

# Infrared spectroscopy and *ab initio* computation in conformer determination of keto ester and diketo triphenylphosphonium ylides

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## ARTICLE INFO

### Article history:

Received 28 April 2009

Received in revised form 20 July 2009

Accepted 21 July 2009

Available online 25 July 2009

### Keywords:

Triphenylphosphonium ylides

Acyl stretching frequencies

HF and DFT calculations

Ylidic conformation

## ABSTRACT

For stabilized triphenylphosphonium keto ester ylides acyl stretching frequencies of the *anti* ester group from HF/6-31G(d) calculations fit experimental values with Scale Factor, SF = 0.866, as estimated earlier for the diester ylides, but Scale Factor = 0.834 has to be used to fit data for the *syn*-keto group and for *syn-anti* diketo ylides. The DFT functional BLYP/6-31G(d), with the literature Scale Factor = 0.9945, generally gives good fits for both keto ester and diketo ylides. For both methods agreement between observed and predicted frequencies is lowest for the *syn-anti* di-*t*-butyl keto ester ylide, although, unlike the situation for diester ylides, one bulky alkyl group does not significantly degrade the fits. Comparison of predicted and observed acyl stretching frequencies is useful in establishing conformations of these stabilized phosphonium ylides.

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## 1. Introduction

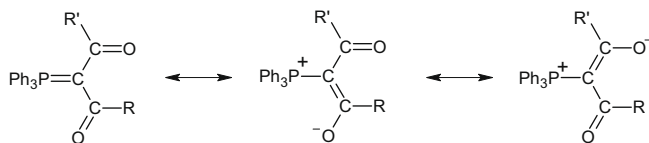
Phosphonium ylides with a single keto or ester substituent can adopt two conformations [1–3] and *syn* and *anti* indicate orientations of the acyl group with respect to phosphorus. The *syn* conformer is generally energetically preferred over the *anti*, due to interactions between anionoid oxygen and cationoid phosphorus and in favorable cases interconversion is slow on the NMR time scale [4,5].

Ylides with two identical acyl groups can adopt three conformations and with different acyl groups four conformers could form, but in most of the stabilized ylides with alkyl acyl groups examined to date one conformer is dominant, usually with *syn-anti* acyl, but sometimes *anti-anti* groups, [6–11]. These generalizations only apply to ylides with alkyl keto or ester groups and Aitken et al. in considering ylides with phenyl or very bulky groups in the ylidic moiety observed a number of systems where two acyl groups adopted the *syn-syn* conformation [12]. There would be resonance between these phenyl groups and the ylidic moiety and such interactions and non-bonding interactions of very bulky groups should not be important in the alkyl ketones and esters that we examined. In the present work we examined triphenylphosphonium derivatives and designated conformations as *syn* or *anti* depending on orientations of the two acyl groups with respect to phosphorus (Scheme 1).

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The classical structures in Scheme 1 are inadequate because there is free rotation about the P–C bond on the NMR time scale and considerable double bond character between the ylidic and acyl carbons. Classical structures can be written as zwitterionic [13] with a P–C single bond and positive charge on phosphorus and negative charge on the ylidic carbon but there should be extensive ylidic resonance with partial charges on these atoms. For alkyl diester ylides *syn-syn* conformers have not been detected, but both *syn-anti* and *anti-anti* conformers have been identified and in the *syn-anti* diester ylides the bulkier alkoxy group is preferentially oriented towards phosphorus in the crystal and in solution [9,11]. In the diesters only one conformer is usually observed, but the crystalline dimethyl diester, X = OMe, is a 1:1 mixture of *syn-anti* and *anti-anti* conformers [10,11], although only one set of <sup>1</sup>H or <sup>13</sup>C NMR signals are observed in solution, possibly because conformers interconvert rapidly on the NMR time scale. The use of Infrared, IR, spectroscopy does not have this limitation, but prediction of frequencies is a problem, and this method lacks the quantitative power of NMR spectroscopy.

Infrared spectra of phosphonium ylides are complicated [14], but stretching frequencies of acyl and cyano groups can usually be identified with limited overlap with other signals. For given structures IR frequencies can be estimated by using a variety of theoretical models, but predicted values are generally too high and empirical corrections are used. Scott and Radom [15a], in a very extensive study of organic and inorganic compounds, showed that the calculated values can be corrected by use of method-specific Scale Factors, SF. The estimated SF value for the HF/6-31G(d) method was 0.8953, and higher level methods gave SF values closer to unity, but overall results were not necessarily



**Scheme 1.** Conformation of *syn-anti* diketo or keto ester ylides, R and R' = alkyl, alkoxy.

better than from this simple method [15b]. However, the SF value for HF/6-31G(d), as applied to triphenylphosphonium diester ylides, gave frequencies which were too high and a value of SF = 0.866 gave reasonable results for a variety of diester and cyano ylides [16]. The literature SF = 0.9945 for the pure DFT functional BLYP/6-31G(d) was used for several triphenylphosphonium ylides of known conformation, and this SF correction could be neglected within the limitations of experimental error, although we apply it to all the results from this method. Silverstein et al. [17] noted that experimental wave numbers can generally be observed to within  $10\text{ cm}^{-1}$ , which sets a limit to the required accuracy of a prediction.

For a number of triphenylphosphonium diester and cyano ylides estimated acyl stretching frequencies from both the DFT functional BLYP/6-31G(d), and HF/6-31G(d) with our revised SF value, agreed reasonably well with experiment [16]. However, for *syn-anti* conformers with a small (Me or Et) *syn* ester group and a large (isoPr or *t*-Bu) *anti* ester group the BLYP/6-31G(d) method gave good results for the *anti* acyl group, but frequencies for the *syn* acyl group were too low by  $33\text{--}61\text{ cm}^{-1}$  and well outside the limits of experimental error. Corresponding values from the hybrid DFT functional B3LYP/6-31G(d), with the literature SF = 0.9614, were slightly higher than experimental values for the larger ester groups and lower for the smaller ester groups, but here the SF value cannot be neglected. The HF/6-31G(d) method with the revised SF gave reasonable fits with the large ester groups, but this SF value was estimated from data on all the diester ylides [16].

The ability of a large alkoxy group in an *anti* ester residue to affect the predicted acyl stretching frequency of the small *syn* ester group indicates that there are interactions between these groups, despite their separation by the ylidic carbon, and they are probably not treated fully by BLYP/6-31G(d). We cannot transpose these groups in diesters where the smaller ester group is always *syn* [16], and were unable to isolate diester ylides with two bulky alkoxy groups, but it is possible to make these structural changes in keto ester ylides where earlier evidence from X-ray crystallography and NMR spectroscopy showed that the keto acyl group is always *syn* and the ester group is *anti*, regardless of the size of its alkoxy residue [6,7,18]. Experimental and predicted stretching frequencies had been compared for some keto esters with a small (methyl) *syn*-keto group and a variable *anti* ester group (Me, Et, isoPr, *t*-Bu) [16]. For this series of ylides (Chart 1) the DFT functional BLYP/6-31G(d) with the near unity SF gave good fits, unlike the situation with some diesters, and the HF/6-31G(d) method, with our revised SF = 0.866, gave good fits for the ester acyl group, but predicted values for the keto acyl group were too high [16]. The ylidic *syn-anti* dimethyl ketone [8a] was also examined and here fits were good with BLYP/6-31G(d), but both HF/6-31G(d) and B3LYP/6-31G(d) gave predicted values for the keto groups which were too high, as discussed later. Examination of a series of keto ester ylides with different keto alkyl groups and various sized ester groups (Chart 1), should complement earlier results [16] on interactions between *syn* and *anti* groups and extend the earlier limited examination of diketo ylides which had indicated that the SF value for HF/6-31G(d), estimated for the ester groups, is inappropriate for keto groups. Behaviors of keto and ester groups may differ because of the geometries of the alkyl and alkoxy groups and the marked electronic delocalization in the latter.

Keto ester ylides	1: R=R'=Me;	2: R=Me, R'=Et;
	3: R=Me, R'= <i>i</i> -Pr;	4: R=Me, R'= <i>t</i> -Bu;
	5: R=Et, R'=Et;	6: R= <i>i</i> -Pr, R'=Et;
	7: R= <i>t</i> -Bu, R'=Et;	8: R= <i>t</i> -Bu, R'= <i>t</i> -Bu;
Diketo ylides	9: R=R'=Me;	10: R=R'=Et;

Compounds **1-4**, and **9** have conformations from X-ray crystallography [9b, 18].

**Chart 1.** General structures for keto ester and diketo ylides.

Conformations of most of the ylidic diesters and the methyl keto ester ylides examined to date have been determined by X-ray crystallography [9b,10,11b,18] and bond lengths and angles are similar to those from the HF/6-31G(d) optimizations.

Observation of  $\pi$ -shielding [6,19] in the  $^1\text{H}$  NMR signals of a terminal methyl hydrogen by a phenyl group indicates that an alkoxy group in an *anti* ester residue is oriented towards phosphorus. Results of this test have been consistent with evidence from X-ray crystallography and we used it in establishing conformations of ester groups [11,20], but the sensitivity is low for *t*-butoxy groups where the shielding effect is spread over nine methyl hydrogens.

## 2. Experimental

### 2.1. Materials

Some of the ylides examined in this work (Chart 1) were known compounds described earlier [7,8a,b], and most of the keto esters with small ester groups and various keto alkyl groups were prepared by standard methods.

The new keto ester ylides, **5-8**, were prepared by classical transylidation [20] of an alkoxy carbonylmethylenetriphenylphosphorane,  $\text{Ph}_3\text{P}=\text{CH}-\text{CO}_2\text{R}'$ , with acyl chlorides,  $\text{R}-\text{COCl}$ , in dry benzene, at  $25^\circ\text{C}$ , under an inert atmosphere. The reaction is an acid-base interaction with a second equivalent of ester ylide, as described for keto ester ylides **1-4** by Castañeda et al. [7]. Elemental analyses confirmed the structures of ylides **5-8**.

*Ethyl 2-triphenylphosphoranylidene-3-oxovalerate*, **5**. Yield 92%, m.p.  $124^\circ\text{C}$ ,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{ppm}}$ : 0.66 (t, 3H,  $\text{CH}_3$ ,  $J = 7\text{ Hz}$ ); 1.10 (t, 3H,  $\text{CH}_3$ ,  $J = 7.5\text{ Hz}$ ); 2.96 (q, 2H,  $\text{CO}-\text{CH}_2$ ,  $J = 7.5\text{ Hz}$ ); 3.77 (q, 2H,  $\text{O}-\text{CH}_2$ ,  $J = 7\text{ Hz}$ ); 7.5 (m, 15H). IR (KBr): 1558, 1658  $\text{cm}^{-1}$ .

*Ethyl 2-triphenylphosphoranylidene-4-methyl-3-oxovalerate*, **6**. Yield 72%, m.p.  $180\text{--}183^\circ\text{C}$ ,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{ppm}}$ : 0.63 (t, 3H,  $\text{CH}_3$ ,  $J = 7\text{ Hz}$ ); 1.04 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ); 3.47 (m, 1H,  $\text{O}-\text{CH}$ ); 4.03 (q, 2H,  $\text{O}-\text{CH}_2$ ,  $J = 7\text{ Hz}$ ); 7.45 (m, 15H). IR (KBr): 1556, 1654  $\text{cm}^{-1}$ .

*Ethyl 2-triphenylphosphoranylidene-4,4-dimethyl-3-oxovalerate*, **7**. Yield 85%, m.p.  $154^\circ\text{C}$ ,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{ppm}}$ : 0.65 (t, 3H,  $\text{CH}_2-\text{CH}_3$ ,  $J = 7\text{ Hz}$ ); 1.30 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ); 3.60 (q, 2H,  $\text{O}-\text{CH}_2$ ,  $J = 7\text{ Hz}$ ); 7.4 (m, 15H). IR (KBr): 1531, 1658  $\text{cm}^{-1}$ .

*t*-Butyl 2-triphenylphosphoranylidene-4,4-dimethyl-3-oxovalerate, **8**. Yield 76%, m.p.  $130\text{--}131^\circ\text{C}$ ,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{ppm}}$ : 1.03 (s, 9H,  $\text{O}-\text{C}(\text{CH}_3)_3$ ); 1.32 (s, 9H,  $\text{CO}-\text{C}(\text{CH}_3)_3$ ); 7.35 (m, 15H). IR (KBr): 1577, 1661  $\text{cm}^{-1}$ .

### 2.2. IR spectroscopy

Spectra were examined on Bruker IFS 56 FT or on Leitz III-G spectrometers.

Unless specified, spectra were measured with a KBr disk. Some IR spectra were of new compounds prepared in the course of this work, but some acyl stretching frequencies were for keto ester ylides synthesized earlier and of known conformation. A few frequencies were from the literature with compounds whose chemical composition was known, but whose conformations were not established, but are consistent with our new evidence.

### 2.3. NMR spectroscopy

The  $^1\text{H}$  NMR spectra were monitored at 60 or 300 MHz in acid-free  $\text{CDCl}_3$  for characterizing structures of novel ylides and in establishing orientations of  $\text{CH}_3$  alkoxy groups with respect to the triphenylphosphonium group. Signal multiplicity allowed distinction between primary, secondary and tertiary alkyl groups.

### 2.4. Computation

The general approach followed methods described earlier [16] with use of Spartan '06 or '08 for Windows. Structures were optimized by using the same method as that for prediction of the IR spectra with no structural constraint. Acyl stretching frequencies are rounded off to the nearest whole number. Convergence conditions were as described earlier [16]. For a few compounds computations are with conformations assumed or known to be incorrect.

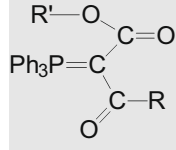
Computations are for isolated molecules, although spectra were monitored in KBr disks, and later we consider evidence on acyl stretching frequencies for some keto ester ylides which had been examined in chloroform [21]. These results, were with compounds with longer keto alkyl groups than those of ylides prepared here.

## 3. Results and discussion

### 3.1. Keto esters and diketone ylides

The DFT functional BLYP/6-31G(d) with the literature SF value gave satisfactory agreement for all the keto ester ylides, except the di *t*-butyl derivative, **8**, where the predicted frequency for the (assumed) *syn*-keto acyl group is significantly too low, but that of the *anti* ester acyl group is in better agreement with experiment (Table 1). Unlike the situation for the diester ylides [16] a *t*-butyl

**Table 1**  
Acyl stretching frequencies of *syn*-*anti* keto ester ylides from BLYP/6-31 G (d) and  $^1\text{H}$  NMR chemical shifts of the terminal  $\text{CH}_3$  of  $\text{R}'$  showing  $\pi$ -shielding.

	$^1\text{H}$ NMR	BLYP/6-31G(d)		Observed
		Calculated	SF Corrected <sup>b</sup>	
<b>1</b> R = Me, $\text{R}' = \text{CH}_3$ <sup>a,c</sup>	3.10(s)	1574	1667	1560 1681
<b>2</b> R = Me, $\text{R}' = \text{CH}_2\text{-CH}_3$ <sup>a,b</sup>	0.63 (t)	1566	1663	1555 1654
<b>3</b> R = Me, $\text{R}' = \text{CH}(\text{CH}_3)_2$ <sup>a</sup>	0.75 (d)	1571	1652	1552 1652
<b>4</b> R = Me, $\text{R}' = \text{C}(\text{CH}_3)_3$ <sup>a</sup>	1.10 (s)	1572	1648	1543 1662
<b>5</b> R = Et, $\text{R}' = \text{CH}_2\text{-CH}_3$ <sup>c</sup>	0.66 (t)	1556	1659	1558 1658
<b>6</b> R = <i>i</i> -Pr, $\text{R}' = \text{CH}_2\text{-CH}_3$ <sup>c</sup>	0.63 (t)	1548	1654	1556 1654
<b>7</b> R = <i>t</i> -Bu, $\text{R}' = \text{CH}_2\text{-CH}_3$	0.65 (t)	1517	1652	1531 1658
<b>8</b> R = <i>t</i> -Bu, $\text{R}' = \text{C}(\text{CH}_3)_3$	1.03 (s)	1523	1639	1577 1661

<sup>a</sup> Conformations of ylides **1–4** are also obtained from X-ray crystallography [18].

<sup>b</sup> For the *syn* methyl *anti* ethyl derivative, **2**, predicted frequencies are 1604 and 1686  $\text{cm}^{-1}$  from B3LYP/6-31G(d).

<sup>c</sup> For *syn*-*syn* and *anti*-*anti* dimethyl derivatives **1** (incorrect conformations) predicted frequencies are 1569–1624 and 1625–1718  $\text{cm}^{-1}$ , respectively. For *anti*-*anti* diethyl derivative **5** (incorrect conformation) predicted frequencies are 1625 and 1712  $\text{cm}^{-1}$ . For *anti* isopropyl keto *anti* ethyl ester **6** (incorrect conformation) predicted frequencies are 1623 and 1710  $\text{cm}^{-1}$ .

**Table 2**

Acyl stretching frequencies of *syn*-*anti* keto ester ylides with SF values for HF/6-31G(d)<sup>a</sup>.

Ylides	Predicted				Observed		
	Calculated		SF Corrected <sup>b</sup>				
<b>1</b> Me keto Me ester	1865	1920	1615	(1555)	1663	1560	1681
<b>2</b> Me keto Et ester	1865	1918	1615	(1555)	1661	1555	1654
<b>3</b> Me keto <i>i</i> -Pr ester	1866	1908	1616	(1556)	1652	1552	1652
<b>4</b> Me keto <i>t</i> -Bu ester	1865	1903	1615	(1555)	1648	1543	1662
<b>5</b> Et keto Et ester	1859	1915	1610	(1550)	1658	1558	1658
<b>6</b> <i>i</i> -Pr keto Et ester	1849	1911	1602	(1542)	1655	1556	1654
<b>7</b> <i>t</i> -Bu keto Et ester	1846	1902	1599	(1540)	1647	1531	1658
<b>8</b> <i>t</i> -Bu keto <i>t</i> -Bu ester	1856	1986	1610	(1550)	1633	1577	1658

<sup>a</sup> With SF = 0.866 unless specified.

<sup>b</sup> Values in parentheses are for *syn*-keto groups with SF = 0.834.

group in the *anti* ester group in the methyl keto *t*-butyl ester ylide, **4**, is predicted to only modestly increase the stretching frequency of the *syn*-keto group by 32  $\text{cm}^{-1}$ , and have a smaller increasing effect on that of the *anti* acyl group, and for the *t*-butyl keto ethyl ester ylide, **7** predicted and observed frequencies are similar. For most of the keto ethyl ester ylides in Table 1 agreements between observed and predicted acyl stretching frequencies are not very sensitive to the bulk of the alkyl groups. Conformations of some of the keto ester ylides were known from X-ray crystallography [18] and  $^1\text{H}$  NMR spectroscopy shows that the ester groups have the *anti* conformation (Table 1). For the diester ylides fits between observed and predicted frequencies were significantly worse when a small alkoxy group in the *anti* ester residue was replaced by an isopropoxy or *t*-butoxy group [16], but for the keto esters such size effects of a single group are much less important. Except for *t*-butyl derivatives predicted and observed frequencies are in good agreement and the frequency of the keto acyl group is always lower than that of the ester acyl group. The hybrid DFT functional B3LYP/6-31G(d), with the literature SF [15], gives frequencies of the ylidic methyl keto ethyl ester, **2**, which are too high for the keto and ester acyl groups, (Table 1 and Ref. [16]), consistent with the HF contribution in this method.

Although the revised SF value of 0.866 for the HF/6-31G(d) method gives satisfactory results for diester ylides [16], it has limitations for keto ester ylides. For the series with a methyl keto group and a variable ester group observed and predicted stretching frequencies are in satisfactory agreement for the ester acyl group, but predicted frequencies with this SF are consistently too high for the *syn* methyl keto acyl group, regardless of the size of the *anti* ester group. The situation is the same with the small *anti* ethyl ester group and variable sized *syn* alkyl keto groups, where the calculation gives too high frequencies for the keto acyl groups (Table 2). The agreement would be worse with the literature SF = 0.8953 [15], but a revised SF = 0.834 gives reasonable fits for the keto groups, while retaining SF = 0.866 for the ester groups. These generalizations break down for the di *t*-butyl keto ester, **8**, where this

**Table 3**

Observed and predicted acyl stretching frequencies for diketone ylides.

Diketone ylides	Predicted				Observed	
	HF/6-31G(d) <sup>a</sup>		BLYP <sup>b</sup>			
<b>9</b> <i>Syn</i> - <i>anti</i> di Me keto	1539	1577	1550	1602	1557	1603
<b>10</b> <i>Syn</i> - <i>anti</i> di Et keto	1533	1574	1543	1590	1535	1590
<b>9</b> <i>Syn</i> - <i>syn</i> di Me keto <sup>c</sup>	1521	1559	1549	1573	—	—
<b>9</b> <i>Anti</i> - <i>anti</i> di Me keto <sup>c</sup>	—	—	1625	1718	—	—

<sup>a</sup> SF = 0.834.

<sup>b</sup> SF = 0.9945.

<sup>c</sup> Incorrect conformation.

method modestly underpredicts the frequencies of both acyl groups (Table 2).

Only two diketone ylides, the dimethyl and diethyl ylides, **9** and **10**, were examined (Table 3). The DFT functional BLYP/6-31G(d) functional gives good agreement in both diketone ylides, but HF/6-31G(d) with SF = 0.866, as for ylidic diesters, gives frequencies that are too high by ca. 50 cm<sup>-1</sup> and the fit is much better with SF = 0.834. As expected from earlier work [16] incorrect conformers give poor agreement between observed and predicted frequencies (Tables 1 and 3).

Conformations of some keto ester and diketone ylides are known in the crystal [9b,18], and for most keto ester and diester ylides the *anti* conformation of an ester group is established by observation of  $\pi$ -shielding of an <sup>1</sup>H NMR signal in the alkoxy group (Refs. [6], [7] and [22], and Section 2). These conclusions agree with those from theoretical treatments. For the *syn-anti* diketone and diester ylides, the *syn* acyl group has a lower stretching frequency than the *anti*, because favorable interaction between an anionoid *syn* acyl oxygen and the cationoid phosphorus slightly increases the CO bond length, reducing the double bond character and therefore the force constant in the stretching vibration.

Some structures from the computations had earlier been compared with those from X-ray crystallography, [9b,18], and bond lengths and angles for some of the ylides are given as Supporting material. For most of the simple ylides that we examined the lengths and angles are not very sensitive to changes in the alkyl groups.

### 3.2. Use of Scale Factors

The application of simple computational methods in the estimation of IR frequencies involves use of SF, although for the DFT functional BLYP/6-31G(d), perhaps fortuitously, SF can be taken as unity [15]. We only used the hybrid functional B3LYP/6-31G(d) with a few phosphonium ylides and this method, with the literature SF value, does not give good agreement with experiment (Table 1 and Ref. [16]).

Some of the compounds used earlier in the establishment of method-specific SF values had simple structures [15], but in the phosphonium ylides there is extensive electronic delocalization involving the whole molecule, so that motions in an acyl group, for example, are coupled with other motions, such as those of phenyl hydrogens and associated alkyl groups. In the keto ester ylides predicting frequencies by the HF/6-31G(d) method requires use of SF values that are group specific, and a single SF is inadequate in treating acyl group IR spectra, with different values for keto and ester acyl groups (Table 2). The selection of SF values would be a major problem if IR spectra were used in conformational assignments of ylides with complicated structures such as those treated in Ref. [12].

### 3.3. Limitations of the DFT functional BLYP/6-31G(d)

Provided that we discount results for the di *t*-butyl keto ester ylide, **8**, this DFT functional satisfactorily predicts acyl stretching frequencies of keto ester ylides, even those with a single bulky alkyl group, although for *syn-anti* diester ylides with one bulky *anti* ester group predicted frequencies for the smaller *syn* ester acyl group are too low [16]. There should be non-covalent interactions between the two ester groups in these conformers. In the crystal the *syn* acyl oxygen is oriented between two phenyl groups, with interactions between the oxygen and phenyl hydrogens, while for the *anti* ester residue the alkoxy group is oriented towards the face of the third phenyl group. These orientations are consistent with structural predictions for isolated molecules and the geometry of a large *anti* ester group may affect that of the small *syn* ester group by an effect relayed through the phenyl groups [16]. In addition the center–center distances between the oxygens

oriented *anti* to phosphorus in a diester ylide can be close to the sum of the van der Waals radii and interactions between these oxygens should also affect the orientation of a *syn* acyl oxygen with respect to phosphorus. Therefore evidence in the crystal and computations for isolated molecules indicates that the geometry of one ester group may affect that of the other, depending on the size of the *anti* ester alkoxy group and the relayed effect on the acyl oxygen of the small *syn* ester group.

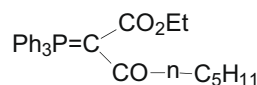
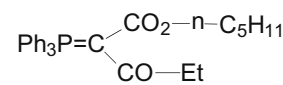
Interactions between ester and keto groups are apparently much smaller than in the diesters, because, except for the di-*t*-butyl keto ester ylide, **8**, the DFT functional BLYP/6-31G(d) satisfactorily predicts keto and ester acyl stretching frequencies (Table 1). The HF/6-31G(d) method, with the revised keto specific and size independent SF, also gives reasonable results (Table 2). For a *syn*-keto group interactions between the alkyl group and oxygen or a (saturated) alkyl residue of the other ester or keto group should be less important than those between the oxygens in ylidic carboxylic ester groups, so that factors that control acyl stretching frequencies are apparently different in ylidic keto esters and diesters and, for the former, should be less sensitive to size of alkoxy groups. The pure DFT functionals have limitations in treating London dispersion forces [15b,23], which should be important in these stabilized triphenylphosphonium ylides, and to that extent the potential ability of the BLYP/6-31G(d) method to fit observed stretching frequencies for acyl groups of many of our phosphonium ylides, and usually within experimental error, may be due to cancellation of errors which is more important in some keto ester ylides than in the diesters. This DFT functional method [15b,24] tends to slightly overestimate lengths of C=O bonds, but it has little effect on bond angles and therefore on conformations. Although the hybrid DFT B3LYP/6-31G(d) was developed to avoid weaknesses in the pure DFT functionals it does not perform well in predicting acyl stretching frequencies for keto ester and diester phosphonium ylides, and the literature SF [15a] is apparently not satisfactory for these ylides.

Recent articles cover in detail the use of various theoretical methods for the prediction of molecular properties [23–26], but some are limited to small molecules [27].

### 3.4. IR spectroscopy of ylides and determination of structure

Examination of IR spectra is useful in identification of functional groups and comparison of signals in the “finger-print” region allows identification of structures [14,17]. Results given here and earlier [16] show that comparison of observed and predicted acyl stretching frequencies is useful in identifying conformations of stabilized phosphonium ylides. The DFT functional BLYP/6-31G(d) provides useful evidence on conformation, although we note its limitations as applied to diester ylides with a secondary or tertiary alkoxy group [16]. The HF/6-31G(d) method is also useful, although structure specific SF values, lower than literature values [15], have to be used for keto and ester acyl groups of phosphonium ylides.

The use of IR spectra for conformer identification has limitations in examining ylides of similar chemical composition and conformation, because acyl stretching frequencies for diketones and keto esters of a given conformation are generally not very sensitive to changes in the alkyl groups and are easily identified (Tables 1–3). As a test we examined the isomeric keto ester ylides, **11** and **12**.

**11****12**

The structure of **11** is known from its synthesis [21] and the observed acyl stretching frequencies in  $\text{CHCl}_3$  are 1550 (keto) and 1640 (ester)  $\text{cm}^{-1}$ . The corresponding predicted values from BLYP/6-31G(d) are 1558 and 1661  $\text{cm}^{-1}$  and HF/6-31 G(d), with the appropriate SF, gives 1547 and 1640  $\text{cm}^{-1}$ . So far as we know **12** has not been synthesized, but the corresponding predicted stretching frequencies from BLYP/6-31G(d) are 1562 and 1661  $\text{cm}^{-1}$ . Therefore comparison of observed and calculated acyl stretching frequencies would not distinguish between these (hypothetical) isomers.

### 3.5. Treatment of incorrect conformations

Observed acyl stretching frequencies for diester and cyano ylides of incorrect conformations [16] estimated largely by the HF/6-31G(d) method with SF = 0.866, do not agree with observed values. In applying this test to the present results we note that this SF value does not give agreement between observed and predicted frequencies of keto acyl groups (Table 3), but the DFT functional BLYP/6-31G(d) does not have this limitation, and we used it for keto ester ylides with incorrect conformations (Table 1). An example of the treatment of a diketone with incorrect conformations is given in Table 3.

## 4. Conclusions

Examination of acyl stretching frequencies of keto groups in a series of keto ester ylides by the HF/6-31G(d) method shows that different SF values are required for keto and ester acyl groups in triphenylphosphonium ylides. The SF estimated in this way with keto esters also gives satisfactory fits of predicted and observed frequencies for di keto ylides with the expected conformation. The DFT functional BLYP/6-31G(d), with a near unity SF, and a simple basis set, gives good agreement with experiment for acyl stretching frequencies in di keto ylides and most keto ester ylides. For the di *t*-butyl keto ester ylide, **8**, the difference between observed and predicted frequencies of the keto group is beyond the experimental error, although differences between observed and predicted frequencies with only a single bulky substituent in the keto or ester group are much less than those for diester ylides with a bulky alkoxy group in the *anti* ester residue. The non-covalent interactions involving *syn-anti* diester groups which may degrade frequency predictions [16] are apparently much less important in keto ester ylides than in diester ylides. Comparison of observed and predicted acyl stretching frequencies is useful in identifying conformations in the simple triphenylphosphonium ylides that we examined, but, as applied to keto ester ylides, it may not distinguish between isomers with the same conformation and transposed keto and ester groups.

Reliance on the use of empirical SF values, which may be structure specific, means that stretching frequencies for given compounds are not predicted, but are compared with those of standards. The conclusion that SF for BLYP/6-31 G(d) can be neglected, within the limits of experimental error, is apparently sensitive to the size of substituents in diester ylides. Reliance on SF values allows the use of economically attractive computational methods in relating molecular spectra to structure for given classes of organic compounds. These generalizations regarding the use of IR spectroscopy may not apply to phenyl keto ylides where both

electronic delocalization in the ylidic system and steric effects have to be considered.

## Acknowledgments

The authors are grateful to Paul Silva and Ximena Ramírez for their valuable work in production of this paper.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2009.07.028.

## References

- (a) I.F. Wilson, J.C. Tebby, J. Chem. Soc. Perkin Trans. 2 (1972) 31; (b) I.F. Wilson, J.C. Tebby, Tetrahedron Lett. (1970) 3769.
- (a) H.I. Zeliger, J.P. Snyder, H.J. Bestmann, Tetrahedron Lett. (1969) 2199; (b) H.I. Zeliger, J.P. Snyder, H.J. Bestmann, Tetrahedron Lett. (1970) 3313.
- D.M. Crouse, A.T. Wehman, E.E. Schweizer, Chem. Commun. (1968) 866.
- (a) G.A. Gray, J. Am. Chem. Soc. 95 (1973) 7736; (b) F.J. Randall, A.W. Johnson, Tetrahedron Lett. (1968) 2841.
- T.A. Albright, M.D. Gordon, W.J. Freeman, E.E. Schweizer, J. Am. Chem. Soc. 98 (1976) 6249.
- A.D. Abell, B.M. Clark, W.T. Robinson, Aust. J. Chem. 42 (1989) 1161.
- F. Castañeda, C.A. Terraza, C.A. Bunton, N.D. Gillitt, M.T. Garland, Phosphorus, Sulfur, Silicon 178 (2003) 1973.
- (a) F. Castañeda, G.I. Recabarren, J. Hu, N.D. Gillitt, C.A. Bunton, Phosphorus, Sulfur, Silicon 178 (2003) 2505; (b) M.P. Cooke Jr., R. Goswami, J. Am. Chem. Soc. 95 (1973) 7891.
- (a) F. Castañeda, C. Aliaga, M.T. Garland, J. Hu, N.D. Gillitt, C.A. Bunton, Phosphorus, Sulfur, Silicon 182 (2007) 151; (b) F. Castañeda, C. Aliaga, C.A. Bunton, M.T. Garland, R. Baggio, Acta Crystallogr. C61 (2005) 496.
- F. Castañeda, C. Jullian, C.A. Bunton, M.T. Garland, R. Baggio, Acta Crystallogr. C63 (2007) 267.
- (a) F. Castañeda, P. Silva, M.T. Garland, A. Shirazi, C.A. Bunton, Phosphorus, Sulfur, Silicon 184 (2009) 19; (b) F. Castañeda, P. Silva, C.A. Bunton, M.T. Garland, R. Baggio, Acta Crystallogr. C 64 (2008) 405.
- R.A. Aitken, N. Karodia, P. Lightfoot, J. Chem. Soc. Perkin Trans. 2 (2000) 333.
- (a) S.M. Bachrach, C.I. Nitsche, in: F.R. Hartley (Ed.), The Chemistry of Organophosphorus Compounds, vol. 3, Wiley, New York, 1994, p. 273 (Chapter 4); (b) M. Kobayashi, F. Sanda, T. Endo, Macromolecules 33 (2000) 5384; (c) H. Schmidbaur, W. Bucher, D. Schentzow, Chem. Ber. 106 (1973) 1251.
- (a) L.C. Thomas, Interpretation of the Infrared Spectra of Organophosphorus Compounds, Heyden, London, 1974; (b) W. Luttkie, K. Wilhelm, Angew. Chem. Int. Ed. Engl. 4 (1965) 875.
- (a) A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502; (b) C.J. Cramer, Essentials of Quantum Chemistry, Wiley, New York, 2002 (Chapter 9).
- C.A. Bunton, P. Silva, F. Castañeda, J. Mol. Struct. 921 (2009) 6.
- R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compounds, fourth ed., Wiley, New York, 1981 (Chapter 3).
- F. Castañeda, C.A. Terraza, M.T. Garland, C.A. Bunton, R.F. Baggio, Acta Crystallogr. C57 (2001) 180.
- (a) M. Nishio, Y. Umezawa, M. Hirota, Y. Takeuchi, Tetrahedron 51 (1995) 8665; (b) M. Nishio, M. Hirota, Tetrahedron 45 (1989) 7201.
- (a) H.J. Cristau, F. Plenat, in: F.R. Hartley (Ed.), The Chemistry of Organophosphorus Compounds, vol. 3, Wiley, New York, 1994, p. 108 (Chapter 2); (b) H.J. Bestmann, Angew. Chem. Int. Ed. Engl. 4 (1965) 583.
- M.P. Cooke Jr., J. Org. Chem. 47 (1982) 4963.
- F. Castañeda, P. Silva, M.T. Garland, A. Shirazi, C.A. Bunton, Phosphorus, Sulfur, Silicon 184 (2009) 2152.
- A.J. Cohen, P. Mori-Sanchez, W. Yang, Science 321 (2008) 792.
- K.E. Riley, B.T. Op't Holt, K.M. Merz Jr., J. Chem. Theory Comput. 3 (2007) 407.
- J. Tirado-Rives, W.L. Jorgenson, J. Chem. Theory Comput. 4 (2008) 297.
- J.P. Perdew, A. Ruzsinszky, L.A. Constantin, J. Sun, G.I. Csonka, J. Chem. Theory Comput. 5 (2009) 675.
- K.S. Raymond, R.A. Wheeler, J. Comput. Chem. 20 (1999) 207.