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ORIGINAL ARTICLE

# Computational study for the ylide isomers from the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of 6-chloro-2-benzoxazolethiol

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**KEYWORDS**

Stable phosphorus ylides;
Dialkyl acetylenedicarboxylates;
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NH-heterocyclic compounds

**Abstract** Stable crystalline phosphorus ylides were obtained in excellent yields from the 1:1:1 addition reactions between triphenylphosphine and dialkyl acetylenedicarboxylates, in the presence of NH-heterocyclic compound, such as 6-chloro-2-benzoxazolethiol. These stable ylides exist in solution as a mixture of the two geometrical isomers as a result of restricted rotation around the carbon–carbon partial double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group. In the recent work, NMR study and the stability of the *Z*- and *E*-isomers were undertaken for the two rotamers of phosphorus ylides involving 6-chloro-2-benzoxazolethiol by atoms in molecules (AIM) and natural population analysis (NPA) methods. The relative energy for the two *Z* and *E* isomers was calculated at both HF/6-31G (d,p) and B3LYP/6-311++G (d,p) in the presence of a solvent medium (ethyl acetate) and gas phases. The results were in good agreement with those that obtained by the $^{1}$H, $^{31}$P and $^{13}$C NMR experimental data.

## 1. Introduction

The development of simple synthetic routes for widely used organic compounds from readily available reagents is one of the major tasks in organic chemistry (Laszo, 1995). Ylides are important reagents in synthetic organic chemistry, especially in the synthesis of naturally occurring products and compounds with biological and pharmacological activities (Wittig, 1980). 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 (Laszo, 1995;

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Johnson, 1966; Cadogan, 1979; Engel, 1988; Hudson, 1990; Corbridge, 1995; Kolodiazhnyi, 1994; Cherkasov and Pudovic, 1994; Maryanoff and Rietz, 1989; Nicolaou et al., 1997; Shen, 1998; Yavari et al., 1998, 2002; Adib et al., 2005a,b; Ramazani et al., 2008; Kalantari et al., 2006; Islami et al., 2005; Maghsoodlou et al., 2006; Habibi-Khorassani et al., 2005, 2006a, b, 2007; Maghsoodlou et al., 2006; Saghatforoush et al., 2006). Phosphorus ylides most often prepare by the treatment of a phosphonium salt with a base. Most of the phosphonium salts are usually made from the reaction of phosphines and an alkyl halide (Cadogan, 1979; Engel, 1988; Hudson, 1990; Corbridge, 1995; Kolodiazhnyi, 1994), though they can be obtained by Michael addition of phosphorus nucleophiles to activated olefins (Johnson, 1966; Cadogan, 1979).

A facile synthesis of the reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxylates **2** and 6-chloro-2-benzoxazolethiol **3** (as a NH-heterocyclic compound) has been earlier reported (Maghsoodlou et al., 2009) for the generation of phosphorus ylides **4** (**a**,**c**) involving the two geometrical isomers such as *Z*- and *E*-isomers. The reaction is shown in Fig. 1. For assignment of the two *Z*- and *E*-isomers as a minor or major form in phosphorus ylides **4** (**a**,**c**) containing a 6-chloro-2-benzoxazolethiol, the *Z*- and *E*-isomers were optimized for all ylide structures at HF/6-31G (d,p) level of theory by Gaussian 03 package program (Frisch et al., 2004). The relative stabilization energies for both the geometrical isomers have been calculated at B3LYP/6-311+ +G (d,p) level. Atoms in molecules (AIM) and the calculation of charge on the atoms by natural population analysis (NPA) and CHelpG keyword at HF/6-31G (d,p) level of theory have been performed 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 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 the stability of *Z*- and *E*-ylide isomers. In addition, $J_{x-y}$, the values of proton and carbon coupling constants and also chemical shifts ($\delta_{\mathrm{H\ iso}}$, $\delta_{\mathrm{C\ iso}}$) have been calculated at mentioned level using SPINSPIN keyword.

## 2. Results and discussion

### 2.1. Calculations

Assignment of the stability of the two *Z*- and *E*-isomers is possible 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 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 more stable form of both the geometrical isomers [*Z*-**4**(**a**,**c**) or *E*-**4**(**a**,**c**)] of ylides (**4a** or **4c**), first their structures were optimized at HF/6-31G (d,p) level of theory by Gaussian03 program package. Also relative stabilization energy of the two isomers has been calculated at HF/6-31G (d,p) and B3LYP/6-311+ +G (d,p) levels (See Figs. 2 and 3). The relative stabilization energies for the two isomers [*Z*-**4** (**a**,**c**) and *E*-**4** (**a**,**c**)] 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 *E*-**4c** forms (0.63 and 1.64 kcal/mol), (0.62 and 0.88 kcal/mol) (0.78 and 1.84) and (0.71 and 1.03) at both HF and B3LYP levels in the gas and solvent phases, respectively. The results of zero point energy (ZPE) have been accumulated in Table 1. They are with the relative stabilization energies in the absence of these corrections in agreement.

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 (Bader, 1990) at HF/6-31G(d,p) level of theory by the AIM2000 program package (Biegler König et al., 2001). In recent years, AIM theory has often 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 the regions of space wherein the electronic charge is locally depleted [$\nabla^2\rho(r) > 0$] or built up [$\nabla^2\rho(r) < 0$] Rozas et al. (2000).

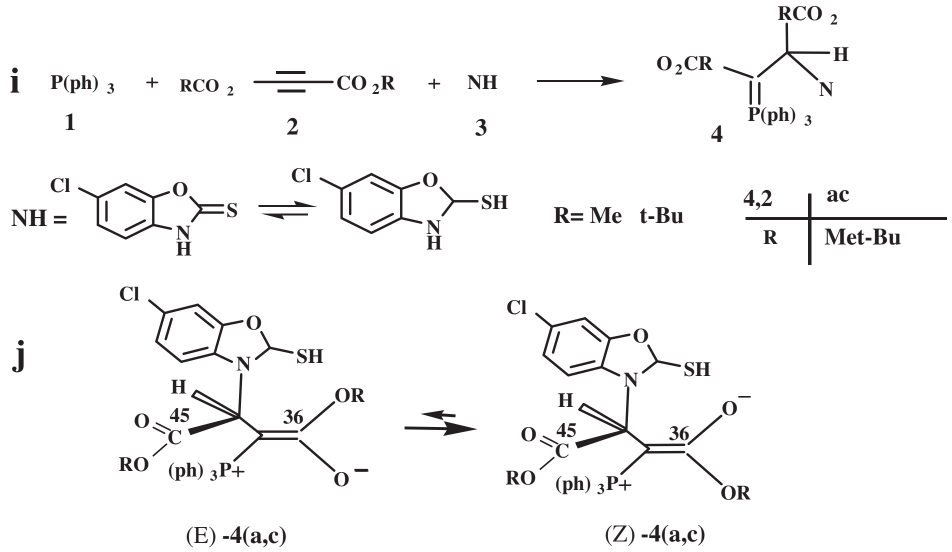

**Figure 1** (i) The reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxylate **2** (**2a** or **2c**) and 6-chloro-2-benzoxazolethiol **3** for generation of stable phosphorus ylides **4** (**4a** or **4c**). (j) The two isomers *E*-**4a** and *Z*-**4a** (minor and major, respectively) of ylide **4a**.

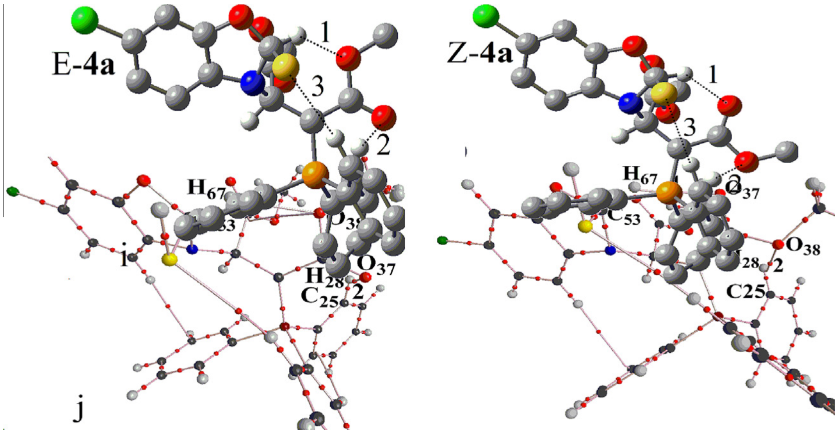

**Figure 2** (i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-**4a** and *Z*-**4a** geometrical isomers of stable ylide **4a**. (j) A part of molecular graphs, including intermolecular hydrogen bond at critical points (BCPs) for the two *E*-**4a** and *Z*-**4a** geometrical isomers of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

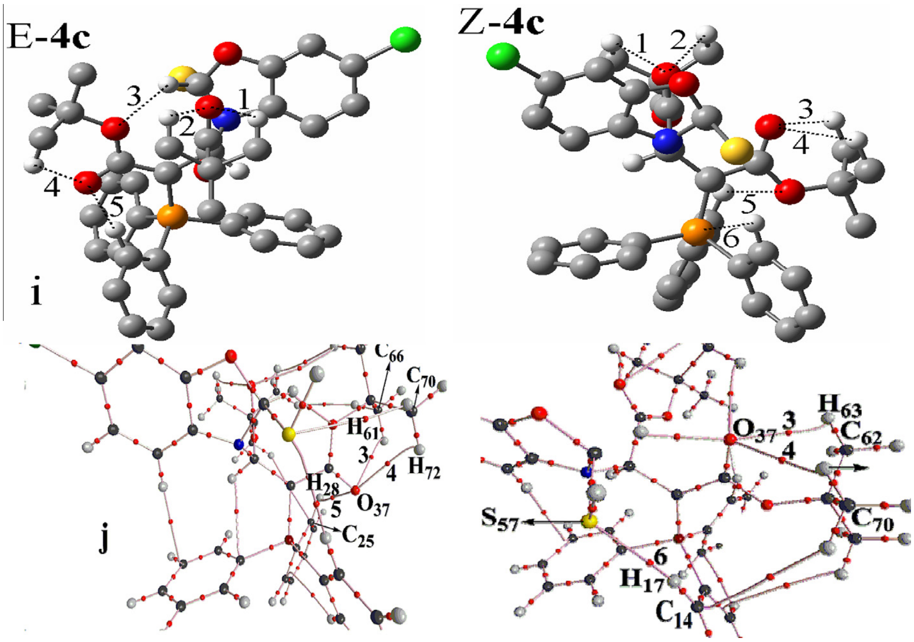

**Figure 3** (i) Intramolecular hydrogen bonds (dotted lines) in the two *E*-**4c** and *Z*-**4c** geometrical isomers of stable ylide **4c**. (j) A part of molecular graphs, including intermolecular hydrogen bond at critical points (BCPs) for the two *E*-**4c** and *Z*-**4c** geometrical isomers of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

**Table 1** The relative energy (kcal/mol) for for the two *Z*- and *E*-isomers of ylides **4a** and **4c**, obtained at HF/6-31G(d,p) and B3LYP/6-311+ +G(d,p) levels in the presence of ethyl acetate solvent medium.

| Conformer | ZPE (HF) | HF | HF (solvent) | B3LYP | B3LYP (solvent) |
|---|---|---|---|---|---|
| *Z*-**4a** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| *E*-**4a** | 0.59 | 0.63 | 0.78 | 0.62 | 0.71 |
| *Z*-**4c** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| *E*-**4c** | 1.53 | 1.64 | 1.84 | 0.88 | 1.03 |

Two interacting atoms in a molecule form a critical point in the electron density, where $\nabla\rho(\mathrm{r}) = 0$, called the bond critical point (BCP). The values of charge density and its Laplacian at these critical points give useful information regarding the strength of the H-bonds (Biegler König et al., 2001). The ranges of $\rho$(r) and $\nabla^2\rho(\mathrm{r})$ are (0.002–0.035) $e/a_0^3$ and (0.024–0.139) $\mathrm{e}/a_0^5$, respectively, if H-bonds exist (Grabowski, 2001). The AIM calculation indicates intramolecular hydrogen bonds

**Table 2** The values of $\rho \times 10^3$, $\nabla^2 \rho \times 10^3$ and Hamiltonian –H(r) × $10^4$ 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* | $\rho \times 10^3$ | $\nabla^2\rho \times 10^3$ | H(r) ×$10^4$ | E2 | *Z* | $\rho \times 10^3$ | $\nabla^2\rho \times 10^3$ | H(r) ×$10^4$ | E2 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 12.91 | 44.05 | −3.09 | 1.79 | 1 | 13.56 | 45.63 | −3.03 | 1.04 |
| 2 | 10.40 | 40.57 | −11.37 | 1.98 | 2 | 7.31 | 30.83 | −12.44 | 1.98 |
| 3 | 7.06 | 24.03 | −11.01 | 2.27 | 3 | 7.26 | 24.67 | −11.24 | 2.41 |

**Table 3** The values of $\rho \times 10^3$, $\nabla^2\rho \times 10^3$ and Hamiltonian –H(r) × $10^4$ 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) × $10^4$ | E2 | *Z* | $\rho \times 10^3$ | $\nabla^2\rho \times 10^3$ | H(r) × $10^4$ | E2 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 11.91 | 46.43 | −13.48 | 1.99 | 1 | 11.93 | 46.37 | −13.11 | 0.57 |
| 2 | 11.52 | 44.89 | −12.97 | 0.52 | 2 | 12.62 | 49.40 | −14.04 | 0.57 |
| 3 | 13.88 | 46.94 | −2.22 | 0.73 | 3 | 12.93 | 49.26 | −12.10 | 0.59 |
| 4 | 13.46 | 51.06 | −12.12 | 0.56 | 4 | 12.52 | 47.87 | −12.46 | 0.58 |
| 5 | 13.01 | 49.56 | −12.28 | 0.56 | 5 | 7.92 | 32.96 | −12.55 | 0.67 |
|  |  |  |  |  | 6 | 7.78 | 25.44 | −11.52 | 0.81 |

**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 both ylides **4a** and **4c**. Bond lengths in angstroms and bond angles in degrees, respectively.

|  | *E*-**4a** | *Z*-**4a** |  | *E*-**4c** | *Z*-**4a** |
|---|---|---|---|---|---|
| $C_{53}{-}H_{67}\cdots O_{38}$ | 2.31[a]<br>(138.6)[b] |  | $C_{66}{-}H_{61}\cdots O_{37}$ | 2.43[a]<br>(111.0)[b] |  |
| $C_{25}{-}H_{28}\cdots O_{37}$ | 2.67<br>(114.2) | 2.31[a]<br>(138.4)[b] | $C_{25}{-}H_{28}\cdots O_{37}$ | 2.43<br>(111.5) |  |
| $C_{53}{-}H_{67}\cdots O_{37}$ |  | 2.64<br>(114.0) | $C_{70}{-}H_{72}\cdots O_{37}$ | 2.67<br>(114.2) |  |
| $C_{25}{-}H_{28}\cdots O_{38}$ |  |  | $C_{62}{-}H_{63}\cdots O_{37}$ |  | 2.43[a]<br>(111.5)[b] |
|  |  |  | $C_{70}{-}H_{72}\cdots O_{38}$ |  | 2.45<br>(145.7) |
|  |  |  | $C_{1}{-}H_{17}\cdots S_{25}$ |  | 2.84<br>(167.1) |

[a] Bond lengths.
[b] Bond angles.

**Table 5** The charges on different atoms for both *Z*- and *E*-isomers in ylides **4a** and **4c** calculated at HF/6-31G (d,p) levels.

| Number of atom | *E*-**4a** | *Z*-**4a** | *E*-**4c** | *Z*-**4c** |
|---|---|---|---|---|
| P1 | 3.24[a]<br>(0.30)[b] (1.87)[c] | 3.24<br>(0.16) (1.87) | 3.25<br>(0.22) (1.88) | 3.24<br>(0.23) (1.87) |
| C35 | −0.82<br>(−0.64) (−0.88) | −0.84<br>(−0.48) (−0.89) | −0.77<br>(−0.61) (−0.87) | −0.81<br>(−0.45) (−0.87) |
| C36 | 0.784<br>(0.78) (−0.95) | 0.773<br>(0.77) (−0.96) | 0.835<br>(0.84) (−0.96) | 0.83<br>(0.72) (−0.97) |
| O37 | 1.83<br>(−0.67) (−0.79) | 1.84<br>(−0.63) (−0.78) | 1.85<br>(−0.68) (−0.81) | 1.86<br>(−0.60) (−0.79) |
| O38 | −1.42<br>(−0.39) (−0.79) | −1.41<br>(−0.41) (−0.79) | −1.43<br>(−0.55) (−0.81) | −1.42<br>(−0.50) (−0.80) |
| C43 | −1.27<br>(0.19) (−0.09) | −1.30<br>(0.20) (−0.08) | −1.29<br>(0.19) (−0.09) | −1.31<br>(0.20) (−0.08) |

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

**Table 6** Selected $^{13}$C NMR chemical shift ($\delta$ in ppm) and coupling constants ($J$ in Hz) for some functional groups in *E*-**4a** isomer as a minor form.

| Groups | $\delta_C$/ppm | $J_{PC}$/Hz |
|---|---|---|
| 2s, 2OMe | 53.0[a] (46.1)[b], 53.6 (47.5) | |
| d, $C_{ipso}$ | 124.9 (126.7) | 92.0[a] (94.2)[b] |
| d, $^3J_{PC}$, $C^{45}$=O | 169.6 (167.3) | 13.9 (12.2) |
| d, $C_{para}$ | 130.0 (133.1), 132.2 (133.4), 132.6 (133.5) | |
| d, P–C=$C^{36}$ | 170.4 (166.7) | |
| d, $C_{meta}$ | 129.2 (127.3) | |
| d, $C_{ortho}$ | 133.5 (136.6) | |

[a] Experimental data in accord with the results reported in the literature (Grabowski, 2001).
[b] Theoretical data.

**Table 7** Selected $^1$H NMR chemical shift ($\delta$ in ppm) and coupling constants ($J$ in Hz) for some functional groups in the *E*-**4a** isomer as a minor form.

| Groups | $\delta_H$/ppm |
|---|---|
| 6H, 2s, 2 (OMe) | 3.81[a] (3.50)[b], 3.83[a] (3.62)[b] |
| 18H, m, arom | 6.88 (6.70), 7.86 (7.92) |

[a] Experimental data in accord with the results reported in the literature (Grabowski, 2001).
[b] Theoretical data.

**Table 9** Selected $^1$H NMR chemical shift ($\delta$ in ppm) and coupling constants ($J$ in Hz) for some functional groups in the *Z*-**4a** isomer as a minor form.

| Groups | $\delta_H$/ppm |
|---|---|
| 6H, 2s, $2CO_2Me$ | 3.21[a] (3.45)[b], 3.80 (3.65) |
| 18H, m, arom | 7.28 (6.94), 7.86 (8.10) |

[a] Experimental data in accord with the results reported in the literature (Grabowski, 2001).
[b] Theoretical data.

and critical points (H-BCP) for the two *Z*-**4** (**a**,**c**) and *E*-**4** (**a,c**) isomers. Intramolecular H-BCPs are shown in Figs. 2 and 3 (dotted line) and also Table 4. For each H- bond E2 stabilization energy obtained via NBO analysis. The results (see Tables 2 and 3) confirmed that H-bonds via NBO analysis are in agreement with AIM analysis. The electron densities ($\rho$), Laplacian of electron density $\nabla^2\rho$(r), and energy density −H(r) are also reported in Tables 2 and 3. A negative total energy density at the BCP reflects a dominance of potential energy density, which is the consequence of accumulated stabilizing electronic charge (Arnold and Oldfield, 2000). Herein, the number of hydrogen bonds in both categories (*E*-**4a** and *Z*-**4a**) and (*E*-**4c** and *Z*-**4c**) are (3 and 3) and (5 and 6), respectively. The values of $\rho$ and $\nabla^2\rho$(r) are in the ranges (0.007–0.012 and 0.007–0.013) $e/a_0^3$, (0.011–0.013 and 0.007–0.012) $e/a_0^3$, (0.024–0.044 and 0.024–0.045) $e/a_0^5$ and (0.044–0.051 and 0.025–0.049) $e/a_0^5$, respectively. In addition the Hamiltonian [−H(r)] is in the range (3.09–11.37 and 3.03–12.44 au) and (2.22–13.48 and 11.52–14.04 au) (see Tables 2 and 3). These HBs show $\nabla^2\rho(r) > 0$ and $H(r) < 0$, which according to the classification of Rozas et al. (2000) are medium-strength hydrogen bonds. In both ylides the dipole moment for the two *E*-**4a** and *E*-**4c** isomers are smaller than the two *Z*-**4a** and *Z*-**4c** isomers in the gas and solvent phases [(8.01, 7.96 D), (10.16, 10.09) and [(11.61, 11.42 D), (14.78, 14.82)]. The value of $-H_{tot}$ (=ΣH(r)) for the two *Z*-**4a** and *Z*-**4c** isomers in the gas phase (26.70 and 75.79 au, respectively) is larger than the two *E*-**4a** and *E*-**4c** isomers (25.47 and 53.06 au, respectively). These differences in the most important geometrical parameters of *Z*-**4** (**a**,**c**) with respect to E-**4** (**a**,**c**), involving a large difference in dipole moment and a considerable difference in −H(r), altogether, make only the slight stability on these isomers in comparison with the *E*-**4** (**a**,**c**) forms. On the basis of theoretical calculations (Table 1), the difference between the relative stability of the *E*-**4c** and *Z*-**4c** isomers is (1.64 k/mol) while it is smaller in the *E*-**4a** and *Z*-**4a**

**Table 8** Selected $^{13}$C NMR chemical shift ($\delta$ in ppm) and coupling constants ($J$ in Hz) for some functional groups in *Z*-**4a** isomer as a major form.

| Groups | $\delta_C$/ppm | $J_{PC}$/Hz |
|---|---|---|
| 2s, 2OMe | 49.6[a] (46.1)[b], 52.3 (47.8) | |
| d, $C_{ipso}$ | 125.6 (127.7) | 92.0[a] (91.9)[b] |
| d, $^3J_{PC}$, $C^{45}$=O | 169.9 (166.6) | 11.4 (10.6) |
| d, $C_{para}$ | 129.8 (126.4), 132.0 (127.7), 132.6 (133.4) | |
| d, P–C=$C^{36}$ | 170.0 (168.2) | |
| d, $C_{meta}$ | 129.2 (127.3) | |
| d, $C_{ortho}$ | 133.4 (136.3) | |

[a] Experimental data in accord with the results reported in the literature (Grabowski, 2001).
[b] Theoretical data.

(0.63 kcal/mol) in gas phase. This result (a slightly difference on stability) is completely consistent with the obtained results on the basis of AIM calculations for determination of the most geometrical parameters (see the value of $-\mathrm{H}_{\mathrm{tot}}$ ($=\Sigma\mathrm{H(r)}$) for the two *Z*-**4a** and *Z*-**4c** isomers). Moreover, the total number of hydrogen bonds in the two *Z*-**4c** and *E*-**4c** (6, 5) is more than the two *Z*-**4a** and *E*-**4a** (3, 3); this leads to 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 more intramolecular hydrogen bonds accompanied by more steric factor of the bulky *tert*-bulky groups (compare with dimethyl groups in both the *E*-**4a** and *Z*-**4a**, Figs. 2 and 3) within the structures of *E*-**4c** and *Z*-**4c** forms makes a good opportunity for the enhancement of energy barrier. Hence, interconversion process between the two isomers needs to pass through very high restricted barrier energy, particular in solution media, for this reason it is possible to see only a single isomer as a lone isomers of **4c**. On the contrary, interconversion process for both the *E*-**4a** and *Z*-**4a** geometrical isomers passes through a considerably low energy barrier, which leads to a plausible observation of the two *E*-**4a** and *Z*-**4a** [see Fig. 1(j)].

In the synthesis of ylides **4a** and **4c** (Maghsoodlou et al., 2009), the $^{1}$H, $^{13}$C and $^{31}$P NMR data showed a lone isomer of **4c** with the experimental abundance percentage of 92% as a major form and also a mixture of isomers *E*-**4a** and *Z*-**4a** with the abundant percentage of 72% for *Z*-**4a** as a major form.

Also, the charge on different atoms which are calculated by NPA and AIM methods and also CHelpG keyword at HF/6-31G (d, p) level are reported in Table 5 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 the mentioned level for the two major *E*-**4** (**a**,**c**) and minor *Z*-**4** (**a**,**c**) geometrical isomers. The total spin–spin coupling constant is the sum of four components: the paramagnetic spin–orbit (PSO), diamagnetic spin–orbit (DSO), Fermi-contact (FC), and spin-dipole (SD) terms. The values of chemical shifts ($\delta$) and coupling constants ($J_{\mathrm{x-y}}$) are reported in Tables 6–9. As can be seen there is good agreement between both the experimental (Maghsoodlou et al., 2009) and theoretical chemical shifts ($\delta$) and coupling constants ($J_{\mathrm{x-y}}$). In the present work, molecular structures of ylides **4** (**a**,**c**) involving four large atoms such as sulfur, phosphorus, nitrogen and chlorine are huge with the large numbers of other atoms, for this reason, employment of basis set higher than B3LYP/6-311++G (d,p) is impossible for the performance of more accurate calculations. This limitation causes a small difference between both the experimental and theoretical coupling constants in some functional groups.

## 3. Conclusion

The assignment of the *Z*- and *E*-isomers as a major or minor form in both the ylides **4a** and **4c** was undertaken by AIM and NPA methods and also CHelpG keyword. Quantum mechanical calculation was clarified how the ylides **4a** and **4c** exist in solution as a mixture of the two geometrical isomers. This result in both media (gas phases and solvent) was in good agreement with the experimental data involving the $^{1}$H, $^{13}$C and $^{31}$P NMR. In addition the NMR study on the basis of theoretical calculations was employed for the determination of chemical shifts and coupling constants of the two major *E*-**4** (**a**,**c**) and minor *Z*-**4** (**a**,**c**) geometrical isomers.

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