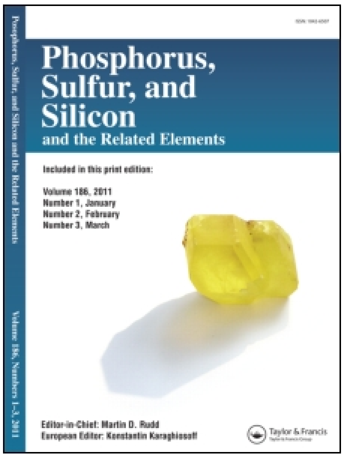

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Cyano Triphenyl Phosphonium Ylides Stabilized by Ester or Keto Groups: Computed Conformations and Crystal Structures

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The mixed stabilized triphenyl phosphonium ylides $Ph_3P{=}C(CN)CO\text{-}R$ and $Ph_3P{=}C(CN)COOR$, $R{=}CH_3$, C_2H_5, $CH(CH_3)_2$, 1a,c and 2a,b, respectively, have sharp ^1H and ^{13}C NMR signals, except for 2b in some conditions. Ab initio geometrical optimizations indicate that in the preferred conformer the acyl oxygen is syn-to phosphorus, with barriers to rotation about the ylidic bond of 15–18 kcal. mol^{-1}, and differences between the syn- and anti-conformers of ca. 4 and 11 kcal. mol^{-1} for the keto and ester derivatives, respectively. These energetic differences are not very sensitive to changes in the alkyl group, R, or the level of computation. The computed geometries indicate that the ylidic moieties are approximately planar with extensive electronic delocalization, as in crystalline 1a and 2a. The ^{13}C NMR signals of the ylidic carbons are shifted strongly up field, consistent with their anionoid character.

Keywords Conformational analysis; NMR spectra; phosphorus ylides; structural computations

INTRODUCTION

The conformations of phosphonium ylides stabilized by electron-withdrawing acyl groups depend on ylidic electronic delocalization and

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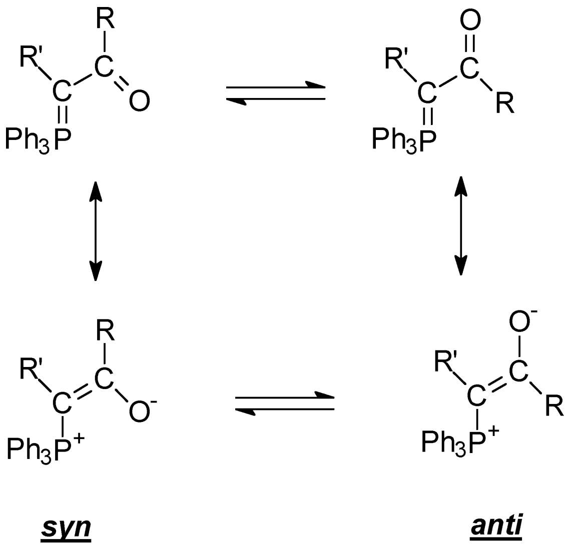
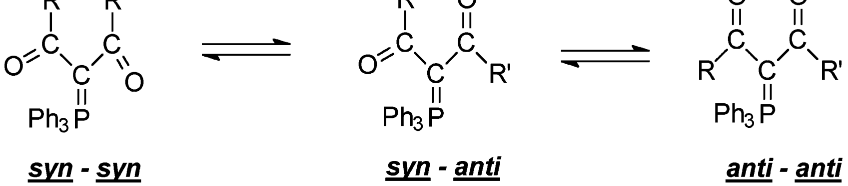


SCHEME 1 Conformations of stabilized phosphonium ylides. R=alkyl, alkoxy; R′=H, alkyl, keto, ester, CN.

on non-bonding steric and dipole-dipole interactions.[1,2] With one stabilizing keto or ester group, two conformers can sometimes be identified with a significant energy barrier to rotation,[3] as expected for the classical structure with an ylidic double bond n(Scheme 1). In general, interaction between cationoid phosphorus, P^+, and anionoid acyl oxygen, O^-, should favor the *syn*- conformer, e.g., **1a**.

A second ester or keto group lowers the barrier to conformational equilibration because rotation then does not completely eliminate electronic delocalization, and therefore allows conformers to equilibrate with low rotational barriers, as shown in Scheme for diesters with classical structures. They are defined as *syn* or *anti,* in terms of the orientation of the acyl oxygen with respect to phosphorus. The corresponding conformations can be written for diketo and keto ester derivatives.[4,5]

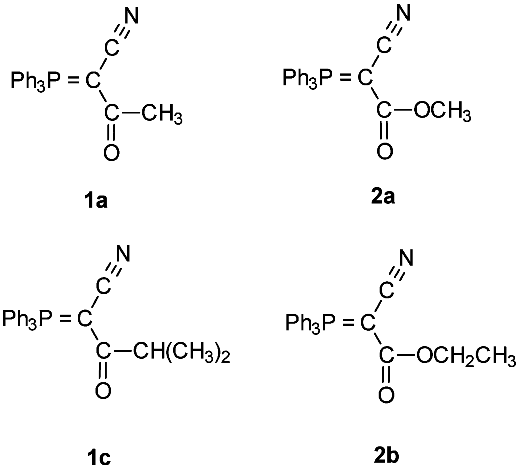


SCHEME 2 Conformational equilibration of diacyl ylides. R=R′=alkyl; R=R′=alkoxy; R=alkyl, R′=alkoxy.

In Scheme 2, we consider not only P—O interactions, which should be favorable, but also O—O interactions that may be unfavorable in diacyl ylides. In the crystal *anti*-alkoxy, or acyl groups may interfere with neighboring ylides; and, with some ylides, conformations differ in the solid and in solution.[5,6]

Electronic effects of the cyano group are similar to those of ester and keto groups, e.g., $\sigma^- = 0.90$, 0.87, and 0.68 for CN, COMe, and CO_2R, respectively,[7] and therefore cyano groups should behave like acyl groups in electronically stabilizing planar phosphonium ylides without significantly disfavoring conformational equilibration. The cyano group is linear, unlike keto and ester groups, and should not interfere sterically with other substituents. Phosphonium ylides stabilized by cyano groups are well characterized and are potentially useful promoters of polymerization.[8] We have examined ylides in solution with one cyano and one keto or ester group by monitoring their ^{1}H and ^{13}C NMR and their IR spectra, and by using ab initio calculations to estimate energy differences between the various conformers.[9] Structures are shown in Scheme, and those of the methyl keto and ester derivatives (**1a**, **2a**) were determined by X-ray crystallography, and we focus our discussion largely on the properties of these compounds. We did not obtain monocrystals of **1c** and **2b**.

Carboxylic esters are typically Z-conformers, as appears to be situation for ylidic esters,[10] and we have seen no exception to this generalization. Some cyano ylides have been isolated and fully characterized, but for the ethyl ester we could not obtain good crystals and the $C\underline{H}_3$ and $C\underline{H}_2$ ^{1}H NMR signals were broad at 25°C in several solvents and we



SCHEME 3

discuss this behavior separately (see Appendix). With this exception, all these cyano ylides gave sharp NMR signals in solution in all conditions.

Recent X-ray crystallography shows that in the methyl keto and methyl ester cyano derivatives the acyl oxygen is, as expected, *syn*- to phosphorus.[4,5,11]

RESULTS AND DISCUSSION

Except for the cyano ethyl ester (**2b**), ^{1}H NMR signals in the ylidic moiety are very simple. We saw no indication of π-shielding of the methyl hydrogen, $C\underline{H_3}$, in an ethyl or isopropyl derivative, as had been seen in other ylides where the alkyl group is oriented towards phosphorus,[4,5] and we conclude that in solution the acyl oxygen in keto and ester derivatives is preferentially oriented towards phosphorus, i.e., in cyano esters the alkoxy group is *anti*- to phosphorus, as in the crystal.

The ^{1}H and ^{13}C NMR signals for several ylides are in Table I. The ^{13}C ylidic signals are doublets due to coupling with phosphorus and are shifted markedly up field, as compared with other ylides,[8,12] consistent with the strong anionoid character at this position. In this article, ylides were written as zwitterions,[8] which fit the strong anionoid character of the ylidic carbon.

Except for the ethyl ester, Appendix, NMR signals are typical of stabilized ylides (Table I). The ^{13}C NMR spectrum of the ethyl ester was obtained with, and without, ^{1}H decoupling. Proton decoupling was use with the other ylides, and the signals had the expected multiplicity for single conformers. The ^{13}C carbonyl signals are weak, and are not always observed with lower field NMR spectrometers.

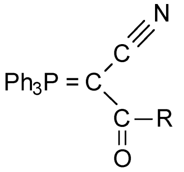
Broad ^{1}H signals were observed with the ethyl ester, **2b**, in some conditions (Appendix), but ^{13}C signals in $CDCl_3$ were sharp.

The assignments of the ^{13}C NMR signals of the *ortho, meta* and *para* carbons of the phenyl groups follow those given for other triphenyl phosphonium ylides by Gray,[13] and Albright et al.,[14] who gave the sequence for P-C coupling constants as *meta*>*ortho*>*para*, although typically values of these parameters decrease with increasing numbers of intervening bonds.[15a] For example, Schraml et al., assigned ^{13}C NMR signals of cyclohexylphenyl phosphines and concluded that the aromatic P-C coupling constants followed the sequence *ortho*>*meta*>*para*.[15b] However, conclusions regarding structures of the ylidic moieties are not affected by questions regarding assignments of ^{13}C signals of the phenyl groups.

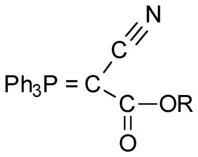
Structural Computations

Geometries of cyano phosphonium ylides with *syn*- and *anti*-conformations and with the acyl group orthogonal to the ylidic plane

TABLE I ^{13}C, ^{1}H and ^{31}P Chemical Shifts^{a} of Keto Cyano and Ester Cyano Ylides 1 and 2, in Solution. 1a, R=CH_3; 1c, R=$CH(CH_3)_2$; 2a, R=CH_3



1



2

Position	**1a**[8]	**1c**	**2a**
R=CH_3	27.9 s	— [2.36,s]	c51.4 [3.64,s]
C=O	194.9 (3.7)	201.3 (3.0)	170.0
OCH_2-CH_3	—	—	—
OCH_2-CH_3	—	—	—
R=$CH(CH_3)_2$	—	19.2 s [1.14 d]	—
R=$CH\ (CH_3)_2$	—	36.7 (6.9) [3.30, m]	—
$C\equiv N$	123.4 (16.7)	122.7 (16.7)	121.7 (15.4)
P=C	49.0 (127.8)	48.7 (140.6)	31.4 (141.7)
ipso	123.5 (93.6)	123.6 (93.6)	123.3 (94.5)
ortho	133.9 (10.3)	133.5 (10.2)	133.6 (10.3)
meta	129.6 (11.3)	129.1 (12.9)	129.0 (12.8)
para	133.4 (2.9)	132.9 (2.9)	133.1 (2.9)
^{31}P	20.7	20.6	22.8

[a] At 25°C in $CDCl_3$, chemical shifts referenced to TMS or external 85% H_3PO_4

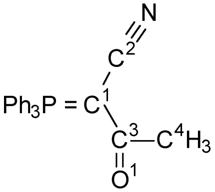
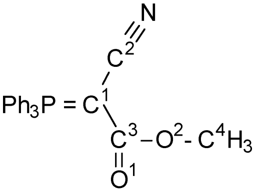
[b] Values in parentheses ( ) are P-C coupling constants J, Hz; and those in square brackets [ ] are ^{1}H chemical shifts.

were optimized, generally with the 6-31G(d) basis set.[9] The conformer with an orthogonal acyl group should be structurally similar to the barrier to interconversion of the *syn-* and *anti-* conformers.

Energies were estimated with B3LYP/6-31G(d) or MP2//6-31G(d) computations.[9] The triphenyl phosphorus group is approximately tetrahedral in the crystal and in solution the phenyl groups are equivalent on the NMR time scale. Our computations are for static structures and we did not use them in defining positions of the phenyl groups.

Some geometries of *syn*-conformers are given in Table II with comparison with X-ray crystallographic data[11] (the numbering is that used in displaying the crystallographic data) and relative energies for the conformers with the acyl oxygen *anti* to phosphorus are given in

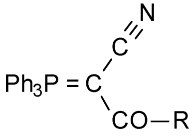
TABLE II Selected Computed and X-Ray Geometric Parameters (Å,°)[a] for (Acetylcyanomethylene) Triphenylphosphorane (1a) and (Methoxycarbonylcyano Methylene) Triphenylphosphorane (2a)

	 **1a**		 **2a**
Bond lengths (Å)			
P-C^{1}	1.75 [1.744(2)]	P-C^{1}	1.74 [1.730 (3)]
C^{1}-C^{3}	1.44[1.410 (3)]	C^{1}-C^{3}	1.44 [1.427 (4)]
C^{3}-O^{1}	1.22[1.239 (3)]	C^{3}-O^{1}	1.21 [1.212 (4)]
C^{3}-C^{4}	1.52 [1.514 (3)]	C^{3}-O^{2}	1.33 [1.350 (4)]
C^{1}-C^{2}	1.42 [1.410 (3)]	O^{2}-C^{4}	1.41 [1.432 (4)]
C^{2}-N	1.14 [1.150 (3)]	C^{1}-C^{2}	1.42 [1.407 (4)]
		C^{2}-N	1.14 [1.145 (4)]
Bond angles (°)			
C^{2}-C^{1}-P	118 [120.3 (17)]	C^{2}-C^{1}-P	121 [120.3 (2)]
C^{2}-C^{1}-C^{3}	121 [121.8 (2)]	C^{2}-C^{1}-C^{3}	121 [120.8 (3)]
C^{3}-C^{1}-P	118 [117.9 (17)]	C^{3-}C^{1}-P	118 [118.8 (2)]
C^{1}-C^{3}-O^{1}	121 [121.6 (2)]	C^{1}-C^{3}-O^{1}	124 [126.0 (3)]
C^{1}-C^{3}-C^{4}	119 [119.0 (2)]	O^{1}-C^{3}-O^{2}	122 [122.5 (3)]
O^{1}-C^{3}-C^{4}	121 [119.4 (2)]	O^{2}-C^{3}-C^{1}	114 [111.5 (3)]
Torsion angles (°)		C^{3}-O^{2}-C^{4}	118 [117.0 (3)]
P-C^{1}-C^{3}-O^{1}	-4.2 [-3.3 (3)]	P-C^{1}-C^{3}-01	-4.1 [4.4 (5)]
Contact distances (Å)			
O^{1}—P	2.94 [2.928 (2)]	O^{1}—P	2.98 [3.022 (2)]
		O^{2}—C^{2}	2.71

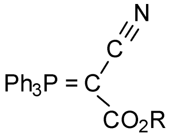
Geometrical optimizations with the HF6-31G(d) basis set. X-ray crystallographic values are in parentheses with the estimated standard deviations.[11] Positions are numbered as in **1a** and **2a**.

Table III. Computed bond lengths and angles for the *anti-* and orthogonal conformers are similar to those for the preferred *syn*-conformers. The energetic differences (Table III) are due largely to nonbonding interactions between phosphorus and an oxygen atom and dipole interactions involving the cyano and keto or ester groups. Natural Atomic Charges in the ylidic moiety of the *syn*-conformers were generally estimated for the B3LYP/6-31G(d) structures, but similar qualitative results were obtained at the HF 6-31 G(d) level.[16]

TABLE III Computed Relative Energies of Cyano Keto Ylides (1) and Cyano Ester Ylides (2)[a]



1



2

R=methyl	*Anti*	Orthogonal	*Anti*	Orthogonal
HF6-31G (d)	13.0	16.8	3.5	16.2
B3LYP	12.0	17.4	3.2[b]	14.6[b]
MP2	10.7	16.5	—	—
R=ethyl				
HF6-31 G (d)	13.2	18.0	3.1	16.4
B3LYP	12.0	18.5	3.4[C]	14.9[C]
R=isopropyl				
HF6-31 G (d)	14.1	17.4	3.5	16.5
B3LYP	12.8	—	3.4	14.9

[a] Computed energies, kcal.mol^{-1}, relative to those of the preferred *syn-* conformer; [b] relative values with BLYP are 5.0 and 13.8; and [c] relative values with LMP2 are 4.5 and 12.6.

The *syn-* conformers are predicted to be energetically preferred for all these cyano derivatives as isolated molecules, as in the crystal.[11] The energy differences between *syn-* and *anti*-conformers are predicted to be significantly higher for the keto than for the ester derivatives (Table III), probably because in the esters the favorable interaction between phosphorus and a *syn-* acyl oxygen is replaced by an interaction with the alkoxy group, and this compensating interaction is absent in the keto derivatives. However, these phosphorus-oxygen interactions disappear in the orthogonal conformers, and the computed energy differences between them and the *syn-* conformers are similar for the keto and ester derivatives (Table III). The computed energy differences between the *syn-* and *anti-* conformers are *ca.* 4 and 13 kcal. mol^1 for the cyano ester and keto derivatives, respectively, and estimated rotational barriers are *ca.* 16 kcal.mol^1 for the keto and slightly lower for the ester derivatives. These energy differences indicate that only the *syn*-conformer should be observed in the present conditions. Predicted relative energy barriers for interconversion of *syn-*, *anti-,* and orthogonal conformers of keto and ester cyano ylides differ from those for stabilized ylides without a cyano group in several respects.[5]

For monostabilized ylides energy barriers for interconversion are such that both *syn* and *anti* conformers can be identified in some cases.[3] For destabilized ylides with keto or ester groups, conformational barriers are low and for some ylides conformations differ in the solid and in solution.[5,6] The derivatives examined in the present work with their linear cyano groups have behaviors intermediate between those of the other ylides, in that energy barriers for interconversion are higher than for diketo or diester derivatives with two trigonal substituent groups. Only one conformer of cyano ylides is detected and it always has the acyl group *syn* to phosphorus and in the ylidic plane. We note that writing structures of stabilized ylides with a classical ylidic double bond is reasonable for some, but not all, stabilized ylides.

Structural Geometries

Geometries of the preferred *syn* conformers in the cyano derivatives are as expected for structures with extensive electronic delocalization, but in the diesters *anti-* conformers are not strongly disfavored, and are often dominant in the crystal,, although not necessarily so in solution.[5,6] Computed bond lengths and angles are almost unaffected by a change in the alkyl groups in these keto and ester derivatives and torsional angles are as expected for ylidic structures with extensive electronic delocalization.[1–6] The non-bonding P—O distances in the cyano derivatives are similar to those for other *syn-* acyl groups and the ylidic and acyl carbons are approximately trigonal, except for the methyl ester where the O^2—C^3—C^1 bond angle is low in the crystal and is predicted to be low for an isolated molecule (Table II). There is probably a favorable dipole interaction in this ester between the cyano and methoxy groups and the estimated C^2—O^2 distance is ca. 2.71 Å, and so on. In considering physical properties of these cyano ylides, we give emphasis to the two compounds for which we could obtain monocrystals allowing comparison of computed geometries of isolated molecules with geometries in the crystal.

Partial Atomic Charges

The concept of partial atomic charge is uncertain theoretically, and values depend on the assumptions involved in the calculations. We estimated Natural Charges, which are numerically higher than the Mulliken Charges, due to differences in the assumptions involved in the estimations, but comparison of values at different positions is qualitatively useful.[16,17]

Phosponium ylides are nonionic, but they have strong dipoles. Values of Natural Chargesare insensitive to alkyl substituents, but differ slightly for *syn* and *anti* groups relative to phosphorus. They are, for the methyl keto, **1a**, and ester, **2a**, *syn* derivatives, from B3LYP//C-31G(d) computations: methyl keto: P, 1.738; C^1, −0.816; C^2, O.261; N, −0.376; C^3, 0.541; O, −0.640, and methyl ester; P. 1.741; C^1, −0.839; C^2, 0.275; N, −0.377; C^3, 0.797; O1, −0.678; O2, -0.538. This numbering is as for the crystals (Table II). Values for the methyl and isopropyl derivatives are very similar, within the second decimal place, data not shown, and numerically slightly higher charges were estimated by using the 6-31G(d) basis set, but trends are as shown above. The ^{13}C chemical shifts, and, in particular, the up field values for the ylidic C^1 are consistent with these estimated atomic charges. The sequences of estimated atomic charges for the *anti* conformers are similar to those given here, but differ for the orthogonal conformers where electronic delocalization is precluded. These values are not shown because we have no evidence on the physical properties of these ylides, which should not exist in the present conditions.

The ylidic carbon is predicted to be strongly anionoid, which fits the marked up field ^{13}C NMR chemical shifts and accords with the views of Kobayashi *et al.*, who write zwitterionic structures for stabilized phosphonium ylides.[8] They observed the following ^{13}C NMR signals for the dicyano triphenylphosphonium ylide with the following chemical shifts, δ, ppm and coupling constants, J, Hz: ylidic C, 5,5, $^1J_{P-C}$ 144.2 ; CN, 121.9, $^2J_{P-C}$ 93.2 (it appears that some assignments were misplaced in the original paper). These up field chemical shifts are reasonable in terms of the following Natural Charges from an HF 6-311G (d) basis set geometry: P 1.76; C −0.93; CN 0.35; CN −0.44.

Conformations of Diester and Cyano Stabilized Phosphonium Ylides

In a hypothetical diester with acyl oxygen *syn* to phosphorus, there should be in a planar ylide, interference between two *anti* alkoxy groups, and in a crystal between them and adjacent molecules. These interferences will be present, but to a lesser extent, in diketo and keto ester phosphonium ylides. Consideration of *ab initio* calculations consistently indicates that interactions between cationoid phosphorus and anionoid acyl oxygen should make the *syn-syn* conformer the preferred diester structure, but, so far as we know, it never is, at least in the crystal.[5] It appears that *ab initio* optimizations of static structures of individual molecules do not allow for the unfavorable interactions between bulky, anionoid, atoms of groups in *anti-* positions in planar ylides, which can

TABLE IV Carbonyl and Cyano Stretching Frequencies of Cyano Keto and Cyano Ester Ylides[a]

Ylide	**1a**[8]	**1c**	**2a**	**2b**
ν(CO), cm^{-1}	1584	1578	1650	1645
ν(CN), cm^{-1}	2172	2174	2179	2177

[1] IR spectra in a KBr disk.

not be neglected, relative to those due to electronic interactions, but are relieved by modest rotations out of the ylidic plane.[6]

These unfavorable steric and dipolar interactions disappear when one trigonal acyl group is replaced by the linear cyano group. The acyl groups in keto and ester cyano ylides are strongly conjugated with the ylidic moiety, as shown by geometries in the crystal, computed geometries and IR stretching frequencies (Table IV). However, the cyano bond lengths are similar to those in simple alkyl cyanides, where electronic delocalizations should be relatively unimportant. It appears that inductive electron withdrawal by CN has a major effect on ylidic stabilizations consistent with values of partial atomic charges at cyano and acyl groups.

CONCLUSIONS

The spectroscopic and computational evidence on cyano, keto, and ester phosphonium ylides indicates that, for isolated molecules, conformers with the acyl group *syn* to phosphorus should be dominant, with essentially no contribution from the *anti*-conformers. Except as noted, ^{1}H NMR signals are sharp. Computed geometries are as expected for near planar ylides with extensive electronic delocalization, and for the methyl derivatives computed bond lengths and angles are similar to those in the crystal.

Comparisons of the crystallographic and computational evidence indicate the marked differences between ylides with a linear cyano group and two trigonal acyl groups.

EXPERIMENTAL

Synthesis

Cyano keto ylide **1a** is prepared by transylidation from cyano methylene triphenylphosphorane.[8] Cyano esters **2a** and **2b** had been prepared earlier by reaction of methyl and ethyl cyanoacetate, respectively, with dihalo triphenylphosphine in the presence of triethyl amine.[18] Cyano isopropylketo **1c** is synthesized as follows: A solution of isobutyryl chloride (10 mmol) in dry benzene (6 ml) is added slowly, at 25°C, to cyano methylenetriphenylphosphorane[19] (20 mmol) in dry benzene (55 ml) under an inert atmosphere. The stirred solution is left at room temperature for 8 h. A white solid of cyano methyltriphenylphosphonium chloride is separated by filtration and most of the solvent is removed by rotary evaporation and the remaining solution, about 15 ml, is diluted with petroleum ether 30–60°C to precipitate **1c**, which is crystallized from ethanol.

Compound 1c

Yield 78%, m.p. 182–183°C; ν_{max}(KBr)/cm^{-1}: 2174 (CN), 1578 (CO). Anal. Calcd. for $C_{24}H_{22}NOP$ (371.4): C, 77.61; H, 5.97; N: 3.77. Found: C, 77.90; H, 5.99; N, 3.78.

Elemental analyses were performed with a Fisons EA 1108 analyzer.

Spectra

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker DRX 300 or Varian INOVA 500 spectrometers and are referenced to TMS or external 85% H_3PO_4. ^{13}C NMR spectra were generally obtained with ^{1}H decoupling, but for **2b** ^{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 cyano and carbonyl stretching frequencies in cm^{-1}.

Structural Optimization

Calculations were made with Spartan 04 or 06 for Windows (Wavefunction) software. Geometries were optimized, generally with the HF 6-31G(d) basis set, although almost identical results were obtained with the HF 6-311G(d) basis set. Except where specified energies and atomic charges were estimated by DFT, B3LYP, with geometries obtained as above.

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APPENDIX

The CH_3 and CH_2 ^{1}H NMR signals of the cyano ethyl ester, **2b**, are broad singlets in $CDCl_3$ at 25°C, and in C_6D_6, and $DMSO_{d-6}$, although ^{1}H signals of the phenyl groups are similar to those in other triphenyl phosphonium ylides. Hydrogen bonding with $CDCl_3$ seems improbable, because broadening is independent of solvent at 25°C.

TABLE V Chemical Shifts of the Cyano Ethyl Ester Ylide, 2b[a]

			Aliphatic groups				
$\underline{C}H_3$	$C\underline{H}_3$	$\underline{C}H_2$	$C\underline{H}_2$	$\underline{C}{=}O$	$C{\equiv}N$	$\underline{C}{=}P$	^{31}P
14.9q,131[b]	1.25t	59.9t,148[b]	4.07q	170	121.9d,15.4[c]	31.1d,140[c]	22.9
			Aromatic carbons				
Ipso	Ortho		Meta			Para	
123.7,93,5[c]	129.2,140[b], 12.8[c]		133.8, 140[b], 10.1[c]			133.2, 140[b], 2.9[c]	

[a] ^{13}C and ^{31}P chemical shifts, δ ppm, are in CDCl$_3$ at 25°C and ^{1}H chemical shifts, δ ppm, are in CD$_2$Cl$_2$ at −14°C; [b] ^{1}H coupling, J Hz; and [c] ^{31}P coupling, J Hz.

Another possibility is ylidic association, but signals are not sensitive to concentration, although in DMSO$_{d-6}$ the $C\underline{H}_3$ and $C\underline{H}_2$ ^{1}H signals sharpen with increasing temperature. At 55°C the $C\underline{H}_3$ signal is a singlet, but the CH$_2$ signal is a quartet, and at 75°C and 90°C the $C\underline{H}_3$ signal is a sharp triplet and the $C\underline{H}_2$ signal is a well resolved quartet. Traces of acid can cause problems with NMR spectra in CDCl$_3$, but at 25°C signals were broad, even though NaHCO$_3$ crystals were used to remove adventitious acid. Broad signals were also observed in CDCl$_3$ (Merck, Darmstadt) stabilized with silver, but the other NMR spectra were obtained in deuterated solvents from Aldrich and we saw no effect of the silver stabilizer.

The original observations on ^{1}H NMR spectra in various solvents were made at 300 and 500 MHz, and at 500 MHz in CD$_2$Cl$_2$ and 25°C both $C\underline{H}_3$ and $C\underline{H}_2$ signals are broad, the former is not well defined, and there is a minor, ill defined, shoulder at 0.8 ppm. We used CD$_2$Cl$_2$ rather than CDCl$_3$ because it would have allowed us to reach lower temperatures, had that been desirable. At −14°C both the $C\underline{H}_3$ and $C\underline{H}_2$ signals were sharp and well defined with the appropriate multiplicities, $C\underline{H}_3$, $\delta = 1.254$ ppm, t, J = 7 Hz; $C\underline{H}_2$, $\delta = 4.065$ ppm, q, J = 7 Hz. There were also very weak unidentified broad signals, at 0.462 and 3.766 ppm. There was no indication of broadening of the ^{1}H aromatic signals in the various solvents.

The ^{13}C NMR spectra in CDCl$_3$, with and without ^{1}H decoupling, had no additional signals above the noise level, and there were no signals of an organic impurity in detectable amounts.[20] The ^{13}C signals were well defined and, with and without ^{1}H decoupling, and had the expected multiplicities and coupling constants (Table V), although the acyl carbon was a broadened singlet which is not unusual in these acyl phosphonium ylides. We were unable to obtain good quality crystals with this derivative, and therefore, we did not use it extensively in the other experimental work.

Sharp NMR signals with the expected multiplicities were obtained with the other cyano ylides discussed here. We do not know the cause of line broadening of ^1H signals of the cyano ethyl derivative **2b**. It is possible that adventitious water interacts with this polar cyano ylide, although we did not see this behavior with other stabilized ylides examined in the course of this, or other work.