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Conformations of monoylidic diester triphenylphosphonium ylides

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HIGHLIGHTS

- ▶ Conformations were determined by spectroscopy, X-ray, HF, BLYP and B3LYP methods.
- ▶ *Anti* conformers are preferred in solution and are dominant in the crystal.
- ▶ Conformations are controlled by electric and non-bonding steric interactions.

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ABSTRACT

In ylidic triphenylphosphonium carboxylic esters the ester oxygen can be oriented towards (*syn*) or away (*anti*) from phosphorus, but except for small ylidic ester groups, *e.g.*, Me, the *anti* conformer is dominant. With suitable crystals conformations are established by X-ray crystallography, but HF and DFT computations, with NMR and IR spectroscopy, are useful methods. Bulky ylidic or nonylidic groups strongly favor the *anti* conformer and even with small carboxylic groups, *e.g.* ethoxy, *anti* conformers are preferred in solution and are dominant in the crystal. The balance of attractive interactions between anionoid oxygen and cationoid phosphorus and nonbonding interactions, controls conformations, as indicated by evidence from NMR and IR spectroscopy, HF and DFT calculations, and X-ray observations.

1. Introduction

Triphenylphosphonium ylides with one aliphatic keto or ester group can have *syn* or *anti* conformations, defined by orientation of the ylidic acyl group relative to phosphorus, Scheme 1, with the acyl oxygen as *syn*, toward, or *anti*, away from, phosphorus. There is electronic delocalization with partial double bonding between the ylidic and acyl carbons, and partial single bonding to phosphorus, allowing *syn–anti* conversions. Coulombic interaction between the anionoid acyl oxygen and cationoid phosphorus should favor the *syn* conformer as in mono keto ylides [1–3].

In some monomethyl ester ylides [2] 1, R = CH_3 and R′ is hydrogen, an alkyl or alkyl substituted group, or an aryl group, with favorable interactions between anionoid acyl oxygen and cationoid phosphorus in a *syn* ylide (Scheme 1). The crystalline monoester **1**, with R = CH_3 and R′ = H, has the expected *syn* conformation, consistent with computation, but the ^{1}H NMR spectrum shows that in $CDCl_3$ there is the *syn* and the minor *anti* conformer [2,4,5]. With R′ a simple alkyl or aryl group the *syn* conformer is preferred, and in solution the *syn–anti* ratio is modestly sensitive to R′ [2]. Effects of R′ on the *syn–anti* ratio can involve steric and electronic effects and conformer conversion is slow on the NMR time scale at room temperature [2].

There are exceptions to the preferred *syn* conformation in some ylidic monoesters, and in an extensive compilation of X-ray evidence, Aitken et al. [6] noted that for some monoylidic esters *anti* conformers are preferred. For example, Cameron et al. [7] showed that the crystalline monoylidic diester **2** (Scheme 2) with R = CH_3 and R′ = t-Bu has the *anti* conformation and the nonylidic ester group is linked to the ylidic carbon by a CH_2 tether group so here conformational control is apparently due to steric rather than electronic effects. The conformation in solution was not examined in detail, but spectral and NMR evidence indicate that only one conformer is present. For this and some other monoylides, [6,7] bulky nonylidic groups are controlling the conformation of the ylidic ester group in the crystal and probably also in solution, although they are not bonded to the ylidic carbon. Small nonylidic ester groups do not control conformations, but the crystalline monoester **3** with R and R′ = CH_2CH_3, has the *anti* conformation [8a] and it was exam-

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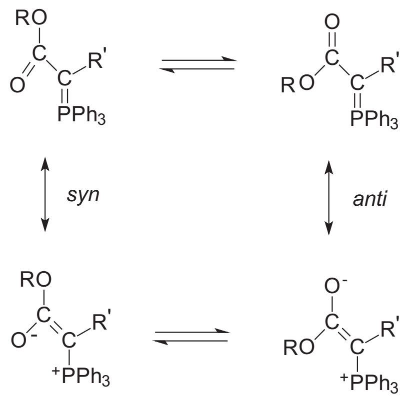


Scheme 1. *Syn* and *anti* conformers of monoylidic methyl esters **1**. R = CH_3; R′ = H, alkyl, aryl [2,5].

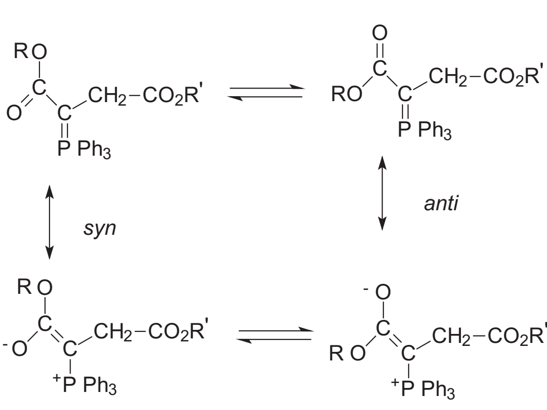
ined in solution, together with other ylidic monoesters with different sized alkoxy groups, Scheme 2. The atom numbering of the ylides examined in this work, Chart 1, follows that applied to the diethyl ylide [8].

In triphenylphosphonium ylides electronic delocalization favors zwitterionic structures with cationoid phosphorus, anionoid oxygen, and an approximately planar ylidic group [3,9], Scheme 1. Conformer conversion involves loss of ylidic resonance and *syn* and *anti* conformers in solution, can generally be identified by NMR spectroscopy and we used it and IR spectroscopy in examining conformations in solution, Scheme 2. Bond lengths and angles were estimated by calculations with HF and DFT methods, which also predicted acyl stretching frequencies, and geometries were compared with observed values for ylides with known crystal structures. In identifying ylides with two alkyl groups the alkyl symbol of the ylidic ester group, R, is given first, followed by that of the nonylidic group, R′, as for simple monoylides [2,4].

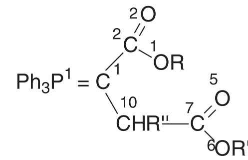
2. Experimental

2.1. Computation

Computations for structural optimization were made with Wavefunction (Windows), '06 or '08 software and optimized with HF/6-31G(d) and DFT methods [10] and with reasonable agreement between these structures and those from X-ray crystallography, BLYP and B3LYP, gives slightly longer acyl bonds than in the crystal but for angles, results are acceptable.



Scheme 2. *Syn* and *anti* conformers of monoylidic diesters. R = alkyl. R′ = alkyl, R = R′; R ≠ R′.



2[a]: R=Me, R'=t-Bu, R''=H
3[b]: R=Et, R'=Et, R''=H
4: R=Et, R'=Me, R''=H
5: R=t-Bu, R'=Me, R''=H
6[b]: R=Et, R'=Et, R''=$^{11}CH_3$
7: R=Et, R'=t-Bu, R''=H
8: R=t-Bu, R'=Et, R''=H

Chart 1. Atomic numbering for calculated and observed monoylidic diester structures. [a]Ref. [7]. [b]Ref [8b].

Positions of bonds and angles for conformers are designated as in X-ray crystallography [8a]. Computed distances and angles are given to the second decimal places and angles to first whole numbers but for the crystal structures full numerical values are given in References 7 and 8a. The sum of the bond angles at the acyl carbons is close to the 360° for a planar carbon and strong delocalization over the ylidic system. Natural population analysis (NPA) for *syn* and *anti* **3** (B3LYP/6-31G(d)) and for *anti* ylide **5** (B3LYP/6-31G(d) and BLYP/6-31G(d)) are in Table 1. Acyl stretching frequencies were estimated with unconstrained structures, and frequencies are rounded off to the nearest whole number. Calculated and observed bond lengths and angles for **2**, **3**, **4** and **6** are in Tables 5–8 (Supplementary data).

2.2. IR spectroscopy

The IR spectra were examined in KBr disks or in $CHCl_3$ solution on a Bruker IFS56 FT or on Leitz III-C spectrometers and the signal maxima were identified by the OPUS deconvolution method with resolution at 4 cm^{-1}. $CHCl_3$ was treated with alumina before use.

There are two strong signals assigned to the ylidic and nonylidic ester C=O groups which are well separated from low frequency signals. It appeared that signals of only the *anti* conformer are strong in both KBr disks and $CHCl_3$ where we had hoped to see *anti* and *syn* signals. The combination of IR acyl stretching frequencies and *ab initio* methods are useful in identification of *anti* conformations of ylidic esters [11]. Predicted signals from the BLYP method and experimental IR acyl stretching frequencies for diester ylides **2–8** are in Table 2.

2.3. NMR spectroscopy

The ^{1}H and ^{13}C NMR signals were examined on a Bruker DRX 300 or Varian Inova 500 spectrometers in acid free $CDCl_3$ and are referred to TMS or 85% H_3PO_4. The ^{1}H NMR signal is useful in characterizing *anti* conformations of novel monoylidic diesters and in establishing orientations of CH_3 alkoxy groups relative to triphenylphosphonium groups by observation of π-shielding [12]. Interactions between a terminal alkyl group and the face of a phenyl

Table 1
Natural population analyses for *syn* and *anti* mono ylidic diethyl diester **3**, $Ph_3P{=}C(CO_2Et){-}CH_2{-}CO_2Et$, and *anti* monoylidic diester **5**, $Ph_3P{=}C(CO_2{-}C(CH_3)_3){-}CH_2{-}CO_2CH_3$.

	Syn ylide **3**	*Anti* ylide **3**	*Anti* ylide **5**
P1	1.720	1.712	1.712 (1.647)
C1	−0.762	−0.781	−0.777 (−0.734)
C2	0.762	0.775	0.778 (0.726)
O2	−0.696	−0.655	−0.665 (−0.627)
O1	−0.577	−0.605	−0.612 (−0.586)
C7	0.847	0.857	0.854 (0.806)
O5	−0.608	−0.633	−0.633 (−0.602)
O6	−0.572	−0.560	−0.548 (−0.520)

Atoms are numbered as in Chart 1. Fractional charges are from B3LYP/6-31G(d) and in parentheses BLYP/6-31G(d).

Table 2
Predicted and observed IR acyl stretching frequencies of monoylidic diester ylides **2**–**8**.

Predicte (cm^{-1})	BLYP		Observed[a] (cm^{-1})	
Anti ethyl ethyl, **3** [8b]	1654	1711	1620	1730
Syn ethyl ethyl, **3**	1593	1724		
Anti ethyl methyl, **4**	1655	1730	1630	1730
Anti ethyl, methyl ethyl, **6** [8b]	1644	1685	1631	1724
Syn ethyl methyl ethyl, **6**	1588	1720		
Anti methyl t-butyl, **2** [7]	1665	1692	1620[b]	1730[b]
Anti t-butyl methyl, **5**	1635	1708	1630	1730
Anti ethyl t-butyl, **7**	1655	1712	1628	1731
Anti t-butyl ethyl, **8**			1622	1730

[a] In a KBr disk unless specified.
[b] In $CHCl_3$ [7].

group may be stabilizing [13]. Selective ^{1}H and ^{13}C NNR data for ylides **2**–**8** are in Table 3.

2.4. Elemental analyses

Elemental analyses were made on a Fison EA 1108 analyzer. The purity of novel compounds **4**, **5**, **7** and **8** for spectral work was shown by elemental microanalysis (Supplementary data).

2.5. Materials

– The methyl, t-butyl diester **2** was made by reaction of monoester $Ph_3P{=}CH{-}CO_2CH_3$ with t-butyl 2-bromoacetate [7].
– The diethyl diester **3** was made from $Ph_3P{=}CH{-}CO_2CH_2{-}CH_3$ and ethyl 2-bromoacetate by transylidation [8b].
– The diethyl 3-methyl-2-triphenylphosphoranylidene succinate **6** was made by methylating the lithium salt of diethyl ester **3** [8b].

In a general method for synthesis of monoylidic diesters, **4** and **5**, a solution of alkyl 2-bromoacetate (12 mmol; alkyl = ethyl or methyl) in dry ethyl acetate (5 mL) was added dropwise to a solution of alkyl 2-(triphenylphosphoranylidene) acetate (24 mmol; alkyl = ethyl or t-butyl) in dry ethyl acetate (100 mL) under an inert atmosphere at 25 °C. After 10 min of stirring the mixture was kept at 40–45 °C for 4 h forming a white solid which was removed by suction filtration and washed with dry ethyl acetate. This solid is the triphenylphosphonium salt ($Ph_3P^{+}{-}CH_2{-}CO_2R\ Br^{-}$; R = Et, t-Bu), formed by transylidation [12b]. After filtration the solvent was removed by rotary evaporation giving a solid which was recrystallized from ethyl acetate–hexane (1:1).

The monoylidic diesters isomers **7** and **8** were made as in the above general procedure but with benzene as solvent at 25 °C for 8 h. Ylide **7** was made by transylidation from $Ph_3P{=}CH{-}CO_2Et$ and t-butyl 2-bromoacetate and ylide **8** was made from $Ph_3P{=}CH{-}CO_2$-t-Bu and ethyl 2-bromoacetate.

Synthetic and spectroscopic details for ylides **3**–**8** and physical properties, are given as Supplementary data.

Ylides formal names are noted as Supplementary data, but given their length, abbreviated simple names and numbers are used in the main text.

3. Results and discussion

3.1. Structural geometries

Bond lengths and angles estimated by HF and DFT methods (Tables 5–8 in Supplementary data) were compared with X-ray crystallographic values, when available. Computations are for *anti*–*syn* conformers, although for some ylides only one conformer is detected in the crystal or in solution. Geometries of the ylidic group in *anti* and *syn* conformers from the B3LYP/6-31G(d) method are

Table 3
^{1}H and ^{13}C NMR selective data for monoylidic diester ylides **2**–**8** showing *anti*–*syn* conformations.

	Et–Et **3** [8b]		Et–Me **4**		Et–Me–Et **6** [8b]		Me–t-Bu **2** [7]	t-Bu–Me **5**	Et–t-Bu **7**	t-Bu–Et **8**
	Anti	*Syn*	*Anti*	*Syn*	*Anti*	*Syn*	*Anti*	*Anti*	*Anti*	*Anti*
^{1}H NMR										
$O^1{-}CH_2{-}C\underline{H}_3$	0.38t 1.94H J = 7.1		0.46t 2.05H J = 7.1	1.19t 0.95H J = 7.1	0.47t 1.7H J = 7				0.45t 3H J = 7.1	
$O^1{-}C\underline{H}_3$							3.34s 3H			
	1.00–1.14 3t; 4.06H				1.10–1.35 3t; 7.3H					
$O^6{-}CH_2{-}C\underline{H}_3$										1.09t 3H J = 7.1
$O^6{-}C\underline{H}_3$			3.50s 2.05H	3.53s 4.09H				3.48s 3H		
$O^1{-}C(C\underline{H}_3)_3$								0.96s 9H		0.94s 9H
$O^6{-}C(CH_3)_3$							1.32s 9H		1.25s 9H	
$C^{10}H{-}R''$	2.92d 1.41H J = 17.4	2.82d 0.65H J = 17.7	3.00d 1.36H J = 17.3	2.88d 0.68H J = 17.1	2.07–2.83 m; 1,1H		2.89d 2H J = 17	2.90d 2H J = 17	2.90d 2H J = 17.3	2.95d 2H J = 17.4
^{13}C NMR										
$C^2O_2{-}$	170.2d J = 12.9	170.9d J = 18.8	170.2d J = 12.7	170.8d J = 18.6			171.3 s	170.5 s	172.2 s	170.6 s
$C^7O_2{-}$	175.2 s	175.4 s	175.1 s	175.5 s			175.1 s	175.2 s	175.5 s	175.4 s

Ylides and atoms are numbered as in Chart 1. ^{1}H and ^{13}C NMR in $CDCl_3$. At 25 °C chemical shifts referenced to TMS or external 85% H_3PO_4. ^{1}H coupling constants J in Hz. $^{31}P{-}^{13}C$ coupling constants in Hz with ^{1}H decoupling.

compared with X-ray geometries in Table 4a, and in Table 4b computational evidence on conformations of ylides which do not form crystals suitable for use of X-ray are compared with those from NMR spectroscopy in $CDCl_3$.

3.2. NMR spectroscopy

The ^1H or ^{13}C, NMR spectra, of diethyl, and ethyl methyl monoylidic diesters **3** and **4** in $CDCl_3$ show that they are *anti–syn* mixtures while X-ray crystallography shows that crystalline **3** has the *anti* conformation [8a] Unlike the methyl ester ylides [2] *anti* conformers are dominant in the crystal and in solution, as shown by π-shielding of NMR signals of the terminal hydrogens of the ylidic alkoxy groups. The ^1H NMR spectrum of the t-butyl methyl monoylidic diester **5** in $CDCl_3$ is that of the *anti* conformer with no indication of a minor *syn* conformer (Table 3). The methyl t-butyl monoylidic diester **2**, the isomer of **5**, is the *anti* conformer in the crystal and probably also in solution, although NMR signals were not assigned [7]. Snyder et al. [2a] reported that large alkyl substituents at ylidic carbon atoms, in monoylidic methyl ester **1** (Scheme 1), favor a relatively high population of *anti* conformers. These conclusions are consistent with NMR evidence on effects of alkyl group size on *syn–anti* ratios in solution.

The dialkyl derivatives **3** and **4** are conformer mixtures in $CDCl_3$ in an approximate 2:1 ratio and assignments are in Table 3 (the conformation for crystalline **3** is *anti* [8a]). The ^1H doublets at 2.8–3.0 ppm in **3**, and **4** are of the ylidic CH_2 tether group, with significant ^{31}P coupling, and the ^1H chemical shifts in conformers, **3** and **4**, are governed by different interactions in the ylidic moieties, as in other monoylides. The ^1H doublets of the ylidic CH2 tether group are similar for any conformer of **2**–**8** and the bulky ylides **2**, **5**, **7** and **8** are assigned as *anti* conformers. Compound **7**, Table 3, is another example of a dominant *anti* conformer in solution. The ^1H methyl of the ylidic ester showed π-shielding at 0.45 ppm and a normal resonance for the ^1H t-butyl group at 1.25 ppm. Moreover *anti* conformer **7** (Table 3) showed only one ^1H doublet at 2.90 ppm for the CH_2 tether group and only two ^{13}C signals at 172.2 and 175.5 ppm for the two ester groups indicating the existence of only one conformer.

The simplicity of the signals of the nonylidic ester groups shows that in solution there is free rotation of this ester group on the NMR time scale.

In the methyl derivative **6**, the ^1H signals of the terminal methyl hydrogens of the two ethyl ester groups and of the methyl hydrogens on the tether group are readily characterized (Table 3) and in solution the *anti*: *syn* ratio of 57:43 indicates that the *anti* conformer preference is less than in the other ylides, Table 3.

3.3. Acyl stretching frequencies and IR spectra

The known *syn* conformation of the crystalline monomethyl derivative, **1b** [5,6] and the *anti* conformations of diethyl and methyl t-butyl derivatives **3** and **2** [7,8a] test computational methods and the use of NMR and IR spectroscopy. Stretching frequencies of ylidic acyl groups are sensitive to conformation and in comparisons of observed and predicted values the latter are corrected with method sensitive Scale Factors, SF, as surveyed by Scott and Radom [14]. For BLYP/6-31G(d) SF = 0.9945, which can be neglected within the accuracy of measurements. The literature SF value for HF/6-31G(d) of 0.8953 [14] overpredicts ylidic acyl stretching frequencies and fits were obtained with SF = 0.834 and 0.866 for ylidic ketone and ester acyl groups, respectively [12d]. Estimated frequencies with B3LYP/6-31G(d), SF = 0.9614, are consistently high [11,15]. The calculations are for molecules in the gas phase at absolute zero, but inclusion of an empirical solvent correction has little effect on the predictions.

The higher frequency signals of the nonylidic ester groups do not provide useful information on ylidic conformations because of free rotation about the tether group. Acyl stretching frequencies estimated in KBr disks for *anti* conformers are compared with calculated values in Table 2. The generally used computations of acyl IR frequencies are unreliable in predicting relative signal strength [11] and for stabilized *syn–anti* dialkyl ester ylides, with known conformations, computed and observed *anti* signals are always the stronger [10b].

The combination of IR spectra of an ylidic ester group and NMR spectroscopy is useful in distinguishing between single and mixed conformers in solution. The IR C=O stretching signals are well separated from other signals and predicted frequencies from HF and

Table 4
Conformations from computation, X-ray crystallography or NMR evidence for monoylidic esters.

Ylide	Calculated geometry[a]				X-ray geometry			
	P=C	C—C	C=O	Torsion angle	P=C	C—C	C=O	Torsion angle
(a) Computation with and without X-ray								
1a Me *syn*	1.71	1.42	1.24	2.2	1.70	1.39	1.23	2.3[b]
anti	1.71	1.43	1.22	176				
3: Et, Et *anti*	1.73	1.42	1.24	169	1.72	1.40	1.23	177[c]
syn	1.73	1.47	1.23	4.2				
2: Me, t-Bu *anti*	1.72	1.43	1.22	169	1.72	1.42	1.22	177[d]
syn	1.73	1.42	1.24	8.2				

Ylide		P=C	C—C	C=O	Torsion angle	NMR evidence
(b) Conformations and ^1H NMR in $CDCl_3$ (without X-ray)						
1 Me	*syn*	1.72	1.43	1.23	169[f]	*Anti*:*syn* = 67:33
	anti	1.72	1.43	1.24	8.4[f]	
6: Et, Me, Et	*anti*	1.74	1.44	1.24	164[e]	*Anti*:*syn* = 57:43
	syn	1.74	1.44	1.25	4.6[e]	
5: t-Bu, Me	*anti*	1.72	1.43	1.3	169[f]	*Anti*:*syn* = 100:0
	syn	1.73	1.43	1.26	8.4[f]	

[f] B3LYP/6.31G(d) unless specified.
[a] B3LYP/6-31G(d), length in Å, angles in °.
[b] Aitken [6].
[c] [8a].
[d] Cameron [7].
[e] BLYP/6-31G(d).

DFT methods, are in reasonable agreement with observed values, but the weakness of *syn* acyl signals limits the utility of this method in examining ratios of mixed conformers. Infrared spectroscopy complements other conformational evidence but is only useful in estimating concentrations when spectra of the individual components can be examined independently.

3.3.1. IR spectra of acyl groups

Observed acyl stretching frequencies of ylidic and nonylidic acyl groups are in reasonable agreement with predicted values for *anti* ylides **2** and **3** (Table 2). There are problems in treating IR spectra of the diethyl and ethyl methyl compounds **3** and **4** which from NMR in $CDCl_3$, are *syn* and *anti* mixtures, although only the *anti* diethyl ylide **3** is present in the crystal [8a]. This solvent effect on conformation was observed with the simpler monoylide **1**a [1a,16]. The strong IR observed signals of the *anti* ylidic acyl groups in **2**, **3** and **6** (Table 2) are 1620, 1620 and 1631 cm^{-1} respectively, as expected for spectra in KBr disks or $CHCl_3$. The X-ray spectra of some crystalline *anti–syn* diylidic diester triphenylphosphonium ylides had shown that the *syn* acyl oxygen is located between the edges of two phosphonium phenyl groups and is close enough to interact with the phenyl hydrogens [14,17] which could affect IR signals of *syn* acyl groups in solution. These types of interactions could be responsible for the weak signals of *syn* acyl groups in **3**, **4** and **6** but we cannot test this speculation by X-ray data for **3** with its *anti* conformer in the crystal. Calculated geometries of *syn* acyl groups in stabilized *syn–anti* diester ylides are consistent with X-ray, NMR and IR evidence regarding locations of acyl groups [11,18].

In crystalline diethyl ester, **3**, the absence of a *syn* conformer could be ascribed to molecular packing, which would not control conformations in solution, while **2**, **5**, **7** and **8** with their t-butyl groups have the *anti* conformation, regardless of positions of this bulky group. Ylides **4** and **3** with small methoxy or ethoxy groups are *syn–anti* mixtures in solution, as are the methyl monoester ylides, *e.g.*, **1** [2].

3.4. Partial atomic charges

Natural Population Analysis (NPA) was used to estimate local charges for known structures or those from computation [10a,12d,19]. The numerical significance of these charges is uncertain, but they indicate factors affecting ylidic conformations. For example, the acyl oxygen in ylidic esters has a significant negative charge and should interact favorably with cationoid phosphorus. However, NPA analysis indicates some anionoid character in the alkoxy oxygen and Coulombic interactions between phosphorus and the acyl oxygen do not control formation of *syn* monoylidic esters in all conditions and steric factors cannot be ignored. Examples of partial charges are given in Table 1 where the dominant *anti* conformer **5** showed NPA values for O1 = −0.612; O2 = −0.665; and P1 = 1.712 from B3LYP/6-31G(d). Assignments of NMR signals of chemically similar groups are consistent with NPA values.

3.5. Examples of conformer identification

Provided that suitable crystals can be isolated X-ray crystallography identifies conformations and results can be compared with those from other methods, e.g., computation. Table 4a shows a simple comparison of conformations from computation and X-ray crystallography. In Table 4, ethyl, ethyl *anti* monoylidic **3** shows bond lengths (Å), calculated from computation: $P^1{=}C^1$ = 1.73; $C^1{-}C^2$ = 1.42 and $C^2{=}O^2$ = 1.24, compared with those observed from X-ray crystallography of 1.72; 1.40 and 1.23 respectively, and torsion angles (°) from computation of 169 and 177 from X-ray crystallography.

A treatment when X-ray is not available is shown in Table 4b. Estimation of torsion angles, with bond strengths and angles, establishes conformation and with NMR evidence establishes conformation ratios. We follow this approach for several of the ylides which were examined in more detail.

3.6. Conformation control

Conformations in the crystal, are sensitive to molecular packing and *syn–anti* ratios may differ from those in solution, as for the methyl ester **1**, R′ = H [5], and the diethyl ylide **3** [8a], Table 6, but the monoylidic diester **2** with a bulky nonylidic t-butyl ester group is a single *anti* conformer in the crystal and probably also in solution, [7]. The monoylidic diesters **5** and **8** with an ylidic t-butyl ester group and a small nonylidic methyl or ethyl ester groups, and could not be examined by X-ray crystallography but NMR and IR spectroscopy, with computations, indicate that it also has the *anti* conformation. The monoylidic diesters with smaller ester groups, **3** and **4** are mixtures of conformers in $CDCl_3$ with *anti–syn ca.* 2:1, consistent with earlier evidence that single conformations in the crystal and in solution are sensitive to bulky ester groups, [7], and are affected by the ylidic ester groups to different extents in the crystal and in solution, Table 4, [6]. Consistently bulky ylidic or nonylidic alkoxy groups favor the *anti* conformation and ylides with small alkoxy groups are generally mixtures in solution, although usually not necessarily so in the crystal [7,8a].

Evidence on stabilized keto ester and diester ylides with known structures illustrates the factors controlling conformational differences [12b,c]. Steric factors affect conformations, for example, in stabilized keto ester ylides the smaller keto group is *syn* and the ester group is *anti,* and in diesters the smaller ester group is typically *syn* and the larger group is *anti,* although crystalline *anti–anti* conformers are observed with some small alkoxy groups [20]. Bulky alkoxy groups, *e.g., iso* propoxy or t-butoxy, apparently do not interact unfavorably with the triphenylphosphonium group [18].

In stabilized ylides, keto ester and diester groups are linked electronically through ylidic resonance, but this link is absent in the monoylidic mono and some diesters where steric effects are important. For an *anti* alkyl ester group orientation of a terminal alkyl hydrogen towards triphenylphosphorus may be modestly attractive [13] and Coulombic interactions between *syn* acyl groups and phosphorus do not control conformations, which in solution and in the crystal are related to sizes of substituent groups [6,7]. Molecular packing, with formation of the more compact *anti* conformer, should be important in the crystal, and affect conformation, but for dilute solutions it is necessary to consider other interactions sensitive to alkyl group size, noting that electronic interactions are limited by a CH_2 tether group .

In monoylidic diesters **2–8** in solution free rotation about the CH_2 tether group [21] should allow the nonylidic ester alkoxy group to interact sterically with the ylidic ester alkoxy group in a *syn* conformer. Interactions between the alkyl groups were examined for hypothetical *syn* conformers of some of the monoylides in Chart 2 (Supplementary data) with assumed rotations of the ylidic alkoxy group and the nonylidic ester group bound to the CH_2 tether group. Structures of hypothetical *syn* conformers from the B3LYP/6-31G(d) calculations were modeled by allowing free rotation of the nonylidic ester groups without changes in bond lengths. The interference between the hypothetical ylidic and nonylidic groups are shown as Supplementary material (Chart 2). For the hypothetical *syn* conformer of methyl t-butyl ylide, **2,** this rotation brings the t-butyl group unfavorably close to the ylidic methoxy group, but for the *anti* conformer the only near contact would be with the small acyl oxygen, and should not be so energetically unfavorable. Similarly for the hypothetical *syn* t-butyl methyl ylide **5** interference between the ylidic t-butyl alkoxy group and the nonylidic methoxy group could destabilize a *syn* conformer. Carboxylic ester groups typically have the preferred Z conformation [21] and in crystalline *syn* ylidic esters the alkyl group are generally oriented away from a nonylidic group, but in solution rotational barriers are week [21] and rotation of the alkoxy group in the ylidic ester allows it in a *syn* conformer to be oriented at some time in an E conformation and toward the nonylidic ester group, with unfavorable inter-alkyl contact. Similar considerations regarding interactions between ylidic, and nonylidic groups apply to other monoylidic aliphatic esters, but should be unimportant when hydrogen is attached to the ylidic carbon, as in **1**. These steric effects are important in *syn–anti* diester ylides with different ester groups where the bulkier alkoxy group has the *anti* conformation [18]. Unfavorable interactions between alkoxy groups could be present in hypothetical aliphatic *syn–syn* diesters which, so far as we know, have not been observed in solution or in the crystal.

Structures of hypothetical *syn* conformers of the t-butyl derivatives **2** and **5** [6,7] were simulated by HF and DFT methods with rotation about the bonds to the ylidic and nonylidic ester groups. This approach was also applied to the minor *syn* conformer of the monoylidic diethyl diester **3** and examples of probable unfavorable encounters between ylidic and nonylidic alkyl groups are shown as Supplementary data. These figures with rotations about bonds involving the CH_2 tether and nonylidic ester group and the ylidic ester group in a *syn* conformer have no quantitative significance but simply show how the ester groups can come into destabilizing contact in solution. For *anti* ylides O—H interactions between the small ester acyl oxygen and nonylidic ester alkyl groups should not be unfavorable. These postulated interactions in *syn* esters should not apply to keto ylides which have *syn* orientations [12b,22].

The presence of a CH_3 substituent on the tether group in **6** decreases the *anti* preference, relative to that in the other monoylides (Table 3), and reduction of the rotational mobility of the nonylidic ester group should decrease interference in a *syn* conformer.

4. Conclusions

In solution and the crystal the *syn* conformer is dominant only in simple monoester triphenylphosphonium ylides with hydrogen or small alkyl groups on the ylidic carbon, consistent with interactions between anionoid acyl oxygen and cationoid phosphorus. However, *anti* conformers are dominant when nonylidic carboxylic ester groups are linked to the ylidic carbon by a CH_2 tether group which limits electronic effects and, depending on sizes of the alkoxy groups, allows unfavorable interactions between nonylidic and ylidic ester groups in *syn* conformers. Conformations in solution are conveniently determined by examination of ^1H and ^{13}C NMR spectra and in the crystal by X-ray crystallography. With large ester groups conformations are the same in the crystal and in solution, but with smaller groups there may be one conformer in the crystal which is only dominant in solution. Molecular packing should be important in the crystal, while the extent of preference for some *anti* conformers in solution depends on sizes of the ester groups. Computed bond lengths and angles of these ylides are similar to values from X-ray crystallography. Stretching vibrations of ylidic acyl groups in IR spectra are sensitive to conformation and computed frequencies for *anti* groups are higher than for *syn* and intensities of the latter are very weak, possibly due to interactions with the triphenylphosphonium group.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012.08.051.

References

[1] (a) L.F. Wilson, J.C. Tebby, J. Chem. Soc. Perkin Trans. 2 (1972) 31;
(b) L.F. Wilson, J.C. Tebby, Tetrahedron Lett. (1970) 3769.

[2] (a) H.I. Zeliger, J.P. Snyder, H.J. Bestmann, Tetrahedron Lett. (1969) 2199;
(b) D.M. Crouse, A.T. Wehman, E.E. Schweizer, Chem. Commun. (1968) 866;;
(c) H.J. Bestmann, J.F.M. Oth, R. Merényi, H. Weitkamp, Tetrahedron Lett. (1966) 3355;
(d) H.I. Zeliger, J.P. Snyder, H.F. Bestmann, Tetrahedron Lett. (1970) 3313.

[3] 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).

[4] (a) T.A. Albright, M.D. Gordon, W.J. Freeman, E.E. Schweizer, J. Am. Chem. Soc. 98 (1976) 6249;
(b) G.A. Gray, J. Am. Chem. Soc. 95 (1973) 7736;
(c) F.J. Randall, A.W. Johnson, Tetrahedron Lett. (1968) 2841;
(d) R. Navarro, E.P. Urriolabeitia, J. Chem. Soc. Dalton Trans. (1999) 4111;
(e) A. Lledós, J.J. Carbó, E.P. Urriolabeitia, Inorg. Chem. 40 (2001) 4913.

[5] P.D. Boyle, Acta Crystallogr. Sect. C52 (1996) 2859.

[6] R.A. Aitken, N. Karodia, P. Lighfoot, J. Chem. Soc. Perkin Trans. 2 (2000) 333.

[7] A.F. Cameron, F.D. Duncanson, A.A. Freer, V.W. Armstrong, R. Ramage, J. Chem. Soc. Perkin Trans. 2 (1975) 1030.

[8] (a) F. Castañeda, P. Silva, C.A. Bunton, M.T. Garland, R.F. Baggio, Acta Crystallogr. C67 (2011) 319;
(b) R. Bacaloglu, A. Blaskó, C.A. Bunton, G. Cerichelli, F. Castañeda, E. Rivera, J. Chem. Soc. Perkin Trans. 2 (1995) 965.

[9] S.M. Bachrach, J. Org. Chem. 57 (1992) 4367.

[10] (a) W.J. Hehre, A Guide to Molecular Mechanics and Quantum Chemical Calculations, Wavefunctions, Inc., Irvine, 2003 (Chapter 16).;
(b) C.J. Cramer, Essentials of Quantum Chemistry, Wiley, New York, 2002 (Chapter 9).

[11] (a) C.A. Bunton, P. Silva, F. Castañeda, J. Mol. Struct. 921 (2009) 6;
(b) C.A. Bunton, F. Castañeda, J. Mol. Struct. 936 (2009) 132.

[12] (a) A.D. Abell, B.M. Clark, W.T. Robinson, Aust. J. Chem. 42 (1989) 1161;
(b) F. Castañeda, C.A. Terraza, C.A. Bunton, N.D. Gillit, M.T. Garland, Phosphorus, Sulfur, Silicon 178 (2003) 1973;
(c) F. Castañeda, C.A. Terraza, M.T. Garland, C.A. Bunton, R.F. Baggio, Acta Crystallogr. C57 (2001) 180;
(d) F. Castañeda, P. Silva, M.T. Garland, A. Shirazi, C.A. Bunton, Phosphorus Sulfur Silicon 184 (2009) 19.

[13] (a) M. Nishio, Y. Umezawa, M. Hirota, V. Takeuchi, Tetrahedron 51 (1995) 8665;
(b) M. Nishio, M. Hirota, Tetrahedron 45 (1989) 7201.

[14] A.P. Scott, L. Random, J. Phys. Chem. 100 (1996) 16502.

[15] F. Castañeda, P. Silva, M.T. Garland, A. Shirazzi, C.A. Bunton, J. Mol. Struct. 1004 (2011) 284.

[16] J.P. Snyder, Tetrahedron Lett. (1971) 215.

[17] G.R Desiraju, T. Steiner, The Weak Hidrogen Bond in Structural Chemistry and Biology, Oxford University Press, 2001 (Chapter 3).

[18] (a) F. Castañeda, P. Silva, M.T. Garland, A. Shirazzi, C.A. Bunton, Phosphorus Sulfur Silicon 184 (2009) 2152;
(b) F. Castañeda, P. Silva, C.A. Bunton, M.T. Garland, R.F. Baggio, Acta Crystallogr. C64 (2008) 405.

[19] (a) A.E. Reid, R.B. Weinstock, F. Weinholl, J. Chem. Phys 83 (1985) 735;
(b) R.F.W. Bader, Chem. Rev. 91 (1991) 893.

[20] (a) F. Castañeda, C. Aliaga, C.A. Bunton, M.T. Garland, R. Baggio, Acta Crystallogr. C61 (2005) 496;
(b) F. Castañeda, C. Jullian, C.A. Bunton, M.T. Garland, R. Baggio, Acta Crystallogr. C63 (2007) 267;
(c) F. Castañeda, C. Aliaga, M.T. Garland, J. Hu, N.D. Gillitt, C.A. Bunton, Phosphorus Sulfur Silicon 182 (2007) 151.

[21] (a) E.I. Eliel, S.H. Wilen, Stereochemistry of Organic Compounds, Wiley, New York, 1994. pp. 635 and 641.;
(b) T.B. Grindley, Tetrahedron Lett. 23 (1982) 1757;
(c) C.E. Blom, H.H. Günthard, Chem. Phys. Lett. 84 (1981) 267;
(d) K.B. Wiberg, K.E. Laidig, J. Am. Chem. Soc. 100 (1987) 5935.

[22] F. Castañeda, G.I. Recabarren, J. Hu, N.D. Gillit, C.A. Bunton, Phosphorus Sulfur Silicon 178 (2003) 2505.