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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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.

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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;

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 ($\delta_{H\ iso}$, $\delta_{C\ iso}$) 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).
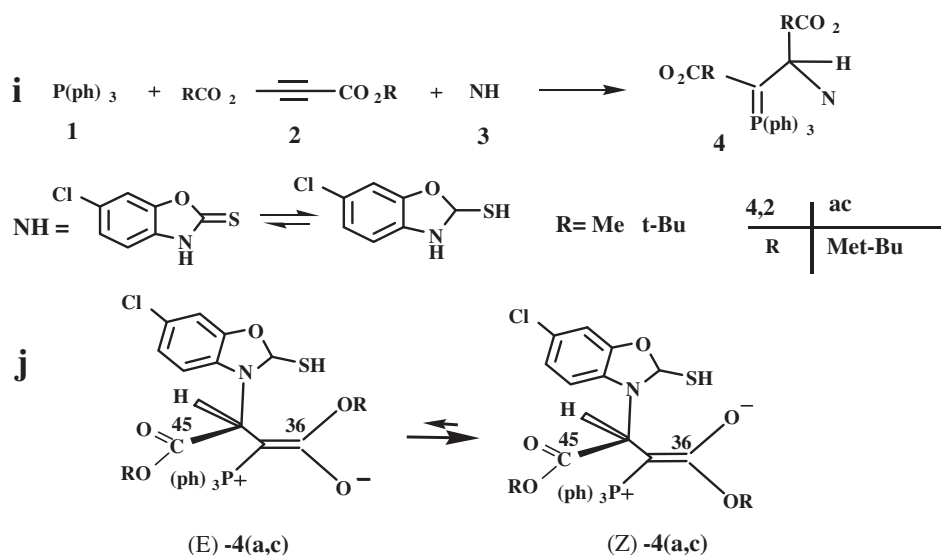

Figure 1   (i) The reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxylate **2** (**2a** or **2c**) and 6-chloro-2-benzoxazolethiol **3** for generation of stable phosphorus ylides **4** (**4a** or **4c**). (j) The two isomers E-**4a** and Z-**4a** (minor and major, respectively) of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