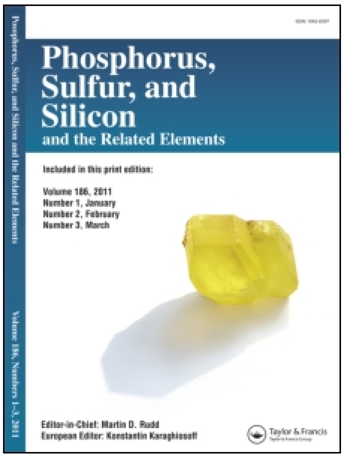


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A Common Conformation of Stabilized Triphenyl Phosphonium Ylidic Diesters with Bulky Alkoxy Groups

Fernando Castañeda[a]; Paul Silva[a]; M. Teresa Garland[a]; Ata Shirazi[b]; Clifford A. Bunton[b]
[a] University of Chile, Santiago, Chile [b] University of California, Santa Barbara, California, USA

To cite this Article Castañeda, Fernando , Silva, Paul , Garland, M. Teresa , Shirazi, Ata and Bunton, Clifford A.(2009) 'A Common Conformation of Stabilized Triphenyl Phosphonium Ylidic Diesters with Bulky Alkoxy Groups', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 8, 2152 — 2168

To link to this Article: DOI: 10.1080/10426500802445373

URL: http://dx.doi.org/10.1080/10426500802445373

Phosphorus, Sulfur, and Silicon, 184:2152–2168, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802445373

A Common Conformation of Stabilized Triphenyl Phosphonium Ylidic Diesters with Bulky Alkoxy Groups

Fernando Castañeda,[1] Paul Silva,[1] M. Teresa Garland,[1] Ata Shirazi,[2] and Clifford A. Bunton[2]
[1]University of Chile, Santiago, Chile
[2]University of California, Santa Barbara, California, USA

The phosphonium ylidic diesters, methyl and ethyl isopropyl and, methyl and ethyl t-butyl triphenylphosphoranylidene malonates, ***1a,b*** *and* ***2a,b****, respectively, have the syn-anti conformation in solution, as in the crystal, and the bulkier alkoxy group is oriented towards phosphorus. The* ^1H *NMR spectra show that in* ***1a,b****, the isopropyl group is oriented towards the face of a phenyl group, consistent with* π *shielding in the* ^1H *signals, and examination of the* ^1H *coupled* ^{13}C *NMR spectra allows assignment of the acyl carbon signals. Computed bond lengths and angles for isolated molecules are similar to those in the crystal, and the geometry and the NMR spectra indicate extensive ylidic resonance. Estimated partial atomic charges on the ester oxygens are more negative when they are oriented towards, rather than away from, phosphorus.*

Keywords Conformations; NMR spectra; optimized structures; phosphonium ylides

INTRODUCTION

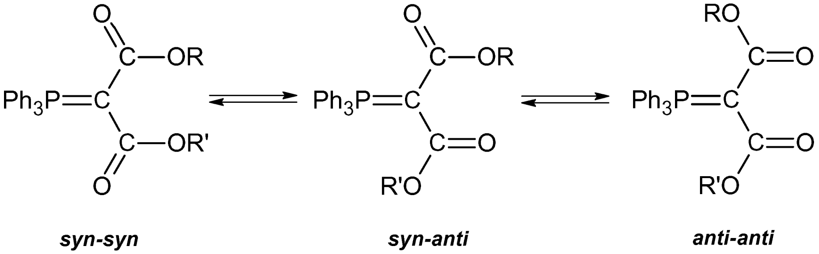
Conformations of triphenyl phosphonium ylides stabilized by two electron-withdrawing carbonyl groups[1,2] have been examined by X-ray crystallography, infrared spectroscopy, and in solution by NMR spectroscopy. The classical structures are shown in Scheme 1 where conformers are designated *syn*- and *anti*- in terms of the orientation of the acyl oxygens relative to phosphorus. These classical structures, with double bonds between the acyl and ylidic carbons and with phosphorus, are an inadequate description because there is extensive electronic

Received 28 April 2008; accepted 1 September 2008.

Support by the CEPEDEQ of the Faculty of Chemical and Pharmaceutical Sciences, University of Chile, for instrumental facilities is gratefully appreciated.

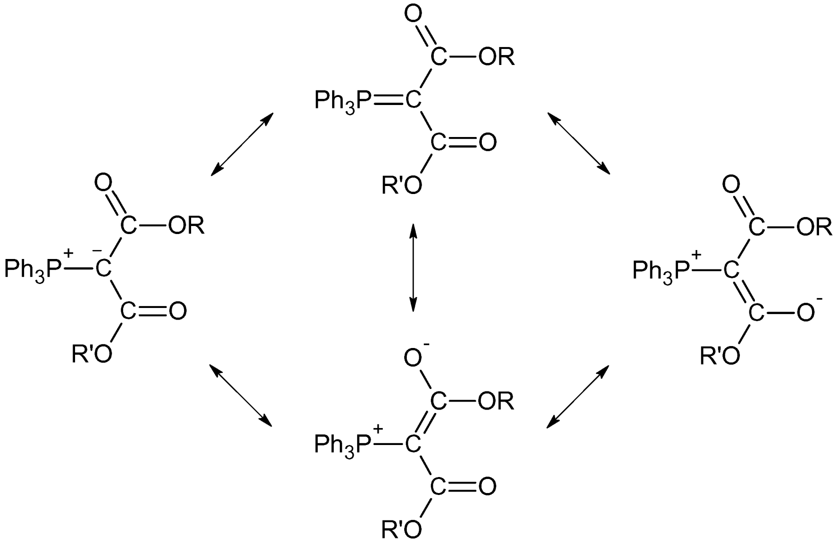
Address correspondence to Fernando Castañeda, Departamento de Química Orgánica y Fisicoquímica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile. E-mail: fcastane@ciq.uchile.cl

delocalization involving the ylidic moiety, as shown in Scheme 2 for a *syn-anti* conformer.[3,4]



SCHEME 1 R = R′ ; R ≠ R′. **1a:** *syn* Me *anti* i-Pr ; **1b:** *syn* Et *anti* i-Pr; **2a:** *syn* Me *anti* t-Bu; **2b:** *syn* Et *anti* t-Bu; **3:** equimolar mixture of *anti* Me *anti* Me and *syn* Me *anti* Me; **4:** *anti* Et *anti* Et; **5:** *syn* Me *anti* Et.

The various conformers of a number of distabilized ylides have been examined by ab initio optimization, generally at the HF/6-31G(d) or B3LYP/6-31G(d) levels.[2,5] Estimated bond lengths and angles are in reasonable agreement with those from X-ray crystallography,[6] but computation indicates that for diesters *syn-syn* conformers should be energetically preferred because of favorable interactions between acyl oxygens and phosphorus.[5] However, so far as we know they never are in the solid, and probably not in solution, because computations for



SCHEME 2 *Syn-anti* conformers of ylidic diesters.

isolated molecules with static structures do not adequately allow for unfavorable, noncovalent interactions involving bulky trigonal ester residues with alkoxy groups positioned *anti-* to phosphorus.

Conformations of ylidic diesters in the crystal are sensitive to small changes in the size of the alkoxy groups.[6,7] For example, in the crystal the diethyl diester, **4**, is *anti-anti-*, but the dimethyl diester, **3**, is a 1:1 mixture of *anti-anti-* and *syn-anti-* conformers, and in the methyl ethyl diester, **5**, the acyl oxygen of the methyl ester group is *syn-* and that of the ethyl ester group is *anti-* to phosphorus (Scheme 1). It therefore seemed that bulky isopropoxy or t-butoxy groups might significantly affect conformations of ylidic diesters.

Computations had indicated that the various conformers of resonance stabilized ylidic diesters have similar relative energies, generally within 3 kcal.mole^{-1}, and that a conformer with one ester group orthogonal to the ylidic plane should be disfavored by no more than another 2 kcal.mole^{-1}, because rotation of only one acyl group out of the ylidic plane does not eliminate ylidic resonance stabilization.[5] Therefore even small changes in the alkyl groups may change the conformation in the solid, and possibly also in solution, but rotational barriers to conversion of conformers should not be large. This behavior is very different from that of the otherwise similar ylides stabilized by only one acyl group, where conformational conversion involves the energetically costly rotation of that stabilizing group out of the ylidic plane and a consequent decrease of ylidic resonance.[3]

The ^{1}H, ^{13}C, and ^{31}P NMR signals are as expected for charge delocalized structures, for example, ^{13}C signals of the ylidic carbons are significantly upfield, as compared with those of other ylides, and π-shielding of ^{1}H signals of terminal methyl groups in the ester moieties of some triphenyl phosphonium derivatives indicates their orientation towards the face of a phenyl group.[1,2,8] The ^{13}C signals of organic compounds are often obtained with elimination of ^{1}H spin–spin coupling, which for these ylides simplifies observation of coupling with ^{31}P, but considerable additional information can sometimes be obtained by examining the ^{1}H coupled ^{13}C NMR spectrum.[9]

In the present article, we examined triphenyl phosphonium ylidic diesters with one small and one large alkoxy group, viz., one methoxy or ethoxy and one isopropoxy or t-butoxy group. In the crystalline diesters, the acyl oxygen of the methyl or ethyl ester group is *syn* to phosphorus and that of the bulky ester group is *anti*, i.e., as in Scheme 1. Geometries of the ylidic diesters (**1a,b** and **2a,b**) have been determined by X-ray crystallography, as described elsewhere,[10] and for both the isopropyl and t-butyl derivatives, the bulkier alkoxy group is *syn* to phosphorus, as is the acyl oxygen of the smaller ester group (Scheme 1).

Crystal structures of ylidic keto esters had also been determined, and the keto oxygen is *syn* and the acyl oxygen of the ester group is *anti* to phosphorus,[1,2] and NMR spectroscopy showed that this was also the conformation in solution, and results with mixed diester ylides indicate that the bulkier alkoxy groups are oriented towards phosphorus.[7,10] However, the observation that in the crystal the dimethyl diester, **3**, is an equimolar mixture of different conformers[7] (Scheme 1) indicates that here conformations may differ in the crystal and in solution.

RESULTS AND DISCUSSION

NMR Spectroscopy

The ^{1}H chemical shifts and coupling constants in the ylidic moieties and ^{31}P and ^{1}H decoupled ^{13}C signals in solution are as expected for ylidic diesters (Table I). The π-shielding of ^{1}H signals of CH_3 of the isopropoxy groups shows that, as in the crystal, this group is *syn* to phosphorus, as for the corresponding keto ester.[1,2] This shielding apparently does not affect the ^{13}C signals. The situation is less obvious for the t-butyl derivatives, because any shielding is averaged over nine hydrogens, but the ^{1}H chemical shift is very similar to that in the corresponding keto ester,[2] which, like the t-butyl diesters in the crystal, has the t-butoxy group *syn* to phosphorus. The ^{1}H chemical shifts of the methyl and ethyl isopropyl diesters **1a,b** are similar with π-shielding of CH_3 in the isopropyl group. The other ^{1}H NMR signals in the ylidic groups of **1a,b** and **2a,b** are as expected, with chemical shifts and coupling constants similar to those observed in other stabilized triphenyl phosphonium ylides.[1,2,5]

The ^{13}C NMR spectra with and without ^{1}H coupling provide evidence on the geometries of the acyl groups, and on the assignment of the phenyl signals, as considered later. Signals of the ylidic carbons are significantly upfield, as compared with those of simple ylides (Table I), and as expected in terms of the strongly anionoid character at this position. This behavior is general for these stabilized ylides, and it has been suggested that their structures should be written as zwitterionic[3,4] (Scheme 2). The ^{13}C signals of the alkyl groups are as expected, and those of the quaternary t-butyl carbons of **2a** and **2b** at 78.58 ppm are broad singlets in the ^{1}H decoupled spectrum, but are broad and partially resolved due to long range coupling in the ^{1}H coupled spectrum. It appears that NMR signals of the t-butyl quaternary carbons are unaffected by the methoxy or ethoxy group.

In crystalline methyl ethyl diester,[7] the acyl group of the methoxy ester group is *syn* to phosphorus and that of the ethyl ester group is

TABLE I Chemical Shifts, ^{1}H, ^{13}C, and ^{31}P, and IR Stretching Frequencies, νc=o of Methyl iso-Propyl 1a, Ethyl iso-Propyl 1b, Methyl t-Butyl 2a, and Ethyl t-Butyl 2b Diester Phosphonium Ylides

^{1}H NMR ($\mathbf{CDCl_3}$)	**1a**	**1b**	**2a**	**2b**
$\text{-OC}\underline{\text{H}}_3$	3.40 s	—	3.45 s	—
$\text{-O-CH}_2\text{-C}\underline{\text{H}}_3$	—	0.88 t	—	0.88 t
$\text{-O-C}\underline{\text{H}}_2\text{-CH}_3$	—	3.86 q	—	3.86 q
$\text{-O-C}\underline{\text{H}}(\text{CH}_3)_2$	4.75 m	4.82 m	—	—
$\text{-O-CH(C}\underline{\text{H}}_3)_2$	0.70 d	0.76 d	—	—
$\text{-O-C(C}\underline{\text{H}}_3)_3$	—	—	0.98 s	1.04 s
^{13}C NMR ($CDCl_3$)				
$\text{-O}\underline{\text{C}}\text{H}_3$	49.7	—	50.4	—
$\text{-O-CH}_2\text{-}\underline{\text{C}}\text{H}_3$	—	14.1	—	14.2
$\text{-O-}\underline{\text{C}}\text{H}_2\text{-CH}_3$	—	58.6	—	58.5
$\text{-O-}\underline{\text{C}}\text{H(CH}_3)_2$	65.0	65.4	—	—
$\text{-O-CH(}\underline{\text{C}}\text{H}_3)_2$	21.0	21.6	—	—
$\text{-O-C(}\underline{\text{C}}\text{H}_3)_3$	—	—	28.2	28.2
$\text{-O-}\underline{\text{C}}\text{(CH}_3)_3$	—	—	78.6	78.4
$\text{P=}\underline{\text{C}}$	52.5	52.9	52.9	52.9
	(d, J=121.3)	(d, J=120.3)	(d, J=120.8)	(d, J=119.5)
$\underline{\text{C}}\text{O}_2$	166.8	167.2	166.6	166.9
	(d, J=11)	(d, J=12.5)	(d, J=10.4)	(d, J=12.8)
	168.7	168.3	169.0	168.5
	(d, J=12.8)	(d, J=13.5)	(d, J=15.2)	(d, J=14.6)
^{31}P NMR ($CDCl_3$)	20.8	20.8	20.9	20.7
Ir ν**c=o** (KBr)	1678	1678	1667	1678
	1638	1612	1649	1613

At 25°C chemical shifts referenced to TMS or external 85% H_3PO_4. ^{31}P–^{13}C coupling constants J in Hz with ^{1}H decoupling. Carbonyl stretching frequencies νC=O, in cm^{-1}.

anti, and the ^{13}C NMR spectra in $CDCl_3$, without and with, ^{1}H coupling confirms that the conformation is as in the crystal.[10,11] Therefore ^{1}H coupled ^{13}C NMR spectra provide useful information in solution, and we first examined the ^{13}C NMR spectrum of the ethyl isopropyl diester with ^{1}H coupling where X-ray crystallography shows that the acyl moiety of the ethyl group is *syn* and that of the isopropoxy group is *anti* to phosphorus.[10]

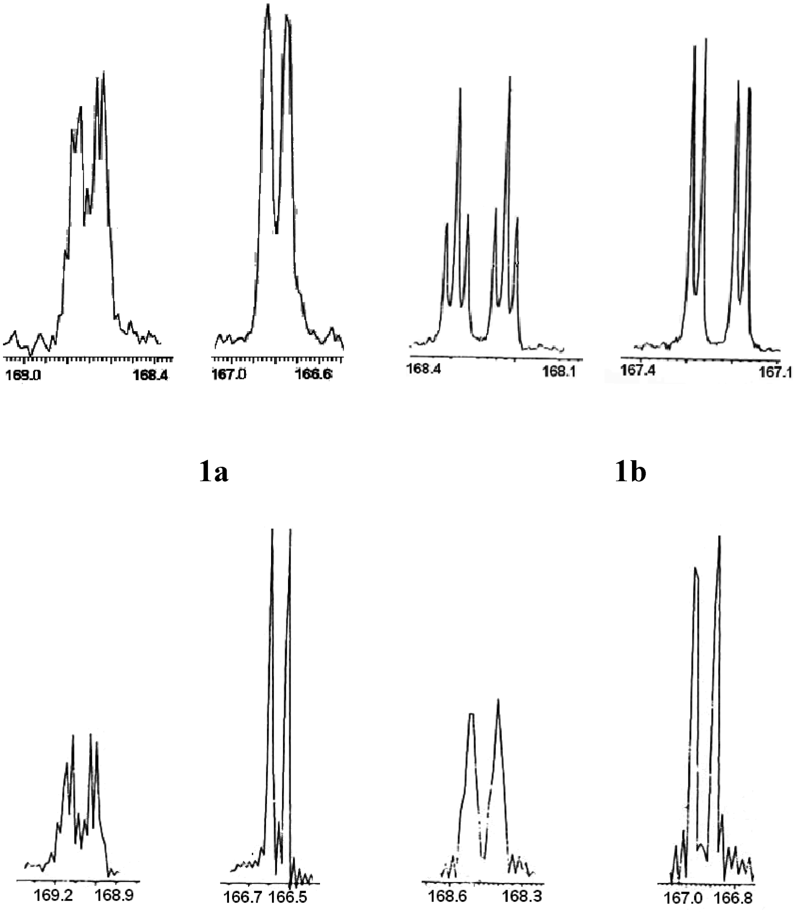
The ^{13}C signals of the two acyl carbons of the ethyl isopropyl diester, **1b**, are doublets at 167.24 and 168.27 ppm, and $^{2}J_{P-C} = 12.5$ and 13.5 Hz, respectively, in the ^{1}H decoupled spectrum due to coupling with ^{31}P. Elimination of ^{1}H decoupling allows long range coupling with the α hydrogens of the alkoxy groups. The upfield signal at 167.24 ppm becomes a doublet of doublets, $^{3}J_{H-C} = 3$ Hz, due to coupling with the α-hydrogen of the isopropyl group, and the downfield signal at

168.27 ppm becomes a doublet of triplets $^3J_{H-C} = 3$ Hz due to coupling with the methylene hydrogens of the ethyl group (Figure 1). As noted, π-shielding in the isopropyl group indicates that this group is oriented towards phosphorus. There is no indication of such shielding in the ethyl group, and we assume that it is oriented away from phosphorus, as in the crystal. These results are generally similar to those observed earlier on the acyl groups of the methyl ethyl diester with the bulkier ethoxy group oriented towards phosphorus.[7,11]

The ^{13}C signals of the acyl carbons of the methyl isopropyl diester, **1a,** with ^{1}H decoupling at 166.8 ppm, J = 11 Hz and 168.7 ppm, J = 12.8 Hz are similar to those of the ethyl derivative, but with ^{1}H coupling, the upfield doublet broadens significantly, although the individual signals are not fully resolved, and the signal at 168.7 ppm broadens considerably and becomes a distorted doublet of quartets (Figure 1) due to long range coupling with $OC\mathit{H}_3$. These observations are consistent with similar conformations in the methyl and ethyl derivatives. The acyl carbon NMR signals of the ethyl t-butyl diester, **2b**, are doublets at 166.9 ppm, J = 12.8 Hz and 168.5 ppm, J = 14.6 Hz, with ^{1}H decoupling, and without ^{1}H decoupling the upfield signal at 166.9 ppm is unaffected, except for slight broadening, and therefore can be assigned to the t-butyl ester group, but that at 168.5 ppm is broadened significantly and is no longer resolved to the base line, due to long range coupling with the methylene ^{1}H of the ethyl group, which allows assignment of both acyl ^{13}C signals (Figure 1).

The ^{13}C NMR spectra of the methyl t-butyl diester, **2a**, with and without, ^{1}H decoupling are as expected in terms of the the spectra of the other diesters. The signals of the acyl carbons are assigned by examination of the effects of ^{1}H coupling. The doublet at 166.6 ppm is unaffected by ^{1}H coupling as is that of the t-butyl ester group. The doublet at 169.0 ppm is assigned to the methoxy ester group, and with ^{1}H coupling, it approximates to a doublet of quartets, with J $\approx$ 3 Hz (Figure 1).

These ^{13}C signals of the acyl carbons without ^{1}H coupling show that conformations of the *syn-anti* diesters are the same in the crystal and in solution, and the bulkier ester group has the upfield ^{13}C signal with the bulkier alkoxy group oriented towards phosphorus. The ^{13}C signals shown in Figure 1 are consistent with the above assignments, except that the upfield doublet signal of the methyl isopropyl ester, **1a**, and the downfield doublet signal of the ethyl t-butyl ester, **2b**, are not fully resolved. Computations of energies of conformers of triphenyl phosphonium ylides stabilized by two ester groups show that barriers to interconversion by rotation about the the ylidic bond are



1a **1b**

2a **2b**

FIGURE 1 ^{13}C NMR signals with long range coupling with ^{31}P and ^{1}H for carbonyl groups of methyl iso-propyl, **1a**, ethyl iso-propyl, **1b**, methyl t-butyl, **2a**, and ethyl t-butyl, **2b**, triphenylphosphonium diester ylides.

small, < 5 kcal.mol^{-1}, and energetic differences between conformers are even smaller.[2,5,12] The samples used in the NMR work gave good X-ray diffraction patterns,[10] characteristic of single crystals, and an earlier study of NMR spectra of keto esters over a wide temperature range gave no evidence for interconversion of conformers,[2] but with the diesters we cannot exclude contributions from small amounts of minor conformers.

The whole ^{13}C spectral range was scanned with ^{1}H coupling, and, except as noted above, the results do not provide evidence on conformations more useful than those given with ^{1}H decoupling, but over the whole range signal multiplicities, due to ^{1}H coupling and separated by ca. 3 Hz, were easily detected. It appears that our results were not limited by lack of resolving power.

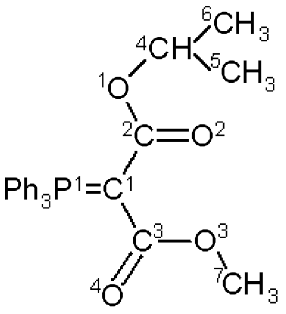
The other ^{13}C signals, including those of quaternary carbons, are similar. Signals of methyl carbons are quartets in the ^{1}H coupled spectrum, but those of the t-butyl methyl groups are split further by long range ^{1}H coupling. The signals of the phenyl and ylidic carbons are also very similar for these diesters. The changes in the ^{13}C signals of the acyl groups on removal of ^{1}H decoupling are consistent with our conclusion that the bulkier alkoxy group is attached to the carbonyl carbon with the upfield chemical shift (Table I).

The ^{1}H and ^{13}C NMR spectra of triphenyl phosphonium ylides indicate that in solution, at room temperature, the phenyl groups are equivalent on the NMR time scale. In the ^{1}H decoupled ^{13}C spectra, the magnitude of phosphorus–carbon coupling is expected to decrease with increasing bond distance, and on this assumption ^{13}C chemical shifts follow the sequence *ipso* < *ortho* < *para* < *meta*. This assignment is confirmed by examining the spectrum without ^{1}H decoupling, which gives additional strong splitting due to the adjacent hydrogens and weaker splitting due to two neighboring hydrogens for the *meta* and *para* carbons, and only one for the *ortho* carbon. In the ^{13}C NMR spectrum of the ethyl isopropyl diester, **1b**, there is overlap between part of the signals of the *para* and *meta* carbons, but the form of the signals fits the expected assignment. The pattern is similar for the phenyl signals of the methyl and ethyl t-butyl diesters, except that here there is overlap between parts of the signals of the *ortho* and *ipso* carbons in the ^{1}H coupled NMR spectrum. The ^{13}C NMR spectra without ^{1}H decoupling are very similar to those seen earlier for other ylidic diesters,[5,12] and NMR signals of phenyl groups of these ylides are not very sensitive to the structures of the ylidic moieties.

Geometrical Optimization

Geometries of the phosphonium ylides were optimized with the HF/6-31G(d) basis set, and energies of the four possible conformations (*syn-syn*, *anti-anti*, and two *syn-anti* conformers) were estimated by B3LYP/6-31G(d) computations.[13] Geometries of the *syn-anti* conformers were also estimated from BLYP/6-31G(d) and B3LYP/6-31G(d) computations. Results from the latter (in Tables II–V) are similar to those

TABLE II Selected Computed and X-Ray Geometric Parameters (Å,°) for Methyl, Isopropyl-2-triphenyl Phosphoranylidene Malonate (1a)



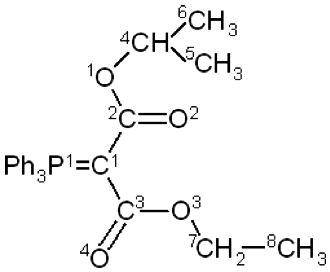
1a

Bond Lengths (Å)	HF	DFT	X-Ray		HF	DFT	X-Ray
P^1-C^1	1.75	1.76	[1.74]	C^2-O^2	1.20	1.22	[1.21]
C^1-C^3	1.45	1.45	[1.44]	C^2-O^1	1.35	1.38	[1.36]
C^3-O^4	1.21	1.24	[1.21]	C^4-O^1	1.43	1.38	[1.44]
C^3-O^3	1.32	1.35	[1.36]	C^7-O^3	1.41	1.38	[1.43]
C^3-$O^{3'}$			[1.36]	$C^{7'}$-$O^{3'}$			[1.44]
C^1-C^2	1.46	1.46	[1.44]				
Bond Angles (°)							
C^3-C^1-C^2	122	123	[122]	O^4-C^3-O^3	121	121	[125]
C^3-C^1-P^1	113	111	[118]	O^4-C^3-$O^{3'}$			[113]
C^2-C^1-P^1	125	125	[119]	O^4-C^3-C^1	122	123	[126]
O^2-C^2-O^1	121	121	[121]	C^1-C^3-O^3	116	116	[109]
O^1-C^2-C^1	113	112	[110]	C^1-C^3-$O^{3'}$			[120]
O^2-C^2-C^1	126	122	[128]				
Torsion Angles (°)							
P^1-C^1-C^3-O^4	−11	−11	[−17]	P^1-C^1-C^3-O^3	170	169	[160]
P^1-C^1-C^2-O^2	−162	−170	[−168]				

Two parts, i.e., C^7-O^3 and $C^{7'}$-$O^{3'}$, of the slightly disordered O^3-C^7H_3 group are shown by X-ray crystallography. X-ray crystallographic values in this and later tables are in parentheses.

from BLYP/6-31G(d) computation, data not shown. As seems to be general for these distabilized ylides, energy differences between conformers are small, unlike the situation for monostabilized triphenyl phosphonium ylides.[14] The computations are for isolated molecules with static structures, and, in both solution and the solid, structures should be sensitive to intra- and intermolecular interactions. Typically these computations indicate that *syn-syn-* conformers of diesters should be

TABLE III Selected Computed and X-Ray Geometric Parameters (Å,°) for Ethyl, Isopropyl-2-triphenyl Phosphoranylidene Malonate (1b)



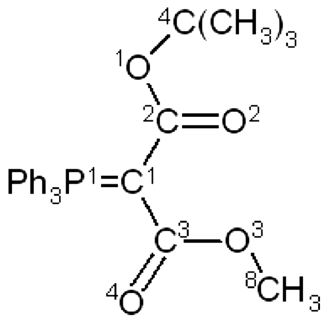
1b

Bond Lengths (Å)	HF	DFT	X-Ray		HF	DFT	X-Ray
P^1-C^1	1.74	1.76	[1.74]	C^7-O^3	1.42	1.35	[1.45]
C^1-C^3	1.45	1.45	[1.43]	$C^{7'}$-$O^{3'}$			[1.45]
C^3-O^4	1.21	1.24	[1.23]	C^2-O^2	1.19	1.22	[1.19]
C^3-O^3	1.32	1.35	[1.38]	C^2-O^1	1.34	1.38	[1.32]
C^3-$O^{3'}$			[1.37]	C^4-O^1	1.43	1.46	[1.44]
C^1-C^2	1.47	1.46	[1.44]				
Bond Angles (°)							
C^3-C^1-C^2	122	123	[123]	O^1-C^2-C^1	113	112	[112]
C^3-C^1-P^1	117	111	[112]	O^4-C^3-O^3	121	122	[121]
C^2-C^1-P^1	125	125	[125]	O^4-C^3-C^1	123	122	[123]
O^2-C^2-O^1	122	121	[120]	C^1-C^3-O^3	116	115	[115]
O^2-C^2-C^1	125	126	[128]				
Torsion Angles (°)							
P^1-C^1-C^3-O^4	−12	−12	[−7]	P^1-C^1-C^2-O^2	−162	−167	[−170]

[a] Two parts of the disordered ethoxylic group, i.e., C^3-O^3 and C^3-$O^{3'}$ or C^7-O^3 and C^7-$O^{3'}$, are shown by X-ray crystallography.

preferred, because of interactions between anionoid acyl oxygens and cationoid phosphorus, but, so far as we know, they are not observed in the crystal, and there is no evidence for their existence in solution, although NMR spectroscopy indicates that for some ylides conformations apparently differ in solution and in the crystal.[15] For hypothetical *syn-syn* ylidic diesters with two bulky trigonal ester groups with alkoxy groups *anti* to phosphorus, there will be unfavorable interactions between them and with neighboring molecules in the solid, and probably in solution; due to the high molecular weights of these phosphonium ylides, intermolecular distances should be small, even with

TABLE IV Selected Computed and X-Ray Geometric Parameters (Å,°) for Methyl, t-Butyl-2-triphenyl Phosphoranylidene Malonate (2a)



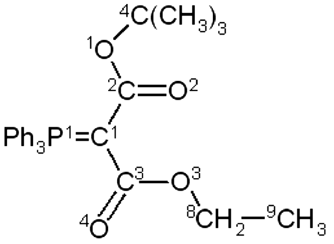
2a

Bond Lengths (Å)	HF	DFT	X-Ray		HF	DFT	X-Ray
P^1-C^1	1.74	1.75	[1.74]	C^2-O^2	1.19	1.22	[1.21]
C^1-C^3	1.44	1.45	[1.43]	C^2-O^1	1.34	1.37	[1.36]
C^3-O^4	1.21	1.24	[1.19]	C^4-O^1	1.44	1.47	[1.46]
C^3-O^3	1.33	1.35	[1.33]	C^8-O^3	1.41	1.43	[1.43]
C^1-C^2	1.47	1.46	[1.45]				
Bond Angles (°)							
C^3-C^1-C^2	122	123	[122]	O^2-C^2-C^1	125	125	[128]
C^3-C^1-P^1	114	111	[117]	O^4-C^3-O^3	121	121	[119]
C^2-C^1-P^1	125	126	[119]	O^4-C^3-C^1	123	123	[125]
O^2-C^2-O^1	122	125	[121]	C^1-C^3-O^3	116	116	[116]
O^1-C^2-C^1	113	112	[110]				
Torsion Angles (°)							
P^1-C^1-C^3-O^4	−8.2	24	[10]	P^1-C^1-C^2-O^2	−147	−157	[−179]

(This structure does not indicate disorder in the methoxy group as shown in the X-Ray crystallography).

dilute (0.1 M) solutions. Triphenyl phosphonium ylides stabilized by cyano and keto or ester groups have *syn* conformations because the linear cyano group does not interfere with trigonal acyl groups.[12] We have usually given computed energies for different conformers as relative to the generally, but incorrectly, predicted lowest energy *syn-syn-* conformer, although there is no physical evidence for it being the preferred structure,[5,15] but results of trapping experiments on diketo ylides[16] can be interpreted in terms the existence of *syn-syn* conformers. However, for the ethyl isopropyl diester, **1b**, our computation indicates that the

TABLE V Selected Computed and X-Ray Geometric Parameters (Å,°) for Ethyl, t-Butyl-2-triphenyl Phosphoranylidene Malonate (2b)



2b

Bond Lengths (Å)	HF	DFT	X-Ray		HF	DFT	X-Ray
P^1-C^1	1.74	1.75	[1.74]	C^2-O^2	1.19	1.22	[1.21]
C^1-C^3	1.44	1.45	[1.43]	C^2-O^1	1.34	1.38	[1.36]
C^3-O^4	1.21	1.24	[1.22]	C^4-O^1	1.44	1.47	[1.48]
C^3-O^3	1.32	1.35	[1.39]	C^8-O^3	1.42	1.44	[1.46]
C^3-$O^{3'}$			[1.29]	$C^{8'}$-$O^{3'}$			[1.46]
C^1-C^2	1.47	1.46	[1.45]				
Bond Angles (°)							
C^3-C^1-C^2	122	123	[123]	O^2-C^2-C^1	125	125	[127]
C^3-C^1-P^1	113	111	[114]	O^4-C^3-O^3	122	122	[122]
C^2-C^1-P^1	125	125	[122]	O^4-C^3-$O^{3'}$			[114]
O^2-C^2-O^1	122	123	[122]	O^4-C^3-C^1	122	122	[124]
O^1-C^2-C^1	113	112	[110]	C^1-C^3-O^3	116	116	[113]
				C^1-C^3-$O^{3'}$			[120]
Torsion Angles (°)							
P^1-C^1-C^3-O^4	9	11	[4]	P^1-C^1-C^2-O^2	147	157	[162]

Two parts, i. e. C^8-O^3 and $C^{8'}$-$O^{3'}$, of the disordered ethoxy group are shown by X-Ray crystallography.

syn-ethyl *anti*-isopropyl conformer should be slightly preferred, as in the crystal, and probably also in solution.

Bond lengths and angles from ab initio computations, at various levels, are similar to those from X-ray crystallography (Tables II–V and ref.[10]). For some of the crystalline ylides, there is minor disorder in some alkoxy groups as shown in Tables II, III, and V. The small differences in computed energies of conformers are understandable, because changes in conformation involve changes in torsional angles, which are energetically less costly than changes in bond lengths and angles. Predicted bond lengths are as expected in terms of extensive ylidic resonance and sums of bond angles at the ylidic and acyl carbons are close to the

TABLE VI Selected Computed and X-Ray Short Contact Distances (Å) for Methyl iso-Propyl, 1a, Ethyl iso-Propyl, 1b, Methyl t-Butyl, 2a, and Ethyl t-Butyl, 2b, Diester Phosphonium Ylides, $Ph_3P^1 = C(COO^1R')CO^4OR$

	P^1—O^1	P^1—O^4	O^2—O^3
1a	3.02 [2.80]	2.85 [3.03]	2.70 [2.62]
1b	3.02 [2.95]	2.84 [2.81]	2.71 [2.69]
2a	3.08 [2.73]	2.86 [2.99]	2.73 [2.70]
2b	3.08 [2.88]	2.74 [2.88]	2.74 [2.70]

X-ray crytallographic values[10] are in parentheses [ ]. The carbonyl oxygen, CO^4, and the alkoxy oxygen $-O^1R'$, are *syn* to phosphorus. The carbonyl oxygen, CO^2, and the alkoxy oxygen $-O^3R$, are *anti* to phosphorus. Atoms are numbered as in Tables II–V.

expected value of 360 degrees for trigonal carbons. The alkoxy groups of the esters appear to adopt the Z- conformation with respect to the bond to the alkoxy group, as for simple esters,[17] and as in the crystals. Bond lengths and angles and some torsional angles in the crystal[10] are compared with those from ab initio geometrical optimization (Tables II–V). Computed bond lengths and angles for the methyl and ethyl t-butyl diesters are similar to those for the corresponding isopropyl diesters, indicating that the geometry of the ylidic moiety is not very sensitive to substituent effects.

There are a number of noncovalent contact interactions in the crystal (Table VI), which are not very different from those estimated for isolated molecules.

Partial Atomic Charges

The extensive electronic delocalization in distabilized phosphonium ylides makes it difficult to show classical organic structures of these compounds. Structures of nonstabilized ylides with only one electron-withdrawing group are generally written with a double bond between to the ylidic and acyl carbons. However, a classical zwitterionic structure can be written for a diester, with charge delocalization involving the acyl groups.[3,4]

$$Ph_3P^+ - C^-(CO_2R)_2$$

Partial charges for individual atoms can be estimated by making simplifying assumptions, and we apply the natural population analysis scheme to the computed structures.[13,18] This treatment gives larger

TABLE VII Partial Atomic Charges[a] and Relative Energies ( )[b] for Ethyl iso-Propyl Diester, 1b, and Ethyl t-Butyl Diester, 2b

			CO_2Et			CO_2-i-Pr			
Ethyl iso-Propyl 1b	P^1	C^1	C^3	O^4	O^3Et	C^2	O^2	O^1i-Pr	Relative Energies[b]
syn-syn	1.73	−0.81	0.80	−0.68	−0.54	0.79	−0.68	−0.54	(0.0)
syn Et-*anti* i-Pr	1.72	−0.83	0.79	−0.68	−0.53	0.80	−0.62	−0.59	(−0.62)
anti Et-*syn* i-Pr	1.72	−0.83	0.80	−0.61	−0.58	0.79	−0.69	−0.54	(2.38)
anti-anti	1.72	−0.86	0.81	−0.59	−0.59	0.79	−0.61	−0.60	(2.43)
			CO_2Et			CO_2-t-Bu			
Ethyl t-Butyl 2b	P^1	C^1	C^3	O^4	O^3Et	C^2	O^2	O^1t-Bu	Relative Energies[b]
syn-syn	1.73	−0.81	0.80	−0.68	−0.54	0.79	−0.68	−0.55	(0.0)
syn Et-*anti* t-Bu	1.72	−0.83	0.78	−0.68	−0.54	0.81	−0.61	−0.59	(3.68)
anti Et-*syn* t-Bu	1.72	−0.83	0.80	−0.61	−0.58	0.80	−0.69	−0.55	(2.49)
anti-anti	1.72	−0.86	0.81	−0.59	−0.59	0.80	−0.62	−0.61	(3.66)

[a] Atoms are numbered as in Tables III and V. Negative charges on ylidic carbon C^1 and on alkoxy oxygens O^1 and O^3 follow orientation towards P.

[b] Energies, in parentheses, are in kcal.mol^{-1} relative to *syn-syn* conformer.

absolute charges than those given by the Mulliken analysis, and numerical values are useful qualitatively rather than quantitatively. Values of B3LYP/6-31G(d) Natural atomic charges for various conformers of the ethyl isopropyl and t-butyl diesters are in Table VII, together with relative energies. Values for the methyl isopropyl and t-butyl diesters are not shown because they are the same, to the second decimal place, as those in Table VII.

The trend in numerical values is similar to those for other ylidic diesters indicating strongly anionoid ylidic and cationoid acyl carbons, consistent with the ^{13}C NMR chemical shifts, but with little apparent dependence on conformation. The ester oxygens are predicted to be anionoid, especially when they are oriented towards phosphorus, but the estimated negative charges on the alkoxy oxygens are not very much lower than those on the acyl oxygens, indicating that interaction of the alkoxy groups with phosphorus cannot be neglected. Interaction of an acyl oxygen with phosphorus is less important than might be expected in predicting conformations, because on rotation about the ester group this interaction is replaced by one with the anionoid alkoxy oxygen. The extent of negative charge on an oxygen is sensitive to both orientation towards phosphorus and chemical bonding. For otherwise similar carbonyl groups the increasing estimated negative charge on oxygen should correspond to an increase in the C-O bond length. Evidence on diesters supports this conclusion,[10] and bonds to a *syn* acyl oxygen are generally slightly longer than to an otherwise similar *anti* oxygen (Tables II–V).

CONCLUSIONS

The diester geometries are predicted from ab initio computation to have the acyl oxygen of the methyl and ethyl ester group *syn-* and that of the isopropyl or t-butoxy ester group *anti-* to phosphorus, in agreement with X-ray crystallographic evidence.[10] Evidence from NMR spectroscopy and computation indicates that conformations of both isopropyl diesters are similar, consistent with the generalization that in mixed *syn-anti* ylidic diesters, the bulkier alkoxy group is always oriented towards phosphorus. Estimated atomic charges are as expected in terms of extended ylidic reasonance. Conformations of the *syn-anti* ylidic diesters, **1a,b**, **2a,b**, are unaffected by size changes in the ester groups, although changes from methyl to ethyl ester groups in **3**, **4**, and **5** change conformations between *anti-anti* and *syn-anti*.[11]

EXPERIMENTAL

Spectra

The ^{1}H, ^{13}C, and ^{31}P NMR spectra in $CDCl_3$ were recorded either on a Bruker DRX 300 or a Varian Inova spectrometer at 300 or 500 MHz, respectively, for ^{1}H, 75 or 125 MHz for ^{13}C, and 121 MHz for ^{31}P, and are referenced to internal TMS or external 85% H_3PO_4. ^{13}C spectra were obtained with and without ^{1}H decoupling. Infrared spectra were monitored on a Bruker IFS 56 FT spectrometer with a KBr disk and carbonyl ester stretching frequencies, wave numbers, are in cm^{-1}.

Structural Optimization

Computations for structural optimization were with Spartan 06 for Windows (Wavefunction) software and geometries were optimized with the HF/6-31G(d) basis set, or occasionally with the HF/6-311G(d) basis set with almost identical results, and with BLYP/6-31G(d) and B3LYP/6-31G(d) methods. Energies and atomic charges were estimated at B3LYP/6-31G(d) levels.

Synthesis

Methyl and ethyl isopropyl diesters, **1a**,**b**, and methyl and ethyl t-butyl diesters, **2a**,**b**, triphenylphosphonium ylides, were synthesized by reaction of isopropyl or t-butyl (triphenylphosphoranylidene)acetate, $Ph_3P{=}CH\text{-}CO_2CHMe_2$ and $Ph_3P{=}CH\text{-}CO_2CMe_3$, with methyl or ethyl chloroformate, respectively.[10]

REFERENCES

[1] A. D. Abell, B. M. Clark, and W. T. Robinson, *Aust. J. Chem.*, **42,** 1161–1167 (1989), and references cited therein.

[2] F. Castañeda, C. A. Terraza, C. A. Bunton, N. D. Gillitt, and M. T. Garland, *Phosphorus, Sulfur, and Silicon*, **178,** 1973–1985 (2003).

[3] S. M. Bachrach and C. I. Nitsche, in *The Chemistry of Organophosphorus Compounds*, F. R. Hartley, ed. (Wiley, New York, 1994), Vol. 3, Ch. 4, pp. 273–299.

[4] M. Kobayashi, F. Sanda, and T. Endo, *Macromolecules*, **33,** 5384–5387 (2000).

[5] F. Castañeda, C. Aliaga, M. T. Garland, J. Hu, N. D. Gillitt, and C. A. Bunton, *Phosphorus, Sulfur, and Silicon*, **182,** 151–160 (2007).

[6] F. Castañeda, C. Aliaga, C. A. Bunton, M. T. Garland, and R. Baggio, *Acta Crystallogr.*, **C61,** 496–499 (2005).

[7] F. Castañeda, C. Jullian, C. A. Bunton, M. T. Garland, and R. Baggio, *Acta Crystallogr.*, **C63,** 267–270 (2007).

[8] H. Günther, *NMR Spectroscopy—Basic Principles, Concepts, and Applications in Chemistry*, 2nd ed. (Wiley, New York, 1998).

[9] R. Riccio, G. Bifulco, P. Cimino, C. Bassarello, and L. Gomez-Paloma, *Pure Appl. Chem.,* **75,** 295–308 (2003).

[10] F. Castañeda, P. Silva, C. A. Bunton, M. T. Garland, and R. Baggio, *Acta Crystallogr.*, **C64,** 405–410 (2008).

[11] F. Castañeda, P. Silva, M. T. Garland, A. Shirazi, and C. A. Bunton, *Phosphorus, Sulfur, and Silicon*, **184,** 19–33 (2009).

[12] F. Castañeda, C. Acuña, M. T. Garland, N. D. Gillitt, A. Shirazi, S. J. Yunes, and C. A. Bunton, *Phosphorus, Sulfur, and Silicon*, **182,** 2541–2554 (2007).

[13] (a) C. J. Cramer, *Essentials of Quantum Chemistry* (Wiley, New York, 2002); (b) W. J. Hehre, *A Guide to Molecular Mechanics and Quantum Chemical Calculations* (Wavefunction, Irvine, CA, 2003).

[14] (a) I. F. Wilson and J. C. Tebby, *J. Chem. Soc. Perkin Trans.,1*, 31–34 (1972); (b) H. I. Zeliger, J. P. Snyder, and H. J. Bestmann, *Tetrahedron Lett*., 2199–2202 (1969); (c) F. J. Randall and A. W. Johnson, *Tetrahedron Lett*., 2841–2846 (1968); (d) D. M. Crouse, A. T. Wehman, and E. E. Schweizer, *Chem. Commun.*, 866–867 (1968).

[15] F. Castañeda, G. I. Recabarren, J. Hu, N. D. Gillitt, and C. A. Bunton, *Phosphorus, Sulfur, and Silicon*, **178,** 2505–2517 (2003).

[16] M. P. Cooke and R. Goswami, *J. Am. Chem. Soc.*, **95,** 7891–7892 (1973).

[17] (a) E. L. Eliel and S. H. Wilen, *Stereochemistry of Organic Compounds* (Wiley, New York, 1994), pp. 618–619; (b) T. B. Grindley, *Tetrahedron Lett*., **23,** 1757–1760 (1982); (c) C. E. Blom and H. H. Günthard, *Chem. Phys. Lett.*, **84,** 267–268 (1981); (d) K. B. Wiberg and K. E. Laidig, *J. Am. Chem. Soc.*, **109,** 5935–5948 (1987).

[18] A. E. Reid, R. B. Weinstock, and F. Weinholl, *J. Chem. Phys.*, **83,** 735 (1985).