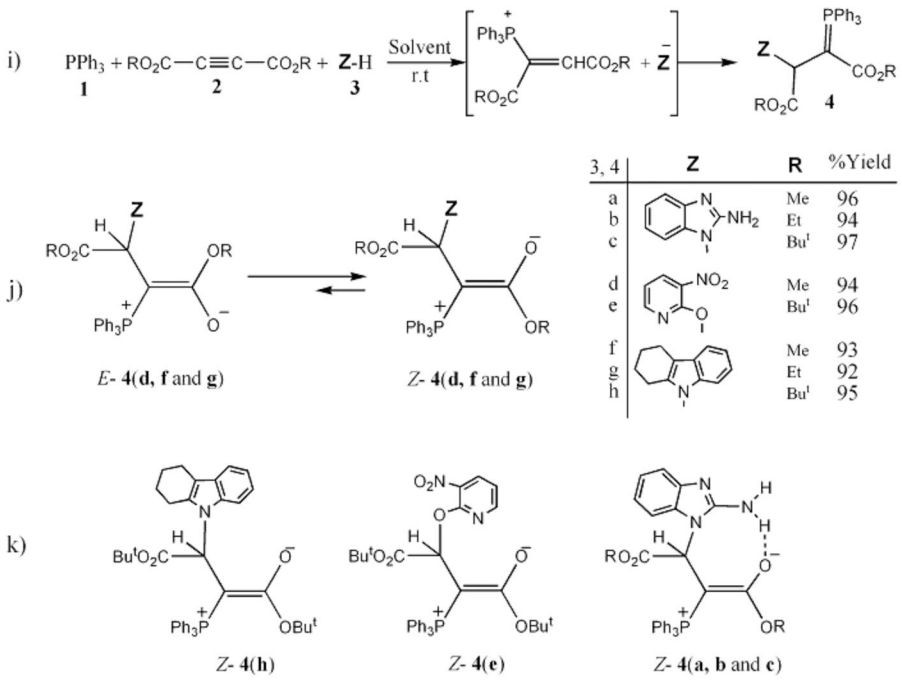

FIG. 1

i) The reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxylate (**2a**, **2b** or **2c**) and 2-aminobenzimidazole, 2-hydroxy-3-nitropyridine or 1,2,3,4-tetrahydrocarbazole **3** (**3a–3h**) for generation of stable phosphorus ylides **4a–4h**. j) *Z*- and *E*-isomers (major and minor) of stable phosphorus ylides (**4d**, **4f** and **4g**) are shown for 2-hydroxy-3-nitropyridine or 1,2,3,4-tetrahydrocarbazole. k) Only one isomer of ylides **4a–4c**, **4e** and **4h** are shown for 2-aminobenzimidazole, 2-hydroxy-3-nitropyridine and 1,2,3,4-tetrahydrocarbazole, respectively

could appear as the major and minor forms, respectively, with the percentage of both isomers as reported in Experimental. For the ^{13}C NMR spectroscopy, the anisotropic effect could not be reported for the methoxy group in the *Z*-isomer because of the small difference of their chemical shifts.

The singlets for methine protons appeared as two doublets at δ 5.65 ($^3J_{PH}$ = 17.4) and δ 5.65 ($^3J_{PH}$ = 17.2), respectively for the *Z*- and *E*-isomers.

On the basis of the well established chemistry of trivalent phosphorus nucleophiles[3–7], it is reasonable to assume that phosphorus ylide **4** results from the initial addition of triphenylphosphine to dialkyl acetylenedicarboxylates and subsequent protonation of the 1:1 adduct by the heterocyclic compounds to form phosphoranes **4** (see Fig. 1i).

The ^1H NMR spectrum of **4a** showed two singlets at δ 3.16 and 3.76 ppm arising from methoxy protons and a doublet at δ 5.03 ppm (1 H, d, $^3J_{PH}$ = 16.4, P-C-CH) for methine proton. The aromatic protons appeared as a multiplet at δ 7.39–7.61 ppm. The ^{13}C NMR spectra of **4a** displayed 17 distinct resonances in a good agreement with only one isomer. The ^1H and ^{13}C NMR spectra of compounds **4b–4h** are similar to those of **4a**, except for the signals from the ester group which appear as characteristic resonance lines with the corresponding chemical shifts. The structural assignments for compounds **4a–4h** were made on the basis of the ^1H and ^{13}C NMR spectra that were supported by their IR spectra. The carbonyl region of these compounds exhibits absorption bands for each compound. The ester absorption is at 1744–1614 cm^{-1}, the conjugation of negative charge in ylide moiety with the adjacent carbonyl group accounting for the reduction in frequency of the carbonyl bands, and allows determination of the ratio between the *Z*- and *E*-isomers.

CALCULATIONS

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 ^{13}C NMR and IR spectroscopy, 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.

In order to determine which is the more stable form of the geometrical isomers *Z*-**4** (**a**, **c**, **d**, **e**, **f** and **h**) and *E*-**4** (**a**, **c**, **d**, **e**, **f** and **h**) in ylides **4a–4h** (**4** (**a**, **c**), **4** (**d**, **e**) and **4** (**f**, **h**) are selected as typical ylides from the different categories of **4a–4c**, **4d–4e** and **4f–4h**, respectively), first the structures were optimized at HF/6-31G (gas phase) and HF/6-31G* (involving polarization functions for hydrogens, solution media, acetone) levels of theory[40] by Gaussian 03 program package[41]. Also relative stabilization energy of the two isomers (Figs 2–7) has been calculated at B3LYP/6-311±G(d,p) (both gas and solution phases) as a result of single point calculations. The relative stabilization energies for both *Z*-**4** (**a**, **c**, **d**, **e**, **f** and **h**) and *E*-**4** (**a**, **c**, **d**, **e**, **f** and **h**) isomers are reported in Table I, as can be seen, the *Z*-**4a**, *Z*-**4c**, *Z*-**4d**,

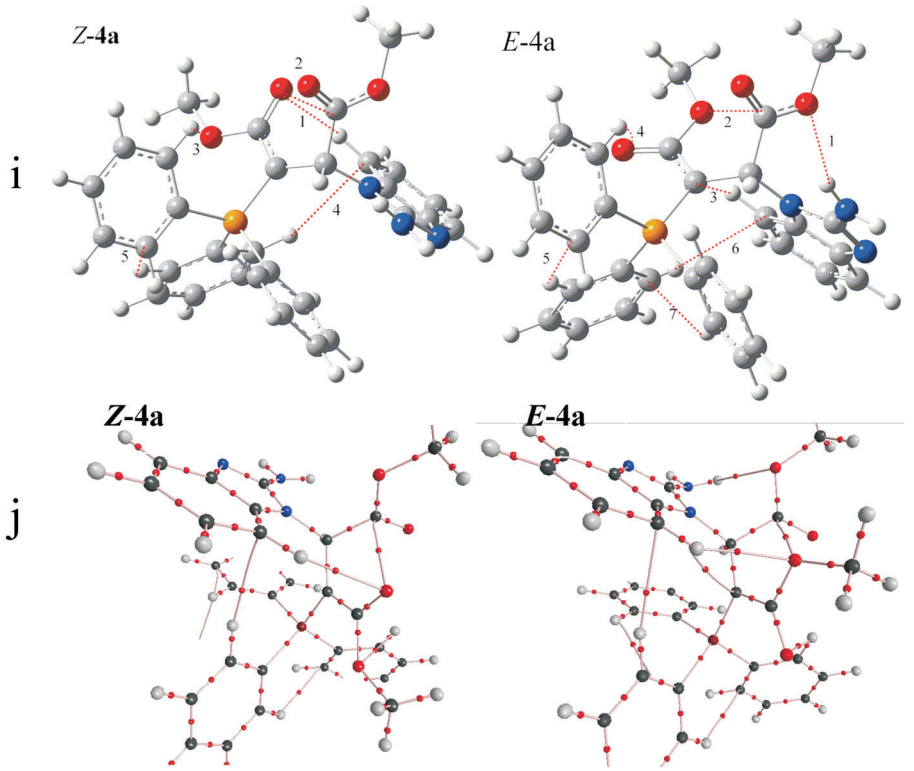

FIG. 2
i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-**4a** and *Z*-**4a** geometrical isomers of stable ylide **4a**. j) A part of molecular map for the two geometrical isomers

Z-**4e**, *Z*-**4f** and *Z*-**4h** isomers are more stable than the *E*-**4a**, *E*-**4c**, *E*-**4d**, *E*-**4e**, *E*-**4f** and *E*-**4h** ones (1.00, 2.71, 0.990, 2.44, 1.19 and 2.47 kcal/mol, respectively) by B3LYP solvation data (acetone).

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[42] at HF/6-31G level of theory by the AIM2000 program package[43]. In recent years, AIM theory was 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

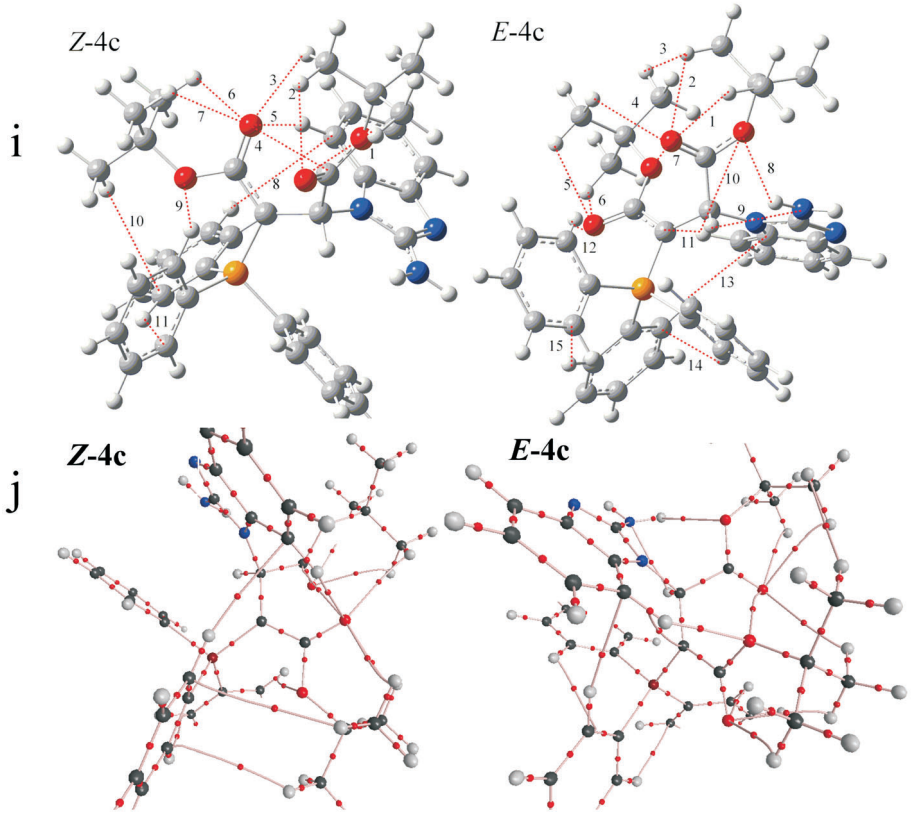

FIG. 3
i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-**4c** and *Z*-**4c** geometrical isomers of stable ylide **4c**. j) A part of molecular map for the two geometrical isomers

charge is locally depleted ($\nabla^2\rho(r) > 0$) or built up ($\nabla^2\rho(r) < 0$)[42]. 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[43]. 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[44]. The AIM calculation indicates intermolecular hydrogen bond critical points (H-BCP) for *Z*-**4** (**a**, **c**, **d**, **e**, **f** and **h**) and *E*-**4** (**a**, **c**, **d**, **e**, **f** and **h**) isomers. Intermolecular H-BCPs along with a part of molecular map are shown in Figs 2–7 (dotted line). The electron density (ρ), Laplacian of electron density $\nabla^2\rho(r)$ and energy density $-H(r)$ are also reported in Tables II–VII. A negative total energy density at the BCP reflects a dominance of potential energy density, which is the consequence of accumulated stabilizing elec-

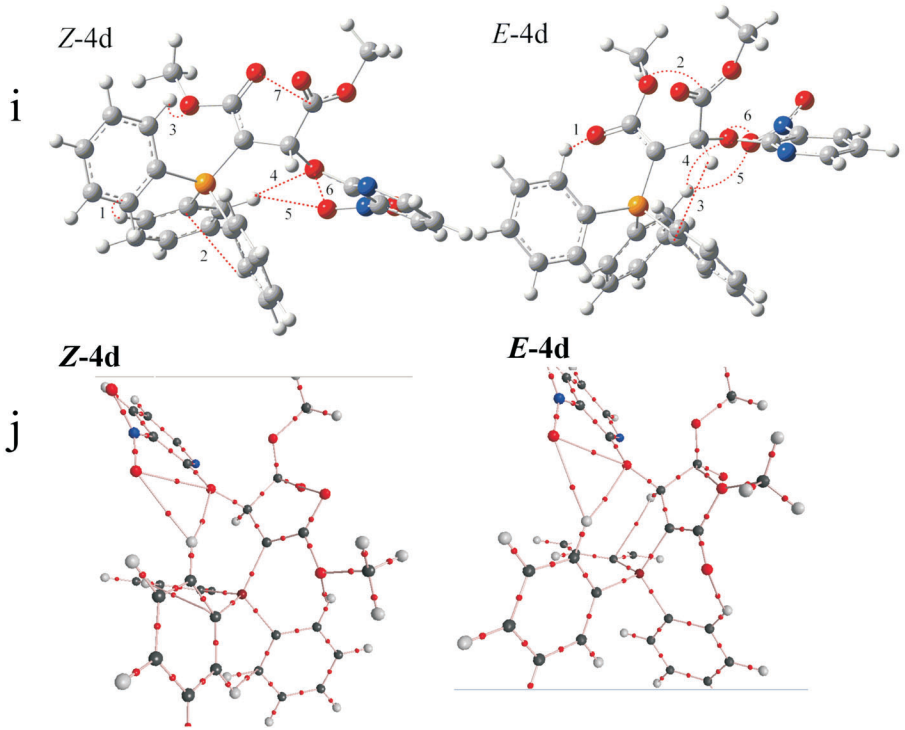

FIG. 4
i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-**4d** and *Z*-**4d** geometrical isomers of stable ylide **4d**. j) A part of molecular map for the two geometrical isomers

tronic charge[45]. Herein, the numbers of hydrogen bonds in all categories (*Z*-**4a** and *E*-**4a**), (*Z*-**4c** and *E*-**4c**), (*Z*-**4d** and *E*-**4d**), (*Z*-**4e** and *E*-**4e**), (*Z*-**4f** and *E*-**4f**) and (*Z*-**4h** and *E*-**4h**) are (5 and 7), (11 and 15), (7 and 6), (13 and 10), (12 and 11) and (15 and 19), respectively. In addition, the values of electron densities (ρ) are in the ranges (0.0028–0.0294 and 0.0031–0.0250 au e/a_0^3), (0.0030–0.0233 and 0.0029–0.0330 e/a_0^3), (0.0054–0.0146 and 0.0065–0.0165 e/a_0^3), (0.0027–0.0143 and 0.0028–0.0189 e/a_0^3), (0.0036–0.0149 and 0.0033–0.0118 e/a_0^3) and (0.0013–0.0158 and 0.0028–0.0146 e/a_0^3), respectively. Also $\nabla^2\rho(r)$ are in the ranges (0.028–0.057 and 0.021–0.063 au e/a_0^5), (0.0097–0.056 and 0.014–0.063 e/a_0^5), (0.026–0.058 and 0.030–0.068 e/a_0^5), (0.009–0.056 and 0.012–0.070

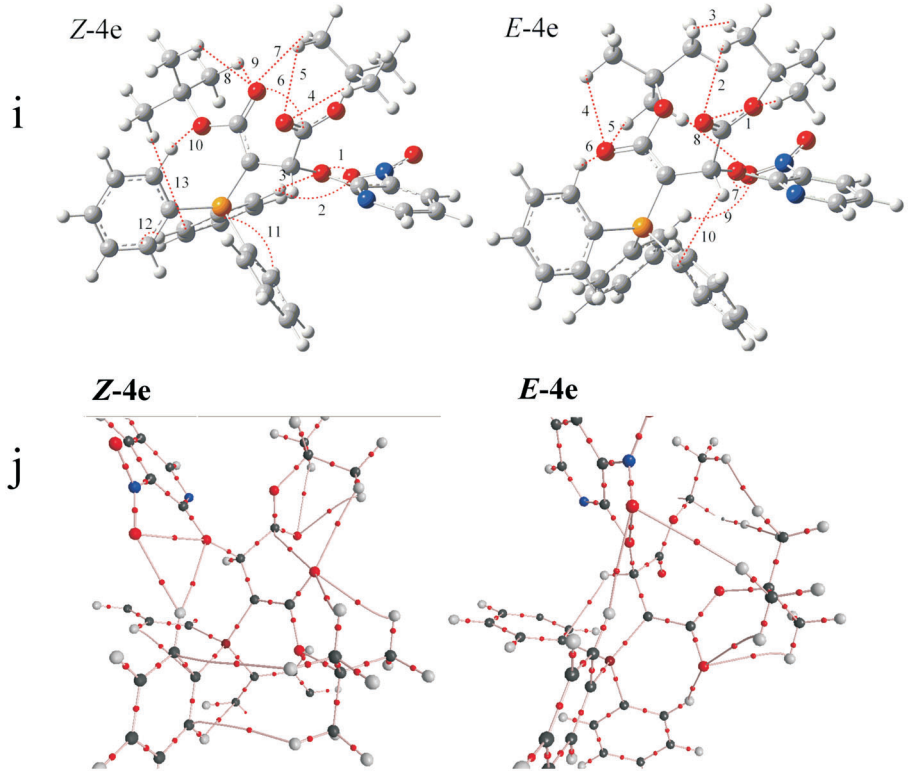

FIG. 5
i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-**4e** and *Z*-**4e** geometrical isomers of stable ylide **4e**. j) A part of molecular map for the two geometrical isomers

e/a_0^5), (0.008–0.059 and 0.012–0.051 e/a_0^5) and (0.014–0.051 and 0.009–0.058 e/a_0^5), respectively. Moreover, the Hamiltonians ($-H(r)$) are in the ranges (4.25×10^{-4}–17.15×10^{-4} and 11.51×10^{-4}–15.90×10^{-4} au), (3.63×10^{-4}–18.59×10^{-4} and 3.55×10^{-4}–22.42×10^{-4} au), (1.02×10^{-4}–15.37×10^{-4} and 1.18×10^{-4}–18.52×10^{-4} au), (0.958×10^{-4}–16.38×10^{-4} and 1.25×10^{-4}–18.18×10^{-4} au), (3.95×10^{-4}–18.93×10^{-4} and 3.67×10^{-4}–19.77×10^{-4} au) and (4.01×10^{-4}–17.42×10^{-4} and 2.97×10^{-4}–17.49×10^{-4} au), respectively (see Tables II–VII).

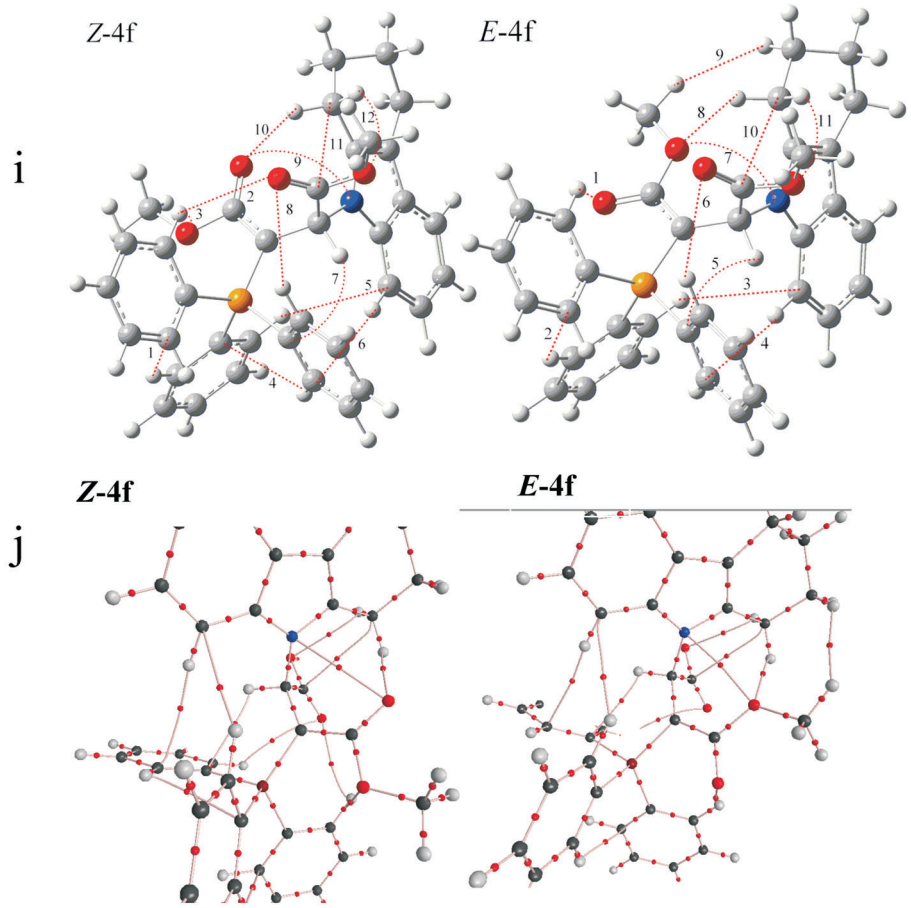

FIG. 6
i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-**4f** and *Z*-**4f** geometrical isomers of stable ylide **4f**. j) A part of molecular map for the two geometrical isomers

These HBs show $\nabla^2\rho(r) > 0$ and $H(r) < 0$, which, according to classification of Rozas et al.[46] are medium-strength hydrogen bonds. In both ylides (**4a**, **4c**), the dipole moments for the two *E*-**4a** and *E*-**4c** isomers (8.25 and 8.18 D, solution media, respectively) are smaller than those for the two *Z*-**4a** and *Z*-**4c** ones (12.2 and 11.7 D, respectively); the values of H_{tot} (= $\sum H(r)$) for the two *E*-**4a** and *E*-**4c** isomers (92.1 and 168.2 au, respectively) are higher than those for the two *Z*-**4a** and *Z*-**4c** ones (55.4 and 120 au, respectively) and the number of hydrogen bonds in *E*-**4a** and *E*-**4c** isomers (7, 15) is higher than that of the *Z*-**4a** and *Z*-**4c** ones (5, 11), respectively. These parameters, as dominate factors on stability, taken altogether,

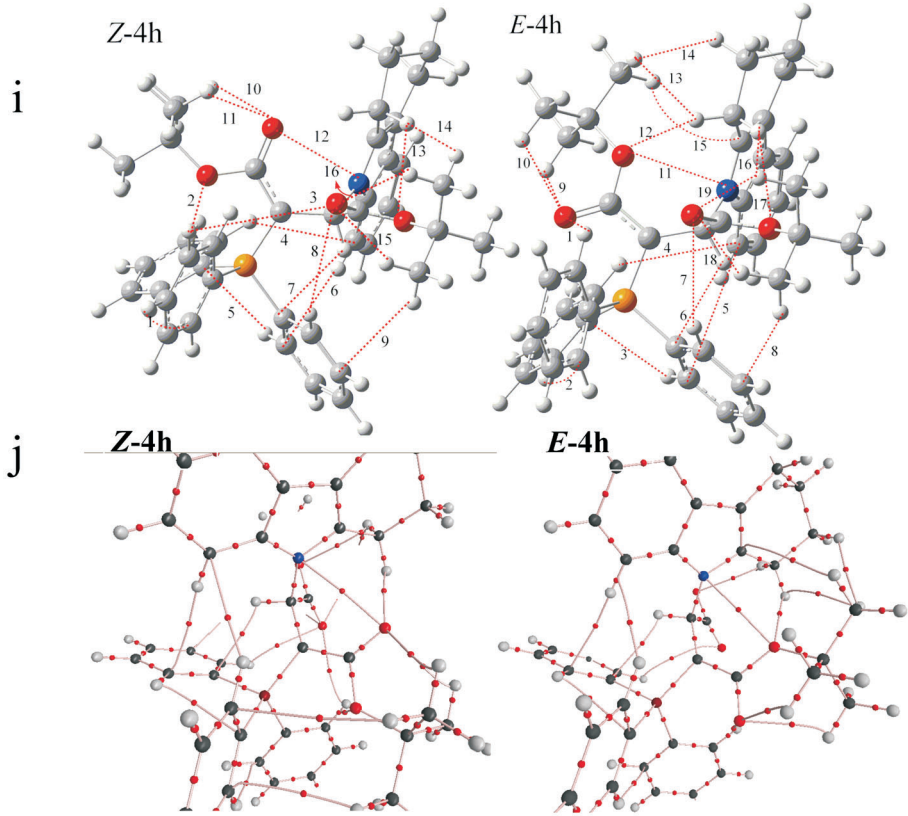

FIG. 7
i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-**4h** and *Z*-**4h** geometrical isomers of stable ylide **4h**. j) A part of molecular map for the two geometrical isomers

TABLE I
The relative stabilization energy (kcal/mol) for both *Z*- and *E*-isomers of ylides **4a**, **4c**, **4d**, **4e**, **4f** and **4h**, obtained at HF/6-31G, B3LYP/6-311±G(d,p) levels (* 2-aminobenzimidazole, ** 2-hydroxy-3-nitropyridine, *** 1,2,3,4-tetrahydrocarbazole)

Rotational isomer	HF	B3LYP
Z-**4a***	0	0
E-**4a***	3.05[a] (1.31)[b]	2.43[a] (1.00)[b]
Z-**4c***	0	0
E-**4c***	4.89 (3.61)	3.65 (2.71)
Z*-**4d***	0	0
E*-**4d***	1.35 (1.02)	1.21 (0.990)
Z*-**4e***	0	0
E*-**4e***	2.21 (2.23)	2.34 (2.44)
Z**-**4f***	0	0
E**-**4f***	1.58 (1.26)	1.35 (1.19)
Z**-**4h***	0	0
E**-**4h***	4.97 (3.36)	2.87 (2.47)

[a] Vacuum data (gas phase). [b] Solvation data (acetone).

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

E-**4a**	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H \times 10^4$	*Z*-**4a**	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H \times 10^4$
1	7.53	33.7	11.5	1	14.2	51.0	4.25
2	14.9	63.2	14.6	2	14.5	57.2	10.9
3	7.72	27.5	12.4	3	7.37	31.7	13.1
4	7.65	32.2	12.6	4	5.35	18.5	10.1
5	9.03	33.0	15.9	5	9.06	34.5	17.2
6	6.20	21.9	11.6				
7	7.66	26.9	13.5				

TABLE III
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-**4c**	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H \times 10^4$	*Z*-**4c**	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H \times 10^4$
1	10.9	42.5	12.0	1	10.2	39.7	11.5
2	10.7	41.7	11.9	2	10.6	41.6	12.2
3	4.03	15.4	9.95	3	5.12	22.6	11.3
4	2.96	14.0	8.53	4	14.0	55.8	11.9
5	12.1	46.6	11.8	5	15.1	53.8	3.53
6	13.7	52.4	11.2	6	12.5	48.1	11.2
7	10.9	41.3	4.52	7	12.1	46.9	11.8
8	13.1	52.8	7.73	8	5.17	18.0	9.96
9	14.3	63.1	22.4	9	6.92	29.8	12.7
10	16.4	60.7	3.55	10	2.92	9.75	5.48
11	7.23	25.5	11.2	11	9.16	36.0	18.6
12	8.80	36.5	13.1				
13	5.58	19.7	10.8				
14	7.70	27.1	13.6				
15	8.95	33.0	16.0				

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

E-**4d**	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H \times 10^4$	*Z*-**4d**	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H \times 10^4$
1	16.6	61.6	5.87	1	8.36	30.5	15.1
2	15.2	67.7	17.5	2	8.51	31.6	15.4
3	10.7	41.1	18.5	3	9.00	38.2	14.1
4	6.55	30.5	13.2	4	5.50	26.2	12.9
5	7.66	35.4	14.5	5	8.90	40.7	15.3
6	14.4	54.1	1.18	6	14.3	53.7	1.02
				7	14.7	58.0	11.1

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

E-**4e**	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H \times 10^4$	*Z*-**4e**	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H \times 10^4$
1	10.6	41.1	11.7	1	14.3	53.6	0.958
2	12.2	47.5	12.4	2	8.36	38.4	15.0
3	5.40	22.1	14.1	3	6.06	28.6	13.2
4	12.2	47.3	11.8	4	10.3	40.4	11.6
5	12.8	49.1	11.3	5	10.8	42.3	12.3
6	18.9	70.0	4.15	6	13.8	55.5	12.6
7	14.4	53.9	1.25	7	6.52	28.6	12.8
8	2.83	12.8	8.04	8	12.6	48.2	11.3
9	4.19	20.5	11.5	9	12.4	47.3	11.3
10	12.2	45.2	18.2	10	8.76	37.4	14.2
				11	8.94	34.1	16.4
				12	8.24	30.6	15.5
				13	2.76	9.15	5.35

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

E-**4f**	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H \times 10^4$	*Z*-**4f**	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H \times 10^4$
1	13.1	50.9	9.90	1	8.97	33.4	16.3
2	8.16	28.9	14.1	2	4.68	20.7	11.4
3	3.76	13.4	8.25	3	8.31	35.5	14.1
4	4.06	14.0	8.24	4	9.28	36.0	17.2
5	11.2	41.5	16.6	5	4.14	14.6	8.70
6	4.29	17.2	9.78	6	4.74	16.2	9.14
7	11.4	41.8	3.68	7	10.7	39.8	16.4
8	11.8	47.3	11.9	8	3.64	8.95	14.5
9	3.31	12.9	8.74	9	9.43	35.2	3.95
10	7.93	37.0	19.8	10	15.0	58.7	11.7
11	9.35	37.3	11.8	11	7.54	34.9	18.9
				12	8.86	35.5	11.9

make a great stability on *E*-**4a** and *E*-**4c** in comparison with the *Z*-**4a** and *Z*-**4c** forms (the results are summarized in Table VIII). For this reason, it is possible to see only a single isomer as a lone isomer (*E*-**4a** and *E*-**4c**) of ylides **4a** and **4c**. In addition, in ylide **4h**, the same behavior and results were observed for *E*-**4h** isomer as a single isomer (see Table VIII). The theoretical results for ylide **4b** are similar to ylides **4a**, **4c** and **4h**, for this reason, the relevant data have not been reported for *E*-**4b** isomer. Although on the basis of theoretical calculations (Table I), *Z*-**4a**, *Z*-**4b**, *Z*-**4c** and *Z*-**4h** isomers have a stability with respect to the *E*-**4a**, *E*-**4b**, *E*-**4c** and *E*-**4h** ones (1.00, no data, 2.70 and 2.47 kcal/mol, in solution media, respectively) and

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

E-**4h**	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H \times 10^4$	*Z*-**4h**	$\rho \times 10^3$	$\nabla^2\rho \times 10^3$	$-H \times 10^4$
1	10.7	43.7	13.3	1	9.00	34.6	17.4
2	8.57	31.0	15.1	2	8.18	35.0	14.1
3	9.64	37.3	17.5	3	4.86	21.4	11.6
4	3.90	14.4	9.16	4	4.05	14.2	8.48
5	4.65	16.2	9.31	5	9.55	37.6	17.8
6	10.7	40.3	16.5	6	5.20	17.9	9.92
7	3.16	12.7	7.89	7	10.8	40.4	16.5
8	2.83	9.76	5.88	8	4.21	17.5	9.88
9	13.9	53.1	11.1	9	12.6	48.2	11.2
10	14.7	57.4	12.6	10	13.1	50.2	11.3
11	8.95	32.9	2.97	11	9.79	36.2	4.01
12	8.22	33.6	11.5	12	8.49	34.3	12.2
13	3.90	15.8	9.34	13	5.09	20.1	12.8
14	6.67	26.8	15.7	14	11.5	44.7	12.1
15	2.90	9.51	5.14	15	10.1	39.7	11.9
16	6.72	27.3	16.0				
17	10.3	40.7	11.2				
18	9.86	38.9	11.9				
19	11.1	43.2	11.7				

seem to be different from the results of predictable properties of the most important geometrical parameters (Table VIII), perhaps, this different behavior is relevant to the huge structures of the ylides **4a**, **4b**, **4c** and **4h** involving three large atoms such as the four oxygen, one phosphorus and three nitrogen (only one nitrogen atom for **4h**) and also a very high 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. On the other hand, same discussion could be employed for *Z*-**4e** (not *E*-**4e**) as a lone isomer in ylide **4e**. Herein, less dipole moment, 9.63, higher H_{tot} = 156 and more hydrogen bonds, 14, as three dominate factors with respect to *E*-**4e**, lead to observe only a single isomer (*Z*-**4e**). In ylides **4d** and **4f**, two stability factors involving higher H_{tot} and higher number of hydrogen bonds are relevant to the *Z*-**4d** and *Z*-**4f** isomers, whereas stability on *E*-**4d** and *E*-**4f** has been only emerged from a result of dipole moment factor. This cause a fairly relative stability on *Z*-**4d** and *Z*-**4f** in comparison with *E*-**4d** and *E*-**4f** isomers in which this is in a good agreement with the experimental results based upon the ^{1}H,

TABLE VIII
The most important geometrical parameters involving the value of H_{tot}, dipole moment and number of hydrogen bonds for the two *Z*- and *E*-isomers of ylides **4a**, **4c**, **4d**, **4e**, **4f** and **4h** (* 2-aminobenzimidazole, ** 2-hydroxy-3-nitropyridine, *** 1,2,3,4-tetrahydrocarbazole)

Rotational isomer	H_{tot}, au	Dipole moment, D	No. of hydrogen bonds
*Z**-**4a**	55.4	8.72[a] (12.2)[b]	5
*E**-**4a**	92.1	5.38 (8.25)	7
*Z**-**4c**	120	8.82 (11.2)	11
*E**-**4c**	168	5.68 (8.18)	15
*Z***-**4d**	84.9	7.66 (11.1)	7
*E***-**4d**	70.8	8.32 (10.6)	6
*Z***-**4e**	156	8.04 (9.63)	14
*E***-**4e**	109	8.28 (10.7)	11
*Z****-**4f**	149	8.43 (11.1)	12
*E****-**4f**	123	5.75 (7.77)	11
*Z****-**4h**	184	8.35 (9.11)	16
*E****-**4h**	214	6.12 (7.62)	19

[a] Vacuum data (gas phase). [b] Solvation data (acetone) at B3LYP/6-311±G(d,p) as a result of single point calculations.

^{13}C and ^{31}P NMR data with slightly more experimental abundance percentage of 77 and 61% for *Z*-**4d** and *Z*-**4f**, respectively. Herein, the result for *Z*-**4g** is similar to *Z*-**4f**, hence no data have been reported for *Z*-**4g** within the text. In conclusion, theoretical calculations indicated that all ylides involving **4a**, **4b**, **4c**, **4e** and **4h** can exist as a lone isomer (i.e. *E*-**4a**, *E*-**4b**, *E*-**4c**, *Z*-**4e** and *E*-**4h**), while the experimental results show that a single isomer is relevant to the *Z*-**4a** *Z*-**4b**, *Z*-**4c**, *Z*-**4e** and *Z*-**4h** isomers. On the other hand, the results for ylides **4d**, **4f** and **4g** are the same in both theoretical and experimental data in which the *Z*-**4d**, *Z*-**4f** and *Z*-**4g** are major forms in comparison with *E*-**4d**, *E*-**4f** and *E*-**4g** as minor forms.

CONCLUSIONS

We have prepared the novel phosphorus ylides using a one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of heterocyclic compounds such as 2-aminobenzimidazole, 2-hydroxy-3-nitropyridine and 1,2,3,4-tetrahydrocarbazole. The present method has the advantage that, not only the reaction is performed under neutral conditions, but also the substances can be mixed without any activation or modifications. Heterocyclic compounds containing phosphorus ylides **4a–4h** may be considered as potentially useful synthetic intermediates. In addition, the assignment of the *Z*- and *E*-isomers as a major or minor form in ylides **4a–4h** was undertaken by the theoretical study. The AIM theory clarified, how the ylides **4a**, **4b**, **4c**, **4e** and **4h** only appear as a single isomer, whereas **4d**, **4f** and **4g** exist in solution as a mixture of these two isomers, and why either *Z*- or *E*-isomer is a more stable form as a major in solution media.

We gratefully acknowledge financial support from the Research Council of University of Sistan and Baluchestan, Iran.

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