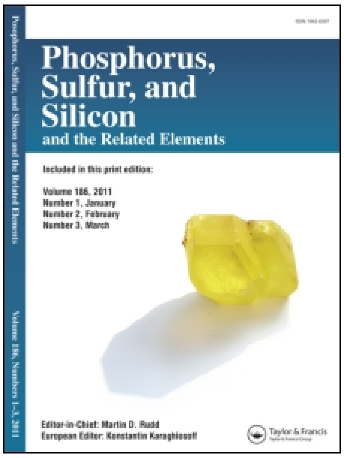

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Comparison of Conformations of Diesters of Stabilized Phosphonium Ylides in Solution and in the Crystal

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Computed bond lengths and angles of methyl ethyl and dimethyl triphenyl phosphonium ylidic diesters, ***1b, c****, respectively, are similar to those in the crystal, as for the diethyl ester,* ***1a****, where both acyl oxygens are anti to phosphorus. The* ^{1}H *and* ^{13}C *NMR spectra of the methyl ethyl diester,* ***1b****, where one acyl oxygen is syn and the other anti to phosphorus, are as expected in terms of the conformation in the crystal, but the dimethyl ester,* ***1c****, in the crystal is an equimolar mixture of conformers. For a given ylidic diester the different conformers have similar energies from B3LYP//6-31G(d) computations, interconversions of conformers should not be slow at ambient temperatures and* ^{1}H *and* ^{13}C *NMR signals in solution are sharp. Estimation of Natural Atomic Charges indicates significant cationoid character on phosphorus and the acyl carbons, and anionoid character on the ylidic carbon and the ester oxygens depending on orientations towards phosphorus.*

Keywords Phosphonium ylides; conformational analysis; structural computations; NMR spectra

INTRODUCTION

Conformations of phosphonium ylides stabilized by two electronic withdrawing substituents, e.g., ester or keto groups, depend on the balance between ylidic resonance and non-bonding interactions, including, for the solid, packing forces in the crystal.[1,2] Electronic delocalization should favor near planar ylidic moieties with favorable interactions between acyl oxygens and cationoid phosphorus, and the bonds between phosphorus and the ylidic carbon, and between it and the acyl carbons,

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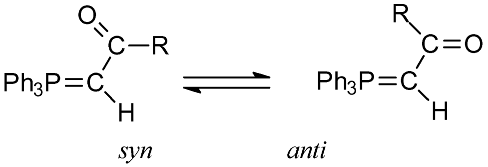
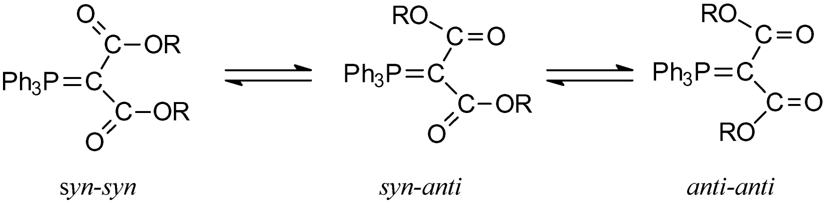


SCHEME 1 R = alkyl, alkoxy.

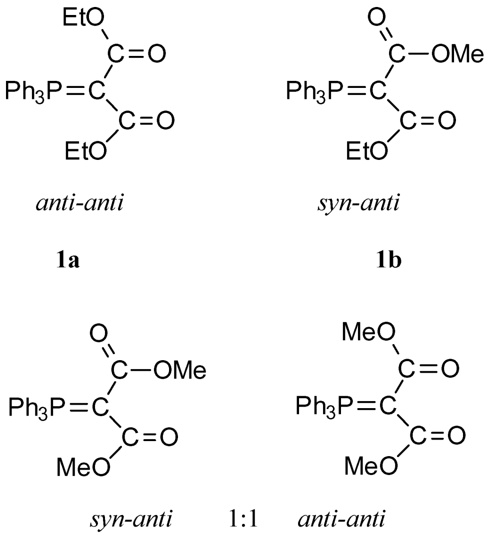
should have orders between one and two. In solution NMR spectroscopy indicates that these stabilized ylides exhibit free rotation about the P—C bond and the sharp signals indicate that one conformer is dominant, or that conformers readily interconvert.[3,4] With some ylides stabilized by a single acyl group, geometrical isomers exist and the two conformers can be identified, as shown in Scheme 1 for a triphenyl phosphonium ylide.[5]

The conformers are designated as *syn* and *anti*, depending on the orientation of the acyl oxygen relative to phosphorus. There are significant energy barriers to interconversions of these monostabilized conformers because ylidic resonance is lost on rotation out of the ylidic plane.[6] The situation is different for distabilized ylides, as shown in Scheme 2 for a symmetrical diester, where rotation of one ester group out of the ylidic plane should not affect resonance interaction involving the other.[3,4]

In Scheme 2, structures are written for simplicity, with a P-C double bond and single bonds between the ylidic and acyl carbons; although this classical structure is inadequate, does not represent bond lengths (C–C, C–P) in the crystal. The phenyl groups are equivalent on the NMR time scale, due to rotation about the bond between phosphorus and the ylidic carbon. At the simplest level, one would expect a *syn-syn* conformer with a planar ylidic moiety to be preferred, as in mono- stabilized ylides, but with diesters there should be interference between the two ester alkoxy groups *anti* to phosphorus. Despite expected favorable electrostatic interactions between acyl oxygens and cationoid phosphorus there is a deviation from planarity of the ylidic moiety in



SCHEME 2 R = alkyl.



anti-anti *syn-anti*

1a **1b**

syn-anti 1:1 *anti-anti*

1c

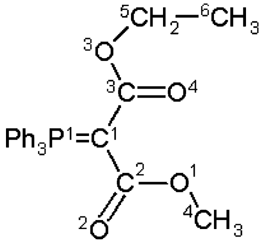
SCHEME 3

the crystalline diethyl ester, **1a**, R = Et, and both acyl oxygens are *anti* to phosphorus, but there are favorable intramolecular interactions between phosphorus and the alkoxy groups.[7] Inter- and intramolecular interactions in the solid are important, but*ab initio* computations at the B3LYP//6-31G(d) level indicate that the independent conformers should have similar energies and low barriers to interconversion, for example, in solution the diethyl ester, **1a**, may be a mixture of equilibrating conformers.[8] A difference in conformation in solution and the solid in some ylidic keto compounds could be indicated by differences in the ^{13}C NMR spectra in these conditions, and packing forces should be important in the solid. Changes in the alkyl groups in the diesters might therefore control conformation in the crystal, and possibly in solution, and in the crystalline methyl ethyl diester, **1b**, the ethoxy group and the acyl oxygen of the carbomethoxy group are *syn* to phosphorus, but the crystalline dimethyl diester, **1c**, is a 1:1 mixture of the *syn-anti* and *anti-anti* conformers,[9] Scheme 3.

In view of the estimated low energy barriers between different conformers of isolated stabilized phosphonium ylides, **1b** and **1c** may have different conformations in solution and in the crystal.

In the present work, we used *ab initio* geometrical optimization to predict geometries of isolated molecules, and ^{1}H and ^{13}C NMR spectroscopy, plus estimation of Natural Atomic Charges, to examine

TABLE I Selected Geometric Parameters (Å, °) for Ethyl Methyl 2-(Triphenylphosphoran ylidene)malonate, 1b, from Computation and X-ray Crystallography[a]



Syn-anti conformer **1b**.

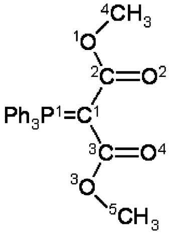
P1-C1	1.75 (1.74)	C2-C1-C3	122 (124)
C1-C2	1.45 (1.43)	C1-C3-O4	126 (127)
C1-C3	1.46 (1.44)	O3-C3-O4	121 (121)
C2-O2	1.21 (1.22)	C1-C3-O3	113 (112)
C3-O4	1.19 (1.20)	O1-C2-O2	121 (121)
C2-O1	1.32 (1.34)	C1-C2-O2	123 (123)
C3-O3	1.35 (1.36)	O1-C2-C1	116 (116)
P1-C1-C2	113 (111)	P1-C1-C2-O2	10 (10)
P1-C1-C3	125 (125)	P1-C1-C3-O4	158 (154)

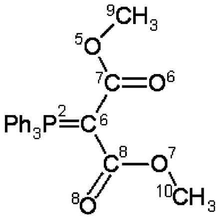
[a] Values in parentheses are for the X-ray crystallographic structure. Positions are designated as in the X-ray crystallographic experiments.[9]

intramolecular interactions. The diester conformations are shown in Tables I and II with positions designated as in the X ray crystallographic results.[9] Positions of the phenyl groups are not specified because rapid rotation about the P—C bond assures their equivalence in solution on the NMR time scale, although interactions involving the phenyl groups could influence conformations.

Estimation of energies of the various conformers of several stabilized triphenylphosphonium ylides indicates that for isolated molecules the *syn-syn* conformer should be preferred, but energy differences between it and the *syn-anti* or *anti-anti* conformers should be small and much lower than energy differences for monostabilized ylides. Rotation of one ester group out of the ylidic plane increases the energy only modestly, and interconversion of conformers in solution should be rapid at *ca.*, 25°C. These small energy differences indicate that in solution interconversion of conformers should be fast on the NMR time scale. However, NMR signal shapes and multiplicities are generally consistent with one conformer being dominant.

TABLE II Selected Geometric Parameters (Å, °) for Dimethyl 2-(Triphenylphosphoranylidene) Malonate, 1c, from Computation and X-ray Crystallography[a]





Anti-anti conformer **1c**		*Syn-anti* conformer **1c**	
P1-C1	1.74 (1.74)	P2-C6	1.75 (1.74)
C1-C2	1.45 (1.43)	C6-C7	1.45 (1.44)
C1-C3	1.46 (1.44)	C6-C8	1.45 (1.43)
C2-O2	1.19 (1.20)	C7-O6	1.19 (1.21)
C2-O1	1.35 (1.36)	C8-O8	1.21 (1.22)
C3-O3	1.36 (1.37)	C7-O5	1.35 (1.36)
C3-04	1.19 (1.20)	C8-O7	1.32 (1.35)
P1-C1-C2	123 (121)	P2-C6-C7	125 (119)
P1-C1-C3	119 (119)	P2-C6-C8	113 (117)
C2-C1-C3	118 (119)	C7-C6-C8	122 (123)
O1-C2-O2	121 (121)	O5-C7-O6	120 (121)
O2-C2-C1	127 (128)	O6-C7-C6	127 (129)
O1-C2-C1	112 (111)	O5-C7-C6	112 (110)
C1-C3-O4	128 (128)	C6-C8-O8	122 (125)
O3-C3-O4	121 (121)	O8-C8-O7	121 (121)
O3-C3-C1	111 (111)	O7-C8-C6	116 (114)
P1-C1-C2-O2	−167 (−162)	P2-C6-C8-O8	11 (9)
P1-C1-C3-O4	163 (158)	P2-C6-C7-O6	167 (155)

[a] Values in parentheses are for the X-ray crystallographic structure. Positions are designated as in the X-ray crystallographic experiments.[9]

In a phosphonium ylidic diester with both acyl oxygens oriented towards phosphorus there could be, in the crystal, interference between the alkoxy groups of the bulky trigonal ester groups and neighboring molecules. Carboxylic esters take up the Z-conformation,[10] with a small preference over the E conformation and *ab initio* computation indicates that this preference is maintained in ylidic esters. Rotation of the bulky trigonal groups in esters should occur readily at ambient temperatures but would involve significant interference between adjacent groups in an ylidic diester with both acyl oxygens *syn* to phosphorus. Rotational interconversion of Z- and E- ester conformers in an ylidic diester with both alkoxy groups *anti* to phosphorus will, therefore, be disfavored by steric interference disfavoring these conformers. These unfavorable interactions are neglected when single point energies are calculated from *ab initio* geometrical optimizations of static structures, which limits their efficacy in predicting conformations of the ylidic diesters. This limitation is less important in treating conformations of monostabililized ylides, or those stabilized by a linear cyano group where Z—E interconversions should not be sterically hindered, and *syn* acyl oxygens in mono keto and ester derivatives are preferred.[11] However, so far as we know *syn*-*syn* conformers of diesters are not preferred in the solid or in solution, and the question of their probable conformation is discussed later. The computations on static structures, as noted, neglect intermolecular interactions and possible rotational mobility of trigonal groups.

RESULTS AND DISCUSSION

Geometrical Optimizations

Ab initio computations were made with geometries from HF 6-31G(d) or 6-311G(d) basis sets,[12] and the predicted structures were indistinguishable by eye. Relative energies are from B3LYP computations with the HF geometries, and for all the diester and diketo systems that we have examined the *syn*-*syn* conformers are predicted to be preferred, but energy differences between them and *anti* conformers are typically within 3 kcal.mole^{-1}and moving one ester group into an orthogonal position has only a small energy effect, typically < 2 kcal.mole^{-1}, consistent with rapid conformational equilibration in solution.[8,11b]

These small energy differences indicate that in solution interconversion of conformers should be fast on the NMR time scale. However, signal shapes and multiplicities are generally as expected in terms of structures of the crystalline ylides.

Bond lengths and angles for conformers, with positions numbered as in the crystal, [9] are in Tables I and II, and for the dimethyl ester, **1c**, we give values for the *anti*-*anti* and *syn*-*anti* conformers. Bond lengths and angles of distabilized ylides, but not necessarily torsional angles, estimated by *ab initio* optimization, are typically similar to those in the crystal where conformations, are apparently sensitive to packing constraints. Computed distances and angles are given to the second decimal place, and angles to the first whole number, but for the crystal structures full numerical values are given in Reference 9. Crystalline **1c** is an equimolar mixture of two interacting conformers and computations are for isolated molecules which complicates comparisons of calculated and observed geometries.

Some bond angles at the acyl carbons differ from the expected 120°for trigonal carbons, probably because of steric effects, or strong interactions between anionoid oxygens, and we see this effect in the crystal and in the computed geometries. However, the sum of the bond angles at these carbon atoms is close to the value of 360°for a planar carbon, consistent with the strong electronic delocalization over the ylidic system.

The computations neglect non-bonding interactions in mobile structures in solution as well as intermolecular interactions in the solid and probably in solution. These phosphonium ylides have molecular weights of *ca*. 400 and at the concentrations, 0.1–0.2 M , used in the NMR measurements in solution, there may be interference between bulky trigonal *anti*-acyl groups of neighboring molecules, as well as between these groups in the same molecule which complicates comparison of NMR data with computation results. These unfavorable non-bonding interactions in diesters are apparently more important than favorable interactions between cationoid phosphorus and *syn*-acyl oxygens which should be partially offset by interactions between *syn* alkoxy groups and phosphorus, as shown later from consideration of Partial Atomic Charges.

In the crystalline methyl-ethyl diester **1b** the bulkier ethoxy group is in the *syn*- position with respect to phosphorus, and the methoxy group is *anti*, and later we consider evidence for this conformation in solution.

NMR Spectroscopy

The ^{1}H and ^{13}C (^{1}H decoupled) NMR spectroscopic signals were examined on a 300 MHz instrument and also on a 500 MHz instrument where the ^{1}H coupled ^{13}C signals were also examined. All experiments were in acid-free $CDCl_3$.[13]

For all the stabilized phosphonium ylides sharp ^{1}H and ^{13}C signals show that in solution rotation about the P-C bond is rapid on the NMR time scale and the ^{31}P chemical shifts indicate significant single bond character, as in the crystal.

For the methyl ethyl and the dimethyl diesters, **1b**, **c**, the marked upfield ^{13}C signals of ylidic carbons confirm their carbanionoid character, consistent with the suggestion that these ylides can be written as zwitterions, rather than with classical P=C bonds.[14] The ^{1}H and ^{13}C signals shown in Table III are in the regions expected in terms of earlier

TABLE III ^{1}H-, ^{13}C-, and ^{31}P NMR Data for Methyl Ethyl Diester, 1b, $Ph_3P{=}C(CO_2Me)CO_2Et$, and Dimethyl Diester, 1c, $Ph_3P{=}C(CO_2Me)_2$

Ylide	^{1}H NMR	^{13}C NMR	^{31}P NMR
1b	0.75 (t,3H, J = 7Hz, $O{-}CH_2{-}CH_3$)	13.94 ($O{-}CH_2{-}CH_3$)	20.87
	3.79 (q,2H, J = 7Hz;$O{-}CH_2{-}CH_3$)	58.56 ($O{-}CH_2{-}CH_3$)	
	3.30 (s,3H, $O{-}CH_3$)	50.22 ($O{-}CH_3$)	
		53.10(d, J = 122.6 Hz, $P{=}C$)	
	7.4–7.8 (m,15H, aromatic)	168.10(d, J = 13.5Hz, CO_2)	
		126.58(d, $^1J_{p-c}$ = 94.1Hz, C_{ipso})	
		128.49(d, $^2J_{p-c}$ = 12.5Hz, C_{ortho})	
		131.82(d, $^4J_{p-c}$ = 3.0Hz, C_{para})	
		133.26(d, $^3J_{p-c}$ = 9.7Hz, C_{meta})	
1c	3.34 (s, 3H, $O{-}CH_3$)	49.15 ($O{-}CH_3$)	20.79
	7.4–7.8 (m, 15H, aromatic)	52.30(d, J = 123.8Hz, $P{=}C$)	
		167.40(d, J = 13.5Hz, CO_2)	
		125.3(d,$^1J_{p-c}$ = 94.2Hz, C_{ipso})	
		127.5(d,$^2J_{p-c}$ = 12.5Hz, C_{ortho})	
		130.9(d,$^4J_{p-c}$ = 2.9Hz, C_{para})	
		132.3(d,$^3J_{p-c}$ = 9.7Hz, C_{meta})	

NMR spectra in CDCl3 at 25°C with TMS as internal reference for 1H and 13C, and H3PO4, as external reference for 31P.

observations. Values of chemical shifts and multiplicities generally do not provide evidence on preferred conformations, except that evidence of π-shielding[15] of terminal methyl hydrogens of alkoxy groups indicates that in solution the group is oriented towards phosphorus, as in **1b**. Although in the crystal the dimethyl ester, **1c**, is an equimolar mixture of *anti-anti* and *syn-anti* conformers we saw only one set of ^{1}H and ^{13}C NMR signals and only one ^{31}P NMR signal in $CDCl_3$. The signals, with the expected multiplicity, do not distinguish between the possibilities that one conformer is dominant in solution, or that conversion of conformers is fast on the NMR time scale, as expected in view of small estimated energy differences between conformers stabilized by two ester groups.[8] The ^{1}H chemical shifts and coupling constants for both diester ylides are consistent with the other structural evidence.

The ^{13}C NMR spectrum of the methyl ethyl diester, **1b**, in $CDCl_3$, provides conformational information by comparison of signals with, and without, ^{1}H decoupling, and some results concerning the ylidic groups, are considered separately. The ^{13}C signals of the phenyl groups are as expected, in view of the equivalence of these groups on the NMR time scale and the spectrum with and without ^{1}H spin-spin decoupling shows that ^{13}C chemical shifts decrease in the sequence*meta* >*para* >

ortho, which accords with the generally accepted assignments based on the magnitude of the coupling constants with ^{31}P.[2] These assignments differ from those given earlier with the chemical shifts decreasing in the sequence *ortho* > *para*> *meta*,[16] but the ^{1}H coupled ^{13}C signals do not fit this sequence because the signal at 128.49 ppm of the *ortho* carbon is a doublet of doublets due to coupling with both ^{1}H and ^{31}P, ($^{2}J_{p-c} = 12.53$ Hz). The signal of the *para* carbon is identified by its area, and is split by ^{1}H and weak ^{31}P coupling ($^{4}J_{p-c} = 3.0$ Hz), but without ^{1}H decoupling part of the signal is under part of the *meta* signal at 133.3 ppm, which itself is also split by ^{1}H and ^{31}P coupling. In the ^{1}H coupled ^{13}C NMR spectrum the splitting patterns of the*meta* and *para* carbons are similar, except that there is a single central peak of the latter because there are two neighboring CH groups, and differ from those of the *ortho* carbon with its single adjacent neighboring CH group. However, only a single central peak was observed in the *para* ^{13}C signal. In the ^{1}H coupled spectrum the ^{13}C signal of the *ipso* carbon becomes a doublet of triplets, J = 7.5 Hz, due to coupling with ^{31}P and the *ortho* ^{1}H. These generalizations regarding the ^{13}C NMR spectra probably also apply to **1c**, although here only the ^{1}H decoupled spectrum was examined.

Ylidic Group in the Methyl Ethyl Diester, 1b

In crystalline **1b** the ethoxy group is *syn* and the methoxy group is *anti* to phosphorus. In solution (Table III) π-shielding[15] of $CH_2C\mathit{H}_3$ indicates that this geometry of the ethoxy group is maintained in solution. The ^{13}C signals of acyl groups of stabilized phosphonium ylides in the ^{1}H decoupled spectra are sometimes broad singlets, which may overlap, and they should be split by coupling with ^{31}P, but they are well defined in **1b**. In $CDCl_3$ at 125 MHz we saw doublets, J = 12.8 and 12.7 Hz at 167.59 and 168.54 ppm, respectively, in the^{1}H decoupled spectrum, indicating different orientations of the acyl groups, and from the chemical shifts we assume that the upfield signal is that of the ethoxy ester acyl carbon. Removal of the ^{1}H decoupling increased the line width of each signal of the doublet at 167.59 ppm, due to long range ^{1}H coupling, although the signals were not resolved. Signals of the doublet at 168.54 ppm are split, and appear to become a somewhat distorted doublet of quartets, and not all the signals are resolved, J = 3 Hz (Figure 1). There is long range coupling with ^{1}H of the methoxy group which in the crystal is *anti* to phosphorus.[9] These observations indicate that the conformation of the methyl ethyl diester, **1b**, is the same in the crystal and in solution, at least as regards the *syn*- position of the ethoxy group,

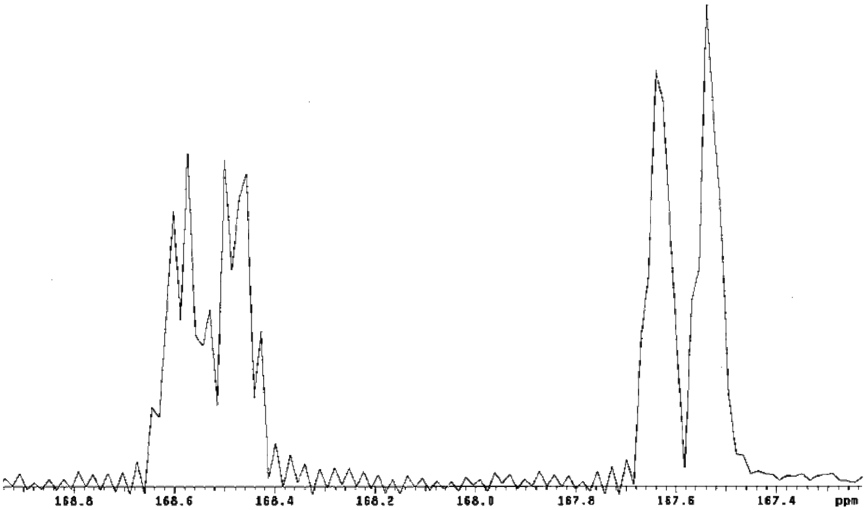


FIGURE 1 ^{13}C NMR signals of the carbonyl groups of **1b** with long-range coupling with ^{31}P and removal of the ^{1}H decoupling.

and later we show evidence, from estimation of Partial Atomic Charges, indicating that the methoxy group is probably *anti* in solution.

The ^{13}C NMR signals of the methoxy and ethoxy groups of **1b** are split by ^{1}H coupling. The $OCH_2\mathit{C}H_3$ signal becomes a quartet, J = 126 Hz, and the $O\mathit{C}H_2CH_3$ signal becomes a triplet, J = 146 Hz, with weak long range coupling with ^{31}P, J = 5 Hz. The $O\mathit{C}H_3$ signal becomes a quartet, J = 145 Hz. It is generally convenient to monitor ^{13}C NMR spectra with ^{1}H decoupling, but with some of these ylides ^{1}H coupling provides additional useful information.

Partial Atomic Charges

The assignment of charge to individual atoms is convenient in considering some molecular properties, although it is essentially an empirical concept. Various approximate treatments have been developed for estimating Partial Atomic Charges,[12] and Natural Charges for some positions in the phosphonium ylides are given in Table IV from B3LYP//HF 6-31G(d) computations on conformers as in the crystal. The *syn*-*anti* conformation of the methyl ethyl diester, **1b**, in the crystal is probably also that in solution, but the *syn*-*anti*- and *anti*-*anti*-conformers of the dimethyl diester, **1c**, are associated in the crystal[9] and partial charges were estimated for both conformers. Partial Atomic Charges for given

TABLE IV Fractional Atomic Charges[a] for Methyl Ethyl Diester, 1b, and Dimethyl Diester, 1c

Methyl ethyl diester, **1b**, *syn-anti* conformer								
Position	P1	C1	C2	C3	O1	O2^b	O3^b	O4
Atomic charge	1.72	−0.83	0.79	0.80	−0.53	−0.68	−0.58	−0.61
Dimethyl diester, **1c**, *anti-anti* and *syn-anti* conformers.								
Position	P1	C1	C2	C3	O1^b	O2	O3^b	O4
Atomic charge	1.72	−0.85	0.79	0.80	−0.58	−0.60	−0.58	−0.61
Position	P2	C6	C7	C8	O5^b	O6	O7	O8^b
Atomic charge	1.72	−0.83	0.79	0.79	−0.58	−0.61	−0.52	−0.68

[a] Atoms are numbered as in Tables I and II. [b] Oxygens oriented towards phosphorus.

groups are similar for these diesters and it appears that substitution of an ethyl for a methyl group has little effect on the charges.

The ylidic carbon is predicted to be strongly anionoid, consistent with the strongly upfield ^{13}C NMR signal, typical of these stabilized ylides, and the partial charges on phosphorus and the acyl carbons are as expected in terms of ylidic resonance, but the alkoxy oxygens are also significantly anionoid and in the *syn* position should interact favorably with phosphorus, as in the crystal. Estimated atomic charges are similar for the *anti-anti* and *syn-anti* conformers of the dimethyl ester, consistent with bond lengths and angles being similar for the two conformers (Table IV). Differences in the anionoid characters of acyl or alkyl oxygens are modestly sensitive to conformation, and, for an acyl group, the anionoid character is consistently slightly higher for oxygens oriented towards, rather than away from, phosphorus, which corresponds to lower carbon-oxygen bond orders and slightly longer bonds differing by *ca.* 0.01 Å, (Tables I and II). This generalization regarding atomic charge and location relative to phosphorus also applies to hypothetical conformers with structures different from those in the crystal (data not shown).

The higher negative partial charge on an alkoxy oxygen *syn*, rather than *anti*, to phosphorus (Table IV) should shift the ^{13}C NMR signal of the $C\mathrm{H}_3$ group slightly upfield, and this hypothesis can be tested by considering these chemical shifts in **1b** and **1c** which are 50.22 and 49.15 ppm., respectively, in $\mathrm{CDCl_3}$(Table III).In crystalline **1c** the $\mathrm{OCH_3}$ groups are largely oriented towards phosphorus, and the more anionoid character on oxygen, as compared to that in **1b** (Table IV), is consistent with the difference in ^{13}C chemical shifts of the methoxy groups (Table III). This analysis involves the assumption that the preferred orientation of $\mathrm{OCH_3}$ in the crystal (Tables 1 and 2) is maintained in solution.

Electronic and Steric Effects on Conformation

Electronic delocalization is important in these stabilized phosphonium ylides with favorable interactions between cationoid phosphorus and anionoid acyl oxygens in ester substituent groups, and to a lesser extent in alkoxy groups. This hypothesis is supported by *ab initio* computations which indicate that *syn-syn* conformers should be energetically preferred, but so far as we know, both acyl oxygens are not *syn* to phosphorus in the crystalline diesters. Differences in computed energies of conformers of diester ylides are small, as are barriers to interconversion, so that non-bonding interactions are probably very important, and estimation of Partial Atomic Charges indicates that alkoxy oxygens should interact with phosphorus, but less readily than acyl oxygens. Minor changes in the alkyl groups, e.g., from Me to Et affect structure in the crystal and probably in solution, and are consistent with small energetic differences between conformers. In hypothetical diesters with two, freely rotating, bulky alkoxy groups *anti* to phosphorus there should be in solution considerable interference between these groups. These interactions are more important than those of an acyl oxygen with phosphorus, although they are neglected in our computations on static structures. In the crystal, where packing is all important, bulky alkoxy groups *anti* to phosphorus are disfavored sterically by interaction with neighboring ylides, and in diesters the bulkier alkoxy group is oriented towards phosphorus. For example, in the methyl ethyl diester, **1b**, the bulkier ethoxy group is oriented towards phosphorus, in the solid and probably in solution, despite the more negative character of the acyl over the ethoxy oxygen. Bond angles at the trigonal ylidic C1 in the crystal are larger towards C3 of the ethyl ester group, than towards C2 of the methyl ester group, although the sum of the bond angles is ca., 360°(Table I). Deviations from the 120° bond angles at trigonal carbons are also evident for the acyl carbons C2 and C3 in the crystal and for computation on an isolated molecule (Table I).

For the dimethyl ester, **1c**, which has associated *anti-anti-* and *syn-anti-* conformers in the crystal, there is reasonable agreement between computed bond angles and those in the crystal, and observed deviations from the expected 120° bond angles are qualitatively as predicted for isolated molecules by *ab initio* geometrical optimization, but the sum of the bond angles is close to the expected value of 360°. This association of *anti-anti* and *syn-anti* conformers in the solid is consistent with the melting point of the dimethyl ester, 192°C, being much higher than those for most triphenyl phosphonium ylides.

For both ylides, **1b** and **1c**, predicted bond lengths are similar to those in the crystal. This generalization is reasonable, because energies for changes in bond lengths are much higher than for changes in bond angles. The inability of geometrical optimization for isolated molecules to provide relative energies of stabilized ylides consistent with the crystal structure is probably due to neglect of packing forces in the solid and the assumption of static structures in the computations, but extensive evidence indicates that energy differences between conformers is small, and their interconversion involves changes in torsional angles rather than in covalencies.

CONCLUSIONS

The ester groups have the Z-conformation in the crystal, and, based on geometrical optimization, also preferentially for isolated molecules. Conformations of various crystalline ylidic diesters differ, depending on the alkoxy groups. In solution the sharp ^{1}H and ^{13}C NMR signals are as expected for stabilized ylides in terms of electronic effects of substituents and rapid interconversion of conformers.

Interference between two trigonal groups *anti*-to phosphorus probably precludes the existence of *syn*-*syn* conformers in the solid and probably also in solution. The situation is different with monostabilized ylides, or when one of the stabilizing groups is linear, as in phosphonium ylides stabilized by cyano and keto or ester groups, where the *syn* conformers are preferred in both the solid and in solution.[11] Ester groups generally exist as Z-conformers about the acyl carbon-oxygen bond,[10] as a result in a hypothetical *syn*-*syn* diester with a static structure there would be an unfavorable interaction between the electron lone pairs of the alkoxy groups and if the ester groups take up the disfavored E-conformation there would be steric interference between the two alkyl groups. We know of no experimental evidence for these ylidic diesters taking up the *syn*-*syn* conformation in the crystal.

EXPERIMENTAL

Diethyl 2-(triphenylphosphoranylidene) malonate, **1a**, was prepared by reaction of dibromotriphenylphosphine and diethylmalonate in the presence of triethylamine as described by Horner and Oediger.[17]

Methyl ethyl and dimethyl 2-(triphenylphosphoranylidene) malonate, **1b** and **1c**, were obtained by transylidation reaction of (methoxycarbonylmethylene) triphenyl phosphorane, $Ph_3P{=}CH{-}CO_2CH_3$, with ethyl and methyl chloroformate, respectively, as reported by Castañeda et al.[9]

^1H, ^{13}C, and^{31}P NMR for **1a**, **1b,** and **1c** were monitored on Bruker DRX 300 or Varian Inova 500 spectrometers and were referenced to TMS or external 85% H_3PO_4. ^{13}C NMR spectra were obtained with and without ^1H decoupling.

Selected geometric parameters and molecular structures for **1b** and **1c** were provided by a Bruker SMART APEX CCD area-detector diffractometer as published by Castañeda et al.[9]

Computations for structural optimization were made with Spartan 06 for Windows (Wavefunction) software, and optimized with HF 6-31G(d) basis set or occasionally with the HF 6-311G(d) basis set with almost identical results. Energies were estimated by density functional B3LYP and HF geometries.

REFERENCES

[1] H. J. Cristau and F. Plenat, In *The Chemistry of Organophosphorus Compounds*, F. R. Hartley, Ed. (Wiley, New York, 1994), Vol. 3, Ch. 2, pp. 108–110.

[2] 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.

[3] (a) A. D. Abell and R. A. Massy-Westropp, *Aust. J. Chem.*, **35**, 2077–2087 (1982); (b) A. D. Abell, B. M. Clark, and W. T. Robinson, *Aust. J. Chem.*, **42**, 1161–1167 (1989); (c) A. D. Abell , J. Trent, and W. T. Robinson, *Aust. J. Chem.*, **41**, 1243–1249 (1988); (d) A. D. Abell and R. A. Massy-Westropp, *Aust. J. Chem.*, **35**, 2277–2287 (1982); (e) M. P. Cooke and K. P. Biciunas, *Synthesis*, 283–285 (1981).

[4] (a) F. Castañeda, C. A. Terraza, C. A. Bunton, N. D. Gillitt, and M. T. Garland, *Phosphorus, Sulfur, and Silicon*, **178**, 1973–1985 (2003); (b) F. Castañeda, G. I. Recabarren, J. Hu, N. D. Gillitt, and C. A. Bunton, *Phosphorus, Sulfur, and Silicon*, **178**, 2505–2518 (2003).

[5] (a) F. J. Randall and A. W. Johnson, *Tetrahedron Lett.*, 2841–2845 (1968); (b) I. F. Wilson and J. C. Tebby, *J. Chem. Soc. Perkin I*, 31–34 (1972); (c) D. M. Crouse, A. T. Wehman, and E. E. Schweizer, *Chem. Commun.*, 866–867 (1968); (d) I. F. Wilson and J. C. Tebby, *Tetrahedron Lett.*, 3769–3770 (1970).

[6] H. I. Zeliger, J. P. Snyder, and H. J. Bestmann, *Tetrahedron Lett.*, 2199–2202 (1969).

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

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

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

[10] (a) E. L. Eliel and S. H.. Wilen, *Stereochemistry of Organic Compounds* (Wiley, New York, 1994), Ch. 10, pp. 618–619; (b) C. E. Blom, H. H. Günthard, *Chem. Phys. Lett.*, **84**, 267–268 (1981); (c) K. B. Wiberg and K. E. Laidig, *J. Am. Chem. Soc.*, **109**, 5935–5948 (1987).

[11] (a) F. Castañeda, C. A. Bunton, R. Baggio, and M. T. Garland, *Acta Crystallogr.*, **C63**, 65–67 (2007); (b) 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).

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

[13] H. J. Bestmann, H. G. Liberda, and J. P. Snyder, *J. Am. Chem. Soc.*, **90**, 2963–2964 (1968).

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

[15] (a) M. Nishio, Y. Umezawa, M. Hirota, and Y. Takeuchi, *Tetrahedron*, **51**, 8665–8701 (1995); (b) M. Nishio and M. Hirota, *Tetrahedron*, **45**, 7201–7245 (1989).

[16] (a) G. A. Gray, *J. Am. Chem. Soc.*, **95**, 7736–7742 (1973); (b) T. A. Albright, M. D. Gordon, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem Soc.*, **98**, 6249–6252 (1976).

[17] L. Horner and H. Oediger, *Chem. Ber.*, **91**, 437–442 (1958).