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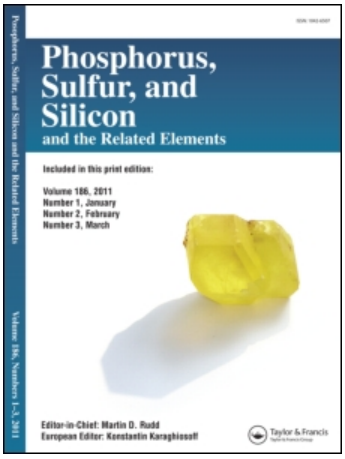

Phosphorus, Sulfur, and Silicon and the Related Elements

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Conformational Differences in Stabilized Diketo and Diester Phosphonium Ylides in a Solid and in Solution

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The diacyl ylid, 3-triphenylphosphoranylidene-2,4-pentanedione ***2*** *can adopt conformations with one oxygen syn- and the other anti- to phosphorus* ***2a*** *as in the crystal, or with both oxygens syn- to phosphorus* ***2b****. In solution,* ^{1}H *and* ^{13}C *NMR signals are sharp, but* ^{13}C *signals in the solid confirm that the two acyl groups are in different positions, and a comparison of the* ^{13}C *signals in solution and a solid shows that conformations differ.* Ab initio *geometrical optimizations give, for* ***2a****, a geometry similar to that in a crystal, and structures of both conformers permit extended ylidic resonance through near planar ylidic and acyl moieties. In crystalline diethyl 2-triphenyl phosphoranylidene malonate* ***3****, the torsional angles of the ester moieties to the plane of the near trigonal ylidic moiety are* -149.2° *and* 170.4°*, due to packing forces and interactions with adjacent molecules, which limit ylidic resonance. The* ^{13}C *NMR spectrum in the solid differs from that in solution, with the two ester groups in different positions, but in solution,* ^{13}C *and* ^{1}H *NMR signals are sharp.* Ab initio *geometrical optimizations indicate that for an isolated molecule, the conformer with torsional angles as in the crystal is energetically unfavored but energetic barriers to interconversion are small, and rapidly equilibrating conformers probably exist in solution.*

Keywords Conformations; NMR spectra; optimized structures; phosphonium ylides

Conformations of stabilized phosphonium ylides with electron-withdrawing substituents, e.g, C=O, are governed by ylidic resonance;

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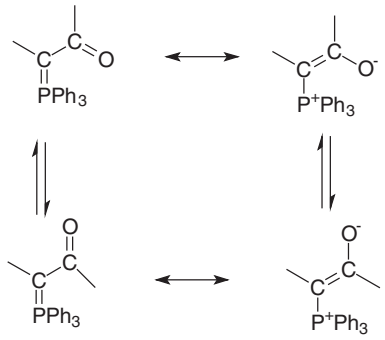

SCHEME 1

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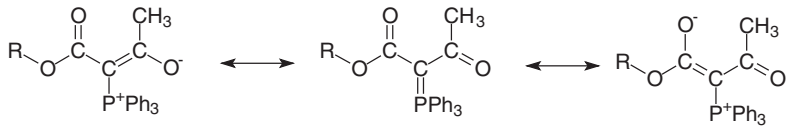
by nonbonding interactions, for example, between anionoid oxygen and cationoid phosphorus; and by dipole-dipole and steric interactions.[1,2]

In a solid, there are intermolecular interactions, and in solution there may be hydrogen-bonding between a solvent and an oxygen, which is oriented away from phosphorus. The classical structures shown in Scheme 1 illustrate conformations in a resonance-stabilized ylid.

There is considerable rotational freedom about the C—P bond, and the phenyl groups shown in Scheme 1 are generally identical in solution on the NMR time scale, but rotation about the ylidic bond can be slow due to ylidic resonance[2,3] Individual conformers of monosubstituted ylides have been identified in solution by their NMR signals. However, when two stabilizing groups are present, ylidic resonance is not completely lost on rotation, and conformational equilibration should be fast.[4,5] Packing forces are important in the crystal, but for mixed keto-ester ylid, **1**, R = Et, the conformer as shown in Scheme 2 is dominant in both a solution and a solid.[5a,7]

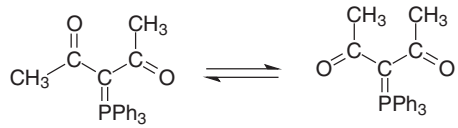
In **1a**,**b**,**c**, the stabilizing acyl groups and the ylidic moiety are in approximately the same plane, with a trigonal ylidic carbon,[5a,7] indicating the important role of ylidic resonance. The diketo ylid **2** in the crystal has keto oxygens *syn*- and *anti*- to phosphorus with respect to ylidic bonds,[5b,6] as shown in Scheme 3, but Cooke and Goswani



1a **1b** **1c**

SCHEME 2

deprotonated the methyl groups in basic, aprotic, media, and isolated cyclic products, consistent with both oxygens being *syn*- to phosphorus, as in **2b**,[8] although the results can be explained in other ways; for example, the formation of the cyclic products could be controlled thermodynamically. ^{1}H and ^{13}C NMR spectra of **2** in solution show that either both oxygens are *syn*- to phosphorus, or rotation is fast on the NMR time scale (Scheme 3), but in the solid, the keto groups have different ^{13}C NMR signals, which is consistent with the crystallographic evidence.[5b,6]



2a: *syn-anti* **2b:** *syn-syn*

SCHEME 3

Unlike the situation with monoacyl ylides, there is no indication of slow conformational equilibration in any of these disubstituted ylides because of extended ylidic resonance in either conformer and favorable interactions between cationoid phosphorus and acyl oxygen. This conclusion is consistent with crystallographic evidence and ab initio geometrical optimizations.[6,7] The only exception to this generalization for stabilized ylides of which we are aware is the diethyl ester **3** where in the crystal there is deviation from coplanarity of the ester groups, and the ylidic moiety of both acyl oxygens are *anti* to phosphorus,[6] but the two ester groups maintain the typical Z-conformation, and the ethoxy oxygens can interact with cationoid phosphorus.[9]

$$Ph_3P = C(CO_2Et)_2 \quad (1)$$

Ylides stabilized by keto and ester groups have well-defined infrared signals due to carbonyl stretching;[2–5] for **2** they are 1601 and 1540 cm^{-1}, and for **3** they are 1711 and 1634 cm^{-1}.

We consider the structural factors that govern conformations of these disubstituted ylides in a solid and in a solution.

RESULTS AND DISCUSSION

Structures of Diketo-ylid

The structure of the *syn*- *anti*- diketo ylid **2a**, obtained earlier[5b] from a geometrical optimization with the HF 6-31G(d) basis set, agrees with

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that in the crystal.[6] Structures from the HF 6-311G(d) basis set also agree reasonably well with that determined by X-ray crystallography.[6] Geometries of the two conformers **2a** and **b** were compared earlier.[5b,6] Computed bond lengths are similar, but there are differences in bond and torsional angles involving the acyl groups. The ^{13}C NMR spectrum in the solid confirms that the two carbonyl groups are not equivalent,[5b,6] but the sharp ^{1}H and ^{13}C signals in solution require that here these groups are equivalent or are rapidly exchanging positions.[5] Chemical evidence[8] supports the first hypothesis, and we now consider computational and NMR spectral evidence.

The conformation of ylid **1**, R = Et, is the same in solid and solution, and chemical shifts of the keto moiety are compared with those of the diketo ylid **2** in solid and in solution.[5] The ^{13}C NMR chemical shifts of the keto CH_3CO group of **1** in $CDCl_3$ with the CH_3 group *anti* and the oxygen *syn* to phosphorus as in Scheme 2 are $\underline{C}H_3$, 29.7 ppm, and $C\underline{O}$ 195.4 ppm,[5a] and the corresponding ^{13}C chemical shifts for the diketo ylid **2** are as follows: $CDCl_3$: $\underline{C}H_3$, 30.6; $\underline{C}O$: 193.1 ppm; in the solid: $\underline{C}H_3$: 28.8; and 50.4 ppm; $\underline{C}$=O: 193.0 and 168.3 ppm.[5b] Comparison of these chemical shifts of the keto ester and diketo ylides (Table I) shows that in the solid diketo ylid, the upfield $\underline{C}H_3$ signal at 28.8 ppm is characteristic of $\underline{C}H_3$ *anti* to phosphorus, and the downfield $\underline{C}O$ signal at 193.0 ppm is characteristic of acyl oxygen *syn* to phosphorus **2a**. The chemical shifts of the diketo ylid in $CDCl_3$: $\underline{C}H_3$, 30.6 ppm, and $\underline{C}O$, 193.1 ppm, are evidence for the *syn-syn* conformer, **2b** in solution, but not in the solid.

As shown earlier,[5b] the *syn-syn* conformer **2b**, for an isolated molecule, should be preferred over the *syn-anti* conformer **2a** by 2.6 or 2.5 kcal.mole^{-1}, with the HF 6-31 G(d) and 6-311G(d) basis sets, respectively, and a conformer with one *syn*-oxygen and the other keto group out of plane by 90° is unfavored by a further 3.6 k.cal. mole^{-1}. The barrier to conformational interconversion should therefore be low in solution with some population of the minor conformer, and it appears that packing forces in the crystal control the differences in conformations of **2a,b**. The *syn* acyl oxygen interacts intramolecularly with phosphorus, and in the solid, both oxygens are close enough to phenyl groups of a nearby ylid for there to be intermolecular interactions.[6] As noted by Bachrach,[10] the use of more extensive basis sets than 6-31G(d) does not significantly improve computations on structures of stabilized ylides. An MP2//6-311G(d) computation gives the energetic difference between **2a** and **2b** as 2.5 kcal.mole^{-1}, and from B3LYP//6-31G(d) or B3LYP//6-311G(d) computations it is 2.6 kcal. mole^{-1}.

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Structures of Diester Ylid

Conformations of keto-ester and diketo ylides **1** and **2**, respectively, in the solid and in solution are governed largely by ylidic resonance with near planarity in the ylidic moiety and the stabilizing groups, and an interaction between an acyl oxygen and cationoid phosphorus. This generalization breaks down for the diethyl ester **3**, where, in the crystal, one carbethoxy group is significantly out of the ylidic plane and neither of the acyl oxygens are oriented toward phosphorus.[6]

In solution, the ^{1}H and ^{13}C NMR signals of diethyl ester **3** are sharp and typical of single, or rapidly interconverting conformers (Table I). However, the ^{13}C NMR signals in the solid show that the ester groups are in similar, but not equivalent, positions, which is consistent with X-ray crystallographic evidence on **3**.[6] We saw only a single $\underline{C}$=O signal, but it was distorted, and the expected two signals were not resolved, although we saw the expected two $\underline{C}H_2$ and $\underline{C}H_3$ signals. The P=$\underline{C}$ signals are doublets due to coupling with ^{31}P, and, as expected, the coupling constants differ in $CDCl_3$ and the solid.

Some of the NMR signals of crystalline **3** are similar to those of the keto ester **1**, R = Et,[5a] where ethoxy and acyl oxygens of the carboethoxy group are oriented respectively toward and away from phosphorus (Scheme 2), and it is understandable that there are similarities with the ^{13}C chemical shifts of the corresponding groups of **3** (Table I) in terms of the conformation in the crystal[6] (Figure 1). Chemical shifts for the ylidic carbons differ because of differences in resonance interactions between cationoid phosphorus and keto and ester groups. Some ^{13}C chemical shifts of diethyl ester **3** are similar in the solid and in solution (Table I), which is understandable because of the small estimated

TABLE I ^{1}H and ^{13}C Chemical Shifts of Diethyl Ester 3 and Diketo 2 in Solution and Solid and Ketoester 1[a]

Diketo **2**	C$\underline{H}_3$	C$\underline{H}_2$	$\underline{C}H_3$	$\underline{C}H_2$	P=$\underline{C}$	$\underline{C}$=O
$CDCl_3$	2.3 s	—	30.6 (6.3)	—	88.8 (102)	193.1 (7.9)
Solid	—	—	28.8, 50.4	—	71.6 (111)	193.0, 168.3
Diethyl ester **3**						
$CDCl_3$	0.83 t	3.84 q	13.1	57.6	51.9 (127)	166.9
Solid	—	—	13.2, 14.1	55.9, 58.4	50.6 (140)	164.5[b]
Keto ester **1a**[c]	0.63 t	3.70 q	14.1	58.7	70.9 (112)	168.1

[a]At 25°C, referred to TMS; values in parentheses are P-C coupling constants J, H_z.
[b]Distorted with a shoulder at 165.8 ppm.
[c]In $CDCl_3$.

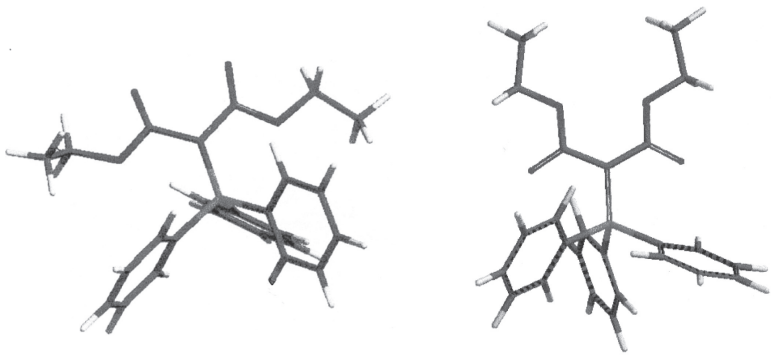

FIGURE 1 Computed structures of diethyl ester **3a** (*anti*-*anti*) as in the crystal **3b** (*syn*-*syn*). C1 is the ylidic carbon, carbonyl C2-O2 and O1 are to the right, and carbonyl C5-O4 and O3 are to the left in **3a**,[6] c.f. Table II.

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differences in energies for the various conformers as shown later and the probable mixture of equilibrating conformers in solution.

The conformation of **1** is apparently the same in solution and the solid,[4,5] with π-shielding of C$\underline{H}_3$ of the ethoxy group by *ca* 0.5 ppm, as compared with ethyl acetate.[11] The conformer of **1**, as in Scheme 2, is predicted to be preferred by 0.4 kcal mol^{-1} over that with the ester acyl oxygen *syn* to phosphorus with a 6-31G(d)//B3LYP optimization [the difference is 0.23 kcal. mol^{-1} from a 6-31G(d) optimization].

The C$\underline{H}_3$ chemical shift of **3** in $CDCl_3$ is 0.83 (Table I), and the π-shielding is slightly less than that of **1** [4,5a] probably because the effect is averaged over 6 rather than 3 hydrogens. It appears that in solution an ethoxy group of **3** can be oriented toward the face of a phenyl group, and we consider the significance of this observation in the differences in computed conformational energies discussed later.

Approximate structures were built for conformers differing in positions of the acyl oxygens relative to phosphorus: *syn*-*syn*, *syn*-*anti*, *anti*-*anti*, and *syn*-orthogonal with one acyl group constrained at a right angle to the ylidic plane. *Syn*-*syn* and *anti*-*anti* conformers are in Figure 1.

A structure was also built with Z-ester groups and torsional angles of the two C=O groups to the ylidic plane P1-C1-C2-O2 and P1-C1-C5-O4 of -149.2° and 170.4°, respectively, as in the crystal,[6] and no geometrical constraints on other parts of the structure. Geometrical optimizations were with the HF 6-311G(d) basis set, and the geometry is similar to that in the crystal (Table II). The constraints were removed and the structure relaxed, with a small change in energy and slightly different torsional angles (-165.5° and 162.2°) to

TABLE II Selected Bond Distances and Angles of Diethyl Ester 3 From Computation and X-Ray Crystallography[a]

	Computation		Crystallography[b]
P1-C1	1.74	(1.74)	1.748
C1-C2	1.46	(1.45)	1.453
C1-C5	1.45	(1.46)	1.440
C2-O2	1.19	(1.19)	1.214
C5-O4	1.19	(1.19)	1.214
P1-C1-C2	122	(122)	122.9
P1-C1-C5	120	(119)	117.8
C1-C2-C5	118	(118)	118.8
C1-C2-O2	127	(127)	125.9
C1-C5-O4	128	(128)	127.9
C1-C2-O1	112	(112)	112.9
C1-C5-O3	111	(111)	111.0
O1-C2-O2	121	(121)	121.2
O3-C5-O4	121	(121)	121.1
Torsion angles			
P1-C1-C2-O2	−149	(−165)	−149.8
P1-C1-C5-O4	170	(162)	170.8

[a]Lengths are in Å, and angles are in degrees. Computed values are with the torsional angles as in the crystal; values in parentheses are after removal of the torsional constraints.
[b] Ref.[6]

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the ylidic plane. Other distances and angles were almost unchanged. The conformation was very similar to that from initial optimization of the *anti*-*anti* conformer with HF 6-31G (d) or 6-311G(d) basis sets, and the structures were indistinguishable by eye.

Our geometrical optimization of **3** indicates that there should be favorable and unfavorable interactions involving anionoid oxygens. The estimated 02–04 distance between acyl oxygens is 2.87 (2.84) Å, and phosphorus ethyl oxygen distances are P1-O1, 2.99 (2.92) Å; P1-O3, 2.83 (2.85) Å. As shown in Table II; these distance are for the structure with the ylidic torsional angles constrained to be as in the crystal, and those in parentheses are with the constraint removed (Table II).

Energies of the various conformers relative to the computationally preferred *syn*-*syn* conformer are as follows: kcal.mole^{-1}: *syn*-*anti*, +1.4; *anti*-*anti*, +3.8, with torsional angles constrained to those in the crystal and +3.4 with the constraint removed; and *syn*-orthogonal, +4.8. These relative energies were estimated at the B3LYP//6-311G(d) level and are similar, with slightly smaller energy differences, to those estimated with the HF 6-31G(d) or 6-311G(d) basis sets. These calculations are

for individual molecules and do not allow for solvent or intermolecular interactions, but conformations of **1** and **2** have been shown to be insensitive to changes in solvent polarity or hydrogen-bond donation, which have only small effects on NMR spectra.[5a,5b] Two optimized structures of **3** are shown in Figure 1, but for all the optimized structures and in the crystal, the ester groups maintain the Z configuration. Crystal packing apparently forces the diethyl ester **3** to take up a conformation that does not provide optimum conjugation between P=C and C=O bonds.[6] Intramolecular interactions between cationoid phosphorus and anionoid oxygen should strongly favor conformations with acyl oxygens *syn* to phosphorus, but with carboalkoxy ylides the alkoxy groups can interact favorably with phosphorus, although probably less strongly than acyl groups. In crystalline **3**, there are evident interactions between ethoxy oxygens and cationoid phosphorus, and an interaction of an acyl oxygen and the phenyl group of a neighboring ylid.[6]

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Geometrical optimization does not provide correct conformations of **3** in solid or solution. Predicted energy differences for isolated molecules are small, and in the crystal packing forces, are very important. The predicted structures in Figure 1 indicate how, in the solid, the two ethoxy groups in **3b** could interfere with adjacent molecules.

There should also be steric effects in solution with possible interference between molecules. Molecular weights of these phosphonium ylides are ca 400, and at concentrations of 0.1–0.2 M typically used in obtaining NMR spectra intermolecular distances, they will not be very much larger than molecular cross sections. Forthermore, intermolecular interactions may not favor the *syn-syn* conformer as compared with the more compact *anti-anti* diethyl ester.

The compact geometry of the carbethoxy groups in crystalline **3** allows effective crystal packing and interactions between ethoxy oxygens and phosphorus. For an *anti-anti* conformer with both acyl groups strictly in the ylidic plane, acyl oxygens would be close enough to allow unfavorable dipole interactions,[6] which would be important if that conformer were dominant in solution. There are balances between a loss of ylidic resonance, due to out-of-plane conformations in the crystalline diethyl ester, favorable interactions between phosphorus and acyl oxygens, and crystal packing forces. The energy of a conformer with one acyl oxygen syn to phosphorus and the other in a plane orthogonal to the ylidic plane should approximate the barrier for the interconversion of conformers. These relatively small energy differences indicate that interconversion of the conformers should be rapid on the NMR time scale. The small energy difference between the *syn-syn* and *syn-anti* conformers, where ylidic resonance is maintained, indicates that rapidly equilibrating conformers of **3** may coexist in solution giving sharp NMR signals.

CONCLUSIONS

Phosphonium ylides stabilized by only one carbonyl or ester group typically show slow rotation about the ylidic bond on the NMR time scale, and it is reasonable to draw the classical structures as zwitterionic with an ylidic double bond and a C–P single bond.

The situation is different when two stabilizing groups are present and the rotation of one group with respect to the ylidic plane does not exclude resonance interactions involving the other. Computation with various basis sets indicates that these rotational barriers should be low, which is consistent with observation of sharp NMR signals in solution over a range of conditions. For the keto-ester ylides, structures in solution and the solid appear to be similar, but they differ for a diketo ylid. However, in all these compounds, the acyl residues are approximately in the ylidic plane, allowing optimum stabilization by resonance. The situation is different for the diethyl ester, where, in the crystal, one carboxyethyl group is twisted slightly, the other is significantly out of the ylidic plane, and the acyl oxygens are oriented away from phosphorus. In the various preferred ab initio optimized geometries of an isolated diethyl ester, at least one acyl oxygen is incorrectly oriented toward phosphorus, and both acyl groups are approximately in the ylidic plane. It appears that in the crystalline diester, interactions with adjacent molecules and packing forces more than offset the loss of interactions between anionoid acyl oxygens and phosphorus, and the decrease of resonance energy due to deviations from planarity. It is not reasonable to draw structures with a classical ylidic double bond. Computed bond lengths and angles are not very sensitive to conformation except when a group is constrained orthogonally to the ylidic plane as in interconversion of conformers. However, nonbonding distances and angles vary markedly for different conformers.

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EXPERIMENTAL

Synthesis

The diacyl ylid **2** was material described earlier.[5a] The diester **3** was prepared by transylidation through an already reported procedure.[6]

Spectra

^{1}H and ^{13}C NMR spectra in solution were monitored on Bruker DRX300 or Varian INOVA 500 spectrometers and were referenced to TMS. ^{13}C NMR spectra in the solid were monitored on a Bruker DRX300

spectrometer as described and were referenced to adamantane at 39.5 ppm with respect to TMS at 0 ppm.[5b] Infrared spectra were monitored on a Bruker IFS 56 FT spectrometer with a KBr disk and carbonyl stretching frequencies in cm^{-1}.

Geometrical Optimization

Calculations were made with Spartan 04-2 for Windows. In general, structures were built with acyl groups approximately in the ylidic plane, and geometries were optimized with the 6-311G (d) basis set, although some obtained with the 3-21G(d), and 6-31G(d) basis sets were similar. The structure of **3** with torsional angles as in the crystal was optimized by making successive STO-3G, 3-21G(d), 6-31G(d), and 6-311G(d) optimizations. Energies were from B3LYP//6-311G(d) computations.

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