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[(Diphenoxyphosphinyl)methylidene]triphenylphosphorane—the double P+-stabilised carbanion: a crystallographic, computational and solution NMR comparative study on the ylidic bonding☆

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Abstract—The crystal and molecular structure of the title compound (**1**) was established by an X-ray diffraction analysis. Some geometrical parameters including a slightly pyramidal shape around its ylidic C_β-atom were determined (*trans*-bent type conformation), providing evidence for a strong electron delocalisation in the $P_\alpha C_\beta P_\gamma O_\delta$ backbone. The charge density redistribution within this molecular unit and its other fully optimised geometries was evaluated in ab initio MO calculations using both the HF and DFT (B3LYP) formalism, which supported such a concept. As a result, the double zwitterionic form (structure **C**) was suggested as the best description of **1**. The absence of an experimentally NMR observable $^2J_{P\alpha-C\beta-H\beta}$ coupling was tentatively rationalised in terms of fast pyramidalisation of the C_β-anionic site. Crystallographic and solution NMR data for ylide **1** were compared with those reported for the other mesomerically stabilised Wittig-type reagents and structurally related anionic species. It was concluded that all aforementioned systems have almost identical P-ylidic bonding most likely governed mainly by very strong electrostatic interactions, with a small contribution of negative hyperconjugation.

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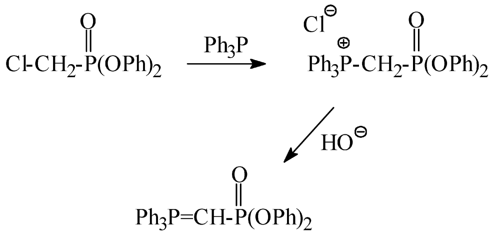
1. Introduction

The phosphonium ylides[2] [(alkylidene)phosphoranes] stabilised by a phosphonate group have found a widespread application in the Wittig synthesis of numerous phosphorus-analogues[3] of bioactive compounds like sugars[4] or nucleosides,[5] including those of antiviral activity.[6] The first discovered and till now the most important example of such air-stable Wittig reagents is [(triphenyl-λ^5-phosphanylidene)-methyl]-phosphonic acid diphenyl ester (**1**), originally prepared by Jones et al.[4a] according to the Scheme 1 (salt method).[7] This compound has been explored to a great extent in stereoselective Wittig condensation with relevant aldehydes to afford systems mentioned above, exclusively via the (*E*)-α,β-unsaturated alkylphosphonates.[5e] The detailed IR[8] and UV[9] spectroscopic investigations of phosphorus ylide (P-ylide) **1** were carried out, as well as routine ^{1}H NMR[4a] and EI-MS[4a,10] measurements. However, until now neither ^{13}C nor ^{31}P NMR solution spectra of **1** were examined, and no studies were described in the literature on the crystal or molecular structure of this phosphono-substituted triphenylphosphonium ylide.



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Scheme 1. Synthesis of ylide **1**.

In the present paper we would like to report the results of joint investigations in this field,[11] involving X-ray crystallography[11a] and ab initio MO calculations (gaseous phase). The latter were carried out both for the solid-state phase of ylide **1** (single-point, high-level approach)[11b] and for its

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☆ Physical image vs structure relation, Part 10. For Parts 8 and 9, see Ref. 1.

Keywords: hyperconjugation; hypervalent elements; resonance; theoretical studies.

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other fully optimised geometries, obtained with the 6-31G** basis set using the Hartree–Fock as well as the DFT formalism. Moreover, multinuclear (^{1}H, ^{13}C, ^{31}P) magnetic resonance spectroscopy studies of **1** were performed in solution.

Our results were confronted with those reported for the other Wittig-type reagents and structurally similar phosphorus-based anionic species, including related crystal structures retrieved from the Cambridge Structural Database (CSD).[12] A comparative study on the 'structure versus spectral data (mainly NMR)' relationship concerning such systems has not been published to date. Moreover, especially interesting from a viewpoint of stereoelectronic interactions in ylides as potentially hypervalent molecules,[13] two as yet controversial bonding issues, i.e. formally double P=C and P=O bonds,[14,15] have been set in opposition to each other in molecule **1** under study.[7] At least potentially then information on both and the chemical (ylidic) bonding, in general, might be forthcoming.

2. Results and discussion

2.1. Crystal structure investigations

The results of a single-crystal X-ray structure analysis of ylide **1**[11a] are gathered in Table 1. A co-ordination sphere around the central atom in phosphonate group [atom P(1)] is best described as the distorted trigonal pyramid, where the basal plane is defined by oxygens O(1), O(2) and O(3). An adjacent ylidic carbon atom C(1) with an almost planar configuration (vide infra) is located on an apex of this pyramid, while the tetra-co-ordinated phosphorus atom P(2) occupies the centre of a second, slightly distorted tetrahedral array of substituents. There is approximately threefold rotational symmetry about an axis defined by the bond P(2)–C(1) (or $P_{\alpha}-C_{\beta}$), resulting in the propeller-like arrangement of phenyl groups around phosphorus P(2); all Ph rings are planar within experimental error. The molecular structure of ylide **1** resulting from an X-ray data analysis is shown in Figure 1.

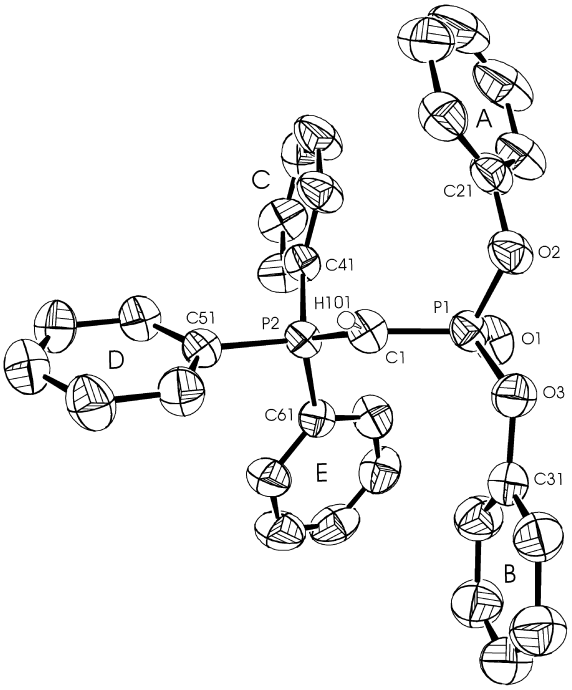


Figure 1. ORTEP representation of **1** showing atom and Ph ring labelling schemes; thermal ellipsoids are drawn at the 40% probability level. Only H atom at C(1) is shown.

The established bond angles involving the *ipso*-C atoms in three Ph ligands at P(2) [C_i-P-C_j of 105.80(12)°, on average] are considerably smaller than corresponding mean angle in $Ph_3P^+-C(sp^3)$ fragments of phosphine complexes [109.08(99)° (CSD search[16] including 79 unique fragments) or 109.04(1.80)° (new search)[17]], yet they are within the range found for a typical phosphonium ylide (101–107°).[14] Consequently, bond angles C(1)–P(2)–C(*n*1) (where *n*=4–6) are more opened than related angles in $Ph_3P^+-C(sp^3)$ moieties [112.91(0.12)° vs 110.33(1.17)°[16] or 109.86(2.14)°[17]]; the typical 'P-ylidic' value ranges from 110 to 118°.[14] The aforementioned results are in good agreement with an expected participation of the π-type orbital interaction between atoms C(1) and P(2) of the ylidic bonding, described as negative hyperconjugation.[13–15,18] Such a back-bond interaction is believed to transfer electron density from the filled nonbonding p orbital of the carbanion [C(1) in **1**] towards the area of vacant antibonding acceptor orbitals (σ*) of the single $P_{\alpha}-C_{ipso}$ bonds,[14,19] giving rise to

Table 1. Important bond distances (Å), bond angles (°) and dihedral angles, including angles between the best planes for the Ph rings (°), determined for **1**

P(1)–O(1)	1.4585(19)	C(1)–P(1)	1.690(3)	P(2)–C(51)	1.807(2)
P(1)–O(2)	1.6067(19)	C(1)–P(2)	1.698(3)	P(2)–C(61)	1.813(3)
P(1)–O(3)	1.6134(18)	P(2)–C(41)	1.809(2)	C(1)–H(101)	0.89(3)
O(1)–P(1)–C(1)	116.0(1)	C(1)–P(1)–O(3)	109.6(1)	C(41)–P(2)–C(51)	106.70(12)
O(1)–P(1)–O(2)	114.1(1)	P(1)–C(1)–P(2)	127.09(16)	C(41)–P(2)–C(61)	104.40(12)
O(1)–P(1)–O(3)	114.1(1)	C(1)–P(2)–C(41)	116.05(13)	C(51)–P(2)–C(61)	106.31(12)
O(2)–P(1)–O(3)	90.4(1)	C(1)–P(2)–C(51)	106.58(12)	P(1)–C(1)–H(101)	115.4(21)
C(1)–P(1)–O(2)	109.8(1)	C(1)–P(2)–C(61)	116.09(13)	P(2)–C(1)–H(101)	117.2(22)
P(1)–C(1)–P(2)–C(41)	−68.1(2)	O(1)–P(1)–C(1)–P(2)	−1.2(3)	B–C	7.6(1)
P(1)–C(1)–P(2)–C(51)	173.3(2)	C(1)–P(1)–O(2)–C(21)	−65.9(2)	B–D	87.8(1)
P(1)–C(1)–P(2)–C(61)	55.1(2)	C(1)–P(1)–O(3)–C(31)	69.9(2)	B–E	67.1(1)
C(41)–P(2)–C(1)–H(101)	105.2(24)	A–B	55.0(1)	C–D	80.7(1)
C(51)–P(2)–C(1)–H(101)	−13.4(24)	A–C	59.2(1)	C–E	64.7(1)
C(61)–P(2)–C(1)–H(101)	−131.6(24)	A–D	50.4(1)	D–E	88.5(1)
O(1)–P(1)–C(1)–H(101)	−174.6(24)	A–E	45.8(1)		

For the labelling of the Ph ring planes, see Fig. 1.

substantial away from an idealised local C_{3v} symmetry at this phosphorus centre.

A planarity of the other important part of ylide **1** molecule, i.e. fragment involving C(1), can be judged by three criteria given by Denmark and co-workers:[20] (1) the sum of all bond angles around C(1) is ca. 359.7°, (2) the distance of C(1) from the P(1)–H(101)–P(2) plane (*d*) is 0.043(3) Å, and (3) the out-of-plane bending, defined as an angle γ (δ[21] or τ[18]) between the C(1)–P(2) bond vector and the C(1)–H(101)–P(1) plane, is 5.3°. So, some deviation from planarity was really found at ylidic carbon C(1) toward a *trans*-bent type conformation,[14,19a] possessing a slightly pyramidal atom C(1) and probably the Ph ring C [with an *ipso*-C(41) atom; see Fig. 2] as an unique-type substituent (R_u),[14,22] observed in nonstabilised (reactive) phosphonium ylides. The length of the aliphatic P(2)–C(41) bond is, however, only 1.809(2) Å vs typical P-ylidic value of 1.82–1.83 Å.[14] Consequently, the second candidate for R_u in **1** is the ring E with the P(2)–C(61) bond length of 1.813(3), as both related C(1)–P(2)–C_{ipso} angles are wider and equal to 116.1(1)°. It is noteworthy that all three P(2)–C(*n*1) distances (*n*=4–6) are elongated with respect to the mean distance P–C_{ipso} in Ph_3P^+–C(sp^3) fragments [1.809(1) Å (weighed av.) vs 1.794(11)[16] or 1.796(14)[17] Å]. Thus, it can be assumed that both tetra-co-ordinate, potentially pentavalent P(V) atoms are (to a first approximation) sp^3 hybridised, from pure geometrical reasons. Instead, from the pyramidality observed at C(1) one can formally deduce for this atom a hybridisation intermediate between sp^2 and sp^3. A significance of the phosphorus d atomic orbitals participation is closely associated with this problem, since planar sp^2 geometry for the ylidic carbanionoid atom was believed in classical approach to optimise the $p_{\pi}-d_{\pi}$ overlap. However, this argument was later rejected, since the short 'P=C' distances found in P-ylides can be accounted for simply by a polarisation effect of the d orbitals or even by considering solely the Coulombic forces.[22] A present understanding of ylidic bonding is outlined in the recent theoretical work by Dobado et al. on such prototype molecular objects.[18] Indeed, the strength of these covalent bonds was found as governed mainly by very strong electrostatic interactions, with only small contribution of negative hyperconjugative π back-donation (vide supra).

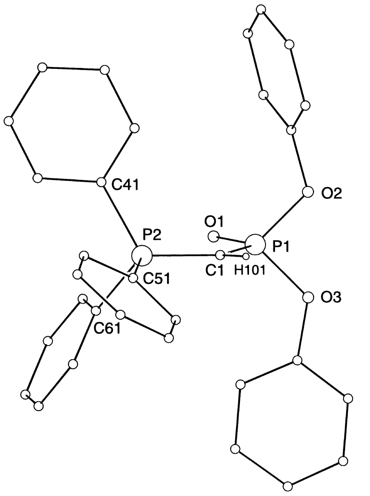
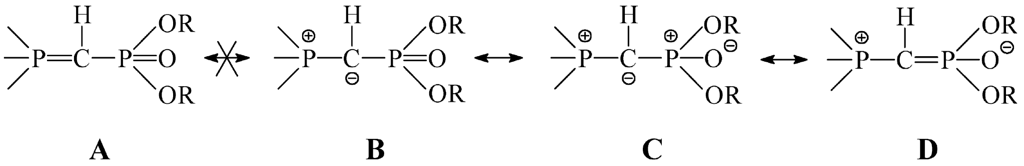


Figure 2. PLUTO view of the pyramidal configuration of the P-ylidic centre in **1** (crystal structure). The H atoms except that at C(1) are removed for clarity.

The most interesting part of molecule of **1** is, however, a close vicinity of its ylidic carbon, i.e. the central region between two phosphorus atoms. Our crystal data unambiguously show that the length of both PC bonds within the $P_{\alpha}C_{\beta}P_{\gamma}$ triad, i.e. P(1)–C(1) and P(2)–C(2), is almost the same [1.694(2) Å, on average]. Moreover, the P(1)–C(1) distance is considerably shorter than the normal single P–C σ-bond in nonhypervalent molecules [1.804(31),[16] 1.80–1.83[14] or 1.803(28)[17] Å]; the P–C distance of 1.808(13) Å was found also for $(PhO)_2P(O)$–C(sp^3) moieties in the structurally close diphenoxy alkylphosphonates.[23] However, both PC linkages are within the typical P=C ylidic distance (1.63–1.71 Å)[14] determined for Y_3P=C moieties (where Y=alkyl, aryl or metallocenyl) in the simple potentially hypervalent phosphonium mono-ylides, like **2**,[12b,24] or related bis-ylides (carbodiphosphoranes), by using reliable ambient as well as low-temperature X-ray data. Therefore, it can be concluded from geometrical considerations (two equal PC ylidic distances), that some multiple bond order in ylide **1** is approximately equally distributed between two differently substituted P atoms.

Such an equality and small pyramidality of the carbanionic atom C(1), i.e. C_{β}, allows one to consider that in the studied molecule an extensive resonance (mesomerism) potentially occurs between three ionic canonical forms of the type **B**-**D**, with the Ph_3P^+ group as an onium centre (Scheme 2; R=Ph, phenyl substituents at P_{α} are omitted for clarity). [In general, a contribution of one of the Wittig's original double-bonded (ylene) form **A** cannot be definitively excluded, however this traditional hypervalent formulation with the P_{α}(V) atom is now regarded as outdated. Indeed, no true multiple-bond character of the P_{α}–C_{β} bond was detected for simple ylides.[18,25]] A particularly favourable delocalisation of a negative charge on C_{β} of the classical[8] 1,2-dipolar (ylide, zwitterionic) form **B** over the whole $P_{\alpha}\underline{\underline{---}}C_{\beta}\underline{\underline{---}}P_{\gamma}\underline{\underline{---}}O_{\delta}$ backbone is easily achieved, on this way. The notation $\underline{\underline{---}}$ used herein for linkages between the atoms α–γ means bond order above 1, arising mainly from hyperconjugative interactions (vide infra). The participation of α-triphenylphosphonium and, especially, γ-phosphonyl groups (including the γ,δ-phosphoryl P=O bond, strongly polarised toward oxygen) seems to be of crucial importance for stabilisation of **1**. This type of electron delocalisation is in good agreement with an observed, nearly planar *cisoid*-relationship between 'terminal' atoms P_{α} and O_{δ}, since the P(2)–C(1)–P(1)–O(1) torsion angle was found to be −1.2(0.3)° (Fig. 2). As the contribution of the covalently bonded ylene form of type **A** in ylides is considered to be small at best (old view)[14,21,26] or negated at all (revised approach),[18,25] there is no important electronic reason preventing rotation about both central partially multiple bonds $P\underline{\underline{---}}C$ of specific nature. Therefore, additional possibility exists (at least potentially) for some geometrical isomerism connected with the classical[8] form **D** of the 1,4-dipolar (betaine) type; isomers *Z* and *E* of this kind were demonstrated for structurally related γ,δ-oxo ylides **3** (R=Ph, G=H or OR).[26b,27]

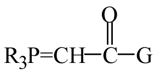


Scheme 2. The charge distribution within a stabilised P-ylidic bonding in **1** shown in terms of the **B**-**D** resonance hybrid, i.e. omitting the outdated form **A**. The participation of literature[8] hypervalent forms **B** and **D** is also questionable (see text).

On the whole, such an electronic picture is consistent with the assignment for two central PC bonds a formal bond order between 1 and 1.5. The $P_{\gamma}O_{\delta}$ bond length in **1** [1.458(2) Å] was found to be practically equal to a literal P═O interatomic distance in common diphenoxy alkylphosphonates [1.461(6) Å].[23] In contrast, a significant (by ca. 0.03 Å) lengthening of the basically single P_{γ}–OPh linkages to 1.610(4) Å (an average value) as compared to 1.581(8) Å value typical of the $(PhO)_2P(O)-C(sp^3)$ moieties,[23] strongly suggests an additional participation of the P_{γ}–OPh bond electrons in the ylidic bonding. The latter finding agrees well with analogous result obtained for ylide **3** (R=Ph, G=OMe) stabilised by the carboxylate group,[28] which can be regarded as the C-ester analogue of P-ester ylide **1**. In this case, the C_{γ}–OMe linkage is also longer than corresponding distances in carboxylic esters [1.374(2)[28] vs 1.336(13)[29] Å]. Moreover, in all recently X-ray studied crystals of oxo ylides **3** (R=Ph, G=OMe, Me or Ph)[28,30] the C═O bonds were found always 0.03–0.05 Å longer than standard carbonyl bonds[29] in esters or ketones, i.e. with the less double-bond character. In consequence, corresponding enolates were proposed as resonance forms really contributing in the conjugation.[30] So, in an arbitrary convention used throughout this work, system **1** can be postulated as an α,γ,δ,δ′,δ″-stabilised ylide, where the dash and double dash signs concern the γ,δ′ and γ,δ″ P–O bonds in P_{γ}–OPh fragments, giving an extra stabilisation to the system (see also Table 3). Indeed, an observed lengthening of the P_{γ}–OPh distances by about 0.03 Å is in line with similar elongation of P(2)–C(n1) distances, where n=4–6 (vide supra).

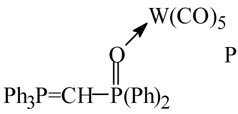
$Ph_3P{=}CH{-}P(Me)_2$

2



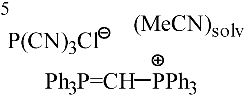
$R_3P{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}G$

3 (R = H or Ph)



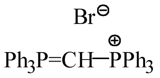
$\overset{\overset{\nearrow W(CO)_5}{O}}{\|}$ $Ph_3P{=}CH{-}P(Ph)_2$

4



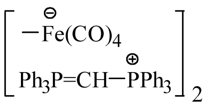
$P(CN)_3Cl^{\ominus}\ (MeCN)_{solv}$ $Ph_3P{=}CH{-}\overset{\oplus}{P}Ph_3$

5



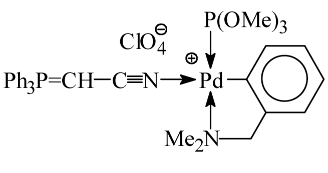
$Br^{\ominus}$ $Ph_3P{=}CH{-}\overset{\oplus}{P}Ph_3$

6



$\left[\overset{\ominus}{-}Fe(CO)_4\ \ Ph_3P{=}CH{-}\overset{\oplus}{P}Ph_3\right]_2$

7



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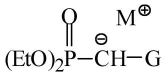


$(EtO)_2\overset{\overset{\displaystyle O}{\|}}{P}{-}\overset{\ominus}{C}H{-}G\ \ M^{\oplus}$

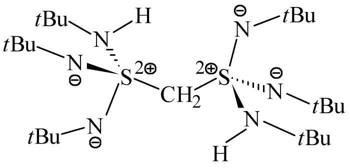
9

$Ph_3P{=}CH_2$

10

A proposed herein model of the typical stabilised P-ylide, containing adjacent negative and positive charges on consecutive atoms C and P (and, e.g. on atoms O and P, as for the phosphoryl group in **1**) seems to be the best description of the real structure, and only this chemical formula obeys the octet rule. Therefore, a double zwitterionic normal-valent form **C** is probably the dominant (if not exclusive) resonance contributor in the case of ylide **1**. Both remaining postulated in the literature,[8] strictly localised Lewis structures **B** and **D** refer to hypervalent states with the ten-valence-electron P(V) atom involved in a formal double P═Y bond. Moreover, the P_{γ}–O_{δ} bond length, being practically identical with the mean P═O distance in phosphonates, suggests the general necessity to describe phosphoryl compounds rather in terms ionic P^+–O^- system[15] and to disregard the form **B** (see also Ref. 7). Analogously, the form **D** can be rejected based on the equality of its both central P–C distances (vide supra). Such a fully ionic description of ylidic bonding is consistent with the recent X-ray study performed by Stalke and co-workers on a structurally related object with two formal S═NR bonds.[31] This compound was experimentally demonstrated to be an ionic system **11** with adjacent S^+–N^- bonds and all nitrogens sp^3 hybridised; neither valence expansion nor d-orbitals participation at sulphur atom was found required to explain the short S–N distances observed. The latter results are in line with chemical bonding in molecules of the type XSO_2Y which are represented mainly by ionic formulation **12**, and only slightly modified by partial π-bonding coming from strong $n_O \rightarrow \sigma^*_{SX(Y)}$ negative-hyperconjugation effects.[13,32] Thus, the high ionicity inherent in the structure **C** of **1** (see also, general formula **13**) most likely[33] leads to overall further reinforcement of its both central P^+–C^- bonds of specific multiple character, e.g. by a favourable orientation of the lone-electron pair(s) of Oδ and, especially, Cβ atoms toward positively charged P atoms; cf. cases of the tetra-co-ordinate yet electronically S(IV) compounds mentioned above. Analogous strengthening of the P–O bond resulting from strong electrostatic attraction, was recently reported for the molecule of H_3P^+–O^-.[15]

Our crystallographic findings concerning ylide **1** are in close correspondence to those reported for other structurally related systems (Table 2). Thus, such metrical parameters are known for the tungsten complex **4** with an additional P═O→W linkage[34] and for compounds **5**,[35] **6**[36] and **7**,[12b,37]



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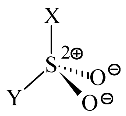

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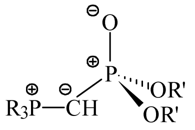


13

which can be treated as ylides containing an electron-withdrawing triphenylphosphonium substituent (Z), in place of the diphenoxyphosphoryl residue. On the other hand, the PC distance in ylides **3** (R=Ph, G=Me or OMe)[28,30b] and **8**,[38] where the ylidic core is directly bound to another carbon instead of phosphorus atom, is only slightly longer (by ca. 0.01 Å). The CC bond in these γ,δ-oxo (or γ,δ-cyano) stabilised Wittig reagents is considerably shorter (1.38–1.39 Å) indicating its some multiple character.[39] So, the charge delocalisation through the presence of stabilising groups (or atoms) in positions α, γ and δ of the ylidic backbone exists most likely also in the systems **3-8**. Inspection of Table 2 reveals that bond angles P–C–Z and Z–C–H generally increase and decrease, respectively, with an increase in the $P_{\alpha}C_{\beta}$ bond length in molecules $Ph_3P{=}CH{-}Z$. Moreover, for **3** (R=Ph) and **6-8** the ylidic β-carbon has an almost ideal trigonal symmetry, as the sum of all bond angles involving this atom approaches 360°. On the whole, molecular parameters discussed above, especially $l(P{=}C)$ and $\sum(\angle Y{-}C{-}X)$, deviate from corresponding values found for semi- and nonstabilised ylides **2** and **10** (Table 2, first three rows); these literature data are listed for comparison only. Two datasets given for the last mentioned compound need some comment. Indeed, the P–C ylidic distance reported for **10** (bold figure among the other 'best values' in brackets; footnote c) is a particularly noteworthy example for the artificial shortening, by ca. 0.02 Å, of such bond length caused by an aspherical valence-electron distribution.[24] In consequence, all other bond distances determined by conventional X-ray methods (Table 2) might also be shorter than they really should be.

The solid-state structures adopted by a lithiated Wadsworth–Emmons reagent **9** (G=CN), i.e. the salt of the phosphonate carbanion, which also might be regarded as the γ,δ-stabilised α-phosphono ylide,[2] has been reported as well. Thus, the THF complex of **9** (G=CN, $M^+{=}Li^+$) was found to be almost perfectly planar carbanionic system with the $P_{\alpha}C_{\beta}$ distance of 1.697(4) Å,[40] very similar to 1.690(3) Å determined for the $P_{\gamma}C_{\beta}$ bond in ylide **1**. In this view, our unexpected observation that both PC distances in **1** are practically equal to the best estimate of 'normal' ylidic $P^+{-}C^-$ distance as ≈1.70[25,26a] or 1.69 Å,[14] indicates that this compound can be considered as both the phosphono-stabilised phosphonium ylide (classical view) and as the phosphono ylide[2,7] internally stabilised by an adjacent phosphonium group, i.e. as the double P^+-stabilised carbanionic system (novel approach). An elongation of all distances $P_{\alpha}{-}C_{ipso}$ and $P_{\gamma}{-}OPh$ by ca. 0.02–0.03 Å, arguing strongly for similar negative hyperconjugative $n{\rightarrow}\sigma^*$ π-back-donation[14,19,32] in **1**, is consistent with this concept. The ionic formula **C** (or **13**, in general) of such a mixed ylide is also in full agreement with the foregoing idea. Undoubtedly, an additional π back-bonding mentioned above results in some multiple character of both $P{-}C_{\beta}$ bonds in the ylide under study.

Table 2. Comparison of P–CH–Z distances (Å) and bond angles (°) determined for single crystals of selected triphenylphosphonium ylides of the $Ph_3P{=}CH{-}Z$ type, **1-8** and **10**

No.	Z	$l(P{=}C)$	$l(C{-}Z)$	∠P–C–Z	∠P–C–H	∠Z–C–H	Σ(∠Y–C–X)	References
10[a,b]	H	1.670	(0.87)	(115.9)	115.9	117.7	349.5	12b,24
10[a,c]	H	**[1.692]**	[(0.88)]	[(115.3)]	[115.3]	[119.3]	[349.9]	24
2[d]	$P(Me)_2$	1.681[e]	1.760	122.3	114.3	120.6	357.2	12b,24
4	$PPh_2(O){\rightarrow}W(CO)_5$	1.701[f]	1.679[f]	127.9	n.a.[g]	n.a.[g]	n.a.[g]	34
1	$P(OPh)_2(O)$	1.698	1.690	127.1	117.2	115.4	359.7	[h]
5	PPh_3^+ $[P(CN)_3Cl]^-$ $[MeCN]_{solv}$	1.701	1.701	129.7	112.7	117.0	359.5	35
6	PPh_3^+ Br^-	1.695[i]	1.710[i]	128.2	115.7	116.1	359.9	36
7	PPh_3^+ $[Fe_2(CO)_8]^{2-}$ $Ph_3P{=}CH^-PPh_3^+$	1.702	1.700	131.5	115.7	112.7	359.9	12b,37
3[j]	C(OMe)(O)	1.704	1.394	120.9	118.0	121.1	360.0	28
3[j]	C(Me)(O)	1.710	1.391	119.6	118.1	122.1	359.8	30b
8[k]	$C{\equiv}N{\rightarrow}Pd^+{-}Aryl$ $[ClO_4]^-$	1.710	1.379	118.4	120.8	120.8	360.0	12b,38

All results obtained from a conventional analysis of the X-ray data, unless specified otherwise.

[a] Nonstabilised, strongly pyramidalised ylide. Averaged data of the two independent molecules; the X-ray dataset collected at 100 K.

[b] Weighed data calculated from reported 'full data refinement' parameters.

[c] Weighed results from the 'high order data refinement' parameters, in brackets.

[d] Semi-stabilised, pyramidalised ylide with the tricoordinated P(III) group Z; $l(P{=}C) \ll l(C{-}P)$.

[e] Originally[24] set as 1.618 Å (typo error).

[f] Av. 1.690 Å, as symmetry of the PCP unit was postulated.

[g] Not available (lacking in CSD).

[h] This work.

[i] Av. 1.703 Å, this molecule is fully symmetrical.

[j] R=Ph, C(O)G=Z.

[k] Determined at 150 K.

2.2. Quantum-chemical MO calculations

An extensive charge delocalisation in the molecule of **1** was further investigated by ab initio molecular-orbital (MO) calculations of electron-density redistribution using the observed crystal geometry (Section 4). Some of the aforementioned X-ray-based qualitative considerations on a bond multiplicity within the $P_{\alpha}C_{\beta}P_{\gamma}O_{\delta\delta'\delta''}$ backbone were also evaluated in this way. Atomic charges at the crucial atoms of ylide **1** and pertinent bond orders obtained at four computational Hartree–Fock levels are given in Table 3. In general, the results are in good agreement with charge-density distribution presented in Scheme 2. Indeed, all RHF–SCF theory levels applied gave positive charges on both P atoms, while oxygen and, especially, the ylidic β-carbon was found to be negatively charged. The Mulliken (or any other, e.g. Löwdin) type of charge partitioning is well-known to be dependent on the basis set,[13,41] and often atomic charges calculated in this way are not true in the absolute sense, especially in computations with more extended basis sets. However, such population analyses are generally rather adequate for studying relative trends. In fact, our results were found to be slightly basis-function sensitive [particularly, the atomic charge at C_{β} (from -0.85 to $-1.25\ e$)], nevertheless analogous trends were observed for an augmentation of initial basis sets with polarisation functions. The major difference in results from the two aforementioned methods concerns the phenyloxy oxygens ($O_{\delta'}$ and $O_{\delta''}$), which were found to be much less negatively charged in the Löwdin approach. It is interesting to note, that the bonds P_{γ}–O involving these oxygens were found theoretically with the less single-bond character (bond order of ca. 0.87, Table 3), in agreement with our considerations based on the X-ray results.

The MO picture of the $P_{\alpha}C_{\beta}P_{\gamma}O_{\delta\delta'\delta''}$ backbone obtained initially for the crystalline-state geometry of **1**, was fully confirmed in additional geometry-unconstrained calculations performed for some other conformations of this molecular system. Although the RHF/6-31G** is the standard level of an electronic theory for studies on hyperconjugative effects,[42] the corresponding more general density functional theory (DFT) approach at a hybrid functional Becke3-LYP level was used as well (Section 4). Geometry and selected structural parameters of the lowest energy P(1)–O(2) rotational conformer (global minimum on the potential energy hypersurface) computed by both methods are given in Figure 3 and Table 4. The most important deviation from the X-ray determined data (Table 1) concerns the C(1)–P(1)–O(2)–C(21) torsion angle in the phosphonate moiety; otherwise, rather good agreement was achieved. Interestingly, the calculated HF/6-31G** bond distances were found to be close to the corresponding single-crystal values (most probably slightly underestimated, vide supra), in comparison with the elongated B3LYP/6-31G** distances (cf. Tables 1 and 4). Moreover, a more realistic picture of the pyramidality at the atom C_{β} is worth noting; $\sum(\angle Y-C_{\beta}-X)=359.47$ (359.63°), $d=0.060$ (0.051 Å) and $\gamma=7.1$ (5.9°) as was established at the HF/6-31G** (or B3LYP/6-31G**) level, respectively. A little difference in values of d and γ, comparing to the conventionally analysed X-ray diffraction data, are due (at least in part) to the longer $C_{\beta}-H_{\beta}$ bond calculated theoretically. It is well known, that all Q–H distances (where Q is a heavy atom) determined for crystals by standard procedures are systematically shortened owing to charge-density distortions, e.g. on the average by 0.1 Å for C–H.[43]

Because of some weakness of population analyses carried out in two foregoing ways, several attempts of calculating atomic charges within the $P_{\alpha}C_{\beta}P_{\gamma}O_{\delta\delta'\delta''}$ backbone of **1** using the more elaborated Bader's atoms in molecules (AIM) topological theory,[44] were undertaken as well.

Table 3. Net atomic charges and A_i-A_j bond orders (in bold) within the PCPO moiety of **1**, for the crystal structure (single-point calculations, four RHF levels) and for an isolated molecule in vacuo (fully relaxed geometries HF/6-31G** and B3LYP/6-31G**); Mulliken (*Löwdin*) charge values, in electrons

Atom(s)	6-31G*	6-31G**	6-311G*	6-311G**	6-31G**^{a,b}	6-31G**^{a,c}
P_{α} [P(2)]	1.123	1.125	1.317	1.302	1.153	0.659
	0.977	*0.979*	*1.097*	*1.101*	*0.965*	
C_{β} [C(1)]	−0.926	−0.847	−1.274	−1.023	−0.885	−0.605
	−0.905	*−0.803*	*−0.941*	*−0.773*	*−0.817*	
P_{γ} [P(1)]	1.549	1.548	1.670	1.651	1.589	1.126
	1.236	*1.236*	*1.104*	*1.104*	*1.239*	
O_{δ} [O(1)]	−0.787	−0.787	−0.770	−0.771	−0.795	−0.620
	−0.727	*−0.728*	*−0.622*	*−0.621*	*−0.731*	
$O_{\delta'}$ [O(2)]	−0.757	−0.757	−0.681	−0.671	−0.777	−0.604
	−0.425	*−0.424*	*−0.266*	*−0.264*	*−0.421*	
$O_{\delta''}$ [O(3)]	−0.762	−0.761	−0.699	−0.691	−0.780	−0.601
	−0.425	*−0.425*	*−0.265*	*−0.264*	*−0.422*	
$P_{\alpha}-C_{\beta}$	**1.337**	**1.329**	**1.232**	**1.256**	**1.333**	
$C_{\beta}-P_{\gamma}$	**1.168**	**1.160**	**1.121**	**1.125**	**1.151**	
$P_{\gamma}-O_{\delta}$	**1.640**	**1.639**	**1.663**	**1.661**	**1.608**	
$P_{\gamma}-O_{\delta'}$	**0.891**	**0.891**	**0.894**	**0.894**	**0.882**	
$P_{\gamma}-O_{\delta''}$	**0.871**	**0.870**	**0.849**	**0.847**	**0.856**	
$-E_{SCF}{}^{d}$	2094.5911	2094.6417	2094.9051	2094.9568	2095.1939	2105.4095

Between atoms A_i and A_j.

[a] Complete geometry optimisation (see Table 4).

[b] HF/6-31G** structure.

[c] B3LYP/6-31G** structure (see Fig. 3).

[d] Total electronic energy in hartrees (1 hartree=2625.50 kJ mol^{-1}).

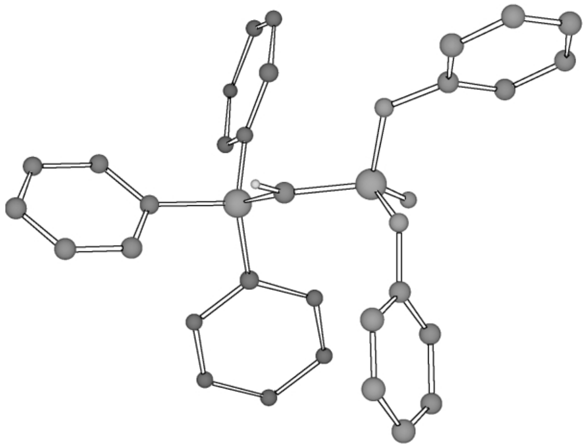


Figure 3. The B3LYP/6-31G**-optimised structure of the lowest found energy rotamer of **1** (only *S* enantiomer shown). The H atoms except that at the ylidic centre are omitted.

Similar type atomic charges obtained from the Weinhold's natural population analysis (NPA)[45] were reported recently for simple γ,δ-oxo ylides **3** (R=H).[46] However, our attempts of such calculations on an X-ray crystal structure of **1** and its HF or DFT fully-optimised geometries failed;[47] the AIM code implemented within the Gaussian 98W package[48] was applied. In consequence, analogous attempts were undertaken for two simple models of ylide **1**, i.e. molecules **13** (R=H or Me), calculated at the B3LYP/6-31G** (**1**, this work) and B3LYP/6-311+G* level ($H_3P^+–CH_2^-$, Ref. 18). Unfortunately, all these AIM runs we have performed so far terminated also with execution errors, most probably owing to an unusual topology[48] of electronic charge density [$\rho(r)$] in the ylidic systems under consideration.

On the whole, the calculational results on a charge distribution, obtained for the fully relaxed conformations of ylide **1** (Table 3, last two columns), are in qualitative agreement with the description its P-ylidic bonding in terms of the valence-bond resonance hybrid of the **B**-**D** canonical assembly (Scheme 2). However, among all these hypothetical contributing structures the double zwitterionic form **C** carrying electrical charges of opposite sign on four adjacent atoms, seems to be especially favoured. In fact, in all calculations performed the P_γ atom is the most positively charged site (Table 3). So, it is likely that stabilising electron-acceptor oxygen substituents at the atom P_γ increase the π back-bonding by an electron withdrawal from P_γ, which becomes more positive giving, in turn, more opportunity for an electron donation from the O_δ lone pairs (see also Ref. 47). This ionic concept is in agreement with an earlier suggestion[8] that the negative charge on C_β in **1** is delocalised to a great extent towards the P═O moiety and two adjacent OPh groups. To the best of our knowledge, a resonance structure **C** was not proposed to date for P-ylides of the type **1**. Curiously enough, this highly ionic structure seems to be the best chemical description (see formula **13**) of this kind of ylidic systems (vide supra). Moreover, it is worth noting that the ab initio calculations at the theory levels applied by us were also not performed for ylides of such a molecular size.

Table 4. Representative bond distances (Å), and angles (°) of the lowest-energy conformation of **1**; the fully optimised HF/6-31G** (roman) and B3LYP/6-31G** (italic) structures

P(1)–O(1)	1.4670 *1.4971*	C(1)–P(1)	1.7083 *1.7157*	P(2)–C(51)	1.8252 *1.8306*
P(1)–O(2)	1.6104 *1.6463*	C(1)–P(2)	1.7047 *1.7117*	P(2)–C(61)	1.8328 *1.8418*
P(1)–O(3)	1.6166 *1.6545*	P(2)–C(41)	1.8270 *1.8367*	C(1)–H(101)	1.0735 *1.0831*
O(1)–P(1)–C(1)	116.1 *116.8*	C(1)–P(1)–O(3)	108.8 *108.3*	C(41)–P(2)–C(51)	107.5 *107.5*
O(1)–P(1)–O(2)	113.4 *114.0*	P(1)–C(1)–P(2)	126.1 *125.8*	C(41)–P(2)–C(61)	105.2 *104.1*
O(1)–P(1)–O(3)	113.4 *114.4*	C(1)–P(2)–C(41)	114.6 *115.0*	C(51)–P(2)–C(61)	105.6 *106.1*
O(2)–P(1)–O(3)	96.8 *95.7*	C(1)–P(2)–C(51)	105.7 *105.3*	P(1)–C(1)–H(101)	118.2 *118.5*
C(1)–P(1)–O(2)	106.5 *105.4*	C(1)–P(2)–C(61)	117.5 *118.2*	P(2)–C(1)–H(101)	115.1 *115.3*
P(1)–C(1)–P(2)–C(41)	−54.9 *−59.1*	C(41)–P(2)–C(1)–H(101)	116.6 *113.8*	C(1)–P(1)–O(2)–C(21)	174.7 *172.1*
P(1)–C(1)–P(2)–C(51)	−173.1 *−177.2*	C(51)–P(2)–C(1)–H(101)	−1.6 *−4.3*	C(1)–P(1)–O(3)–C(31)	77.1 *71.4*
P(1)–C(1)–P(2)–C(61)	69.5 *64.5*	C(61)–P(2)–C(1)–H(101)	−119.0 *−122.6*		
O(1)–P(1)–C(1)–P(2)	−13.4 *−12.2*	O(1)–P(1)–C(1)–H(101)	175.4 *175.1*		

Fig. 3. For an atom labelling, see Fig. 1.

2.3. Solution NMR investigations

In view of all above results, the multinuclear (^1H, ^{13}C, ^{31}P) magnetic resonance data obtained for **1** in $CDCl_3$ solution are also interesting. Perhaps the most striking observation was an 'absence' in the routine ^1H NMR spectrum either of two-bond coupling constants between the carbanionic proton H_β and two phosphorus atoms ($^2J_{PH\beta}$). This phenomenon was observed previously by other authors.[4a] Thus, only minimal, if any, broadening of this methine signal was found (δ_H 1.46–1.49; a small high-frequency shift accompanies increasing concentration of the sample). No adequate spin-spin interactions $P\leftrightarrow H_\beta$ were also observed in the ^1H-coupled ^{31}P spectrum, in which the PPh_3 phosphorus signal (two overlapping very broad multiplets; $^2J_{PP}=45.5$ Hz, $^3J_{P\alpha Har}\approx 12$ Hz) was unambiguously identified at 20.4 ppm. It is worth mentioning, that for a simple ylide **10** ^{31}P chemical shifts of 18.4 or 20.3 ppm were measured,[26b,49] whereas for *E* and *Z* isomers of the C-ester analogue **3** (R=Ph, G=OMe) such shifts were of 16.30 and 17.83 ppm, respectively.[27g,50] It is well-known, that for most triphenylphosphonium ylides $^2J_{PH}$ values are in the range from 18.5 to 27 Hz depending on their geometry,[27a–e,g,50] however, the P,H_β-coupling of only 7.0 or 7.5 Hz was reported for the parent, unsubstituted ylidic system **10**.[27a,d,51]

Analogous NMR effects were observed, at ambient temperature, for structurally similar phosphonium ylide **3** (R=Ph, G=OMe) and related compounds.[27a–d,f,g,50] In this case, the collapse of the H_β signal and an absence of the P,H_β-coupling were attributed[27] to the equilibration between *E*/*Z* geometrical isomers (occurring via infrequent rotation about the partially multiple C_β–C_γ bound) and/or extremely facile H^+-exchange process (transylidation)[27d] operating simultaneously between the ylide and acidic contaminants, like its conjugated acid (phosphonium salt)[27b–g] or water.[27d,f,g] In fact, after careful exclusion of such protic-catalyst traces with basic NMR-tube reagents[27d,g] (Section 4), we were able to see the H_β signal in the ^1H NMR spectrum of **1** as a relatively good resolved doublet ($^2J_{PH}=5.2$ Hz, at ca. 21°C). The expected doublet of doublets was not found, however. Therefore, it can be concluded that the geminal coupling of the β-proton with other P nucleus (P_α, vide infra) is most likely smaller than the half-height linewidth (0.5–0.6 Hz) of both components of the H_β doublet observed. Moreover, only the P_γ signal was substantially altered in the ^1H-coupled ^{31}P NMR spectrum recorded under such experimental conditions, which appeared now in form of the double doublet ($^2J_{PP}=45.5$ Hz and $^2J_{P\gamma H\beta}=5.2$ Hz).[52] Much larger coupling, $^2J_{PP}=125.1$ Hz, was determined for the phosphino-substituted ylide **2**.[24] In contrast, very similar P,H_β-coupling of 4.2 and +5.0 Hz was reported for the phosphono system **9** (G=CN, $M^+=Li^+$ or K^+) in Py-d_5[40] and DMSO-d_6,[53] respectively ($\delta_{H\beta}$ 1.72).[40] Thus, the absence of an observable $^2J_{P\alpha H\beta}$ for **1** is rather surprising. However, for diethyl phosphono-substituted ylide **14** (R=Et) also only one of two $^2J_{PH\beta}$ was reported (7.5 Hz).[5e] An origin of this coupling was not discussed.

The ^{13}C nucleus of the PCHP fragment in **1** (C_β) resonates at rather low frequency, δ_C 6.55–6.57 (concentration dependent), reflecting very well an expected carbanionic character of this center.[26b,54] Its signal is considerably high-frequency shifted from that reported for the nonstabilised ylide **10** (δ_C from −6.4 to−4.1),[26b,c,55] most likely due in part to the presence of neighbouring phosphonyl group. The β-carbon appears in the $^{13}C\{H\}$ NMR spectrum of **1** as sharp double doublet, indicating two one-bond couplings to adjacent phosphorus atoms ($^1J_{PC\beta}$): 123.0 and 221.2_5 Hz for *C*PPh and *C*P(O)OPh, respectively. The other characteristic carbon-phosphorus coupling constants[54] of the Ph ring carbons allow complete ^{13}C NMR assignment of the compound studied (Section 4). A coupling $^1J_{C\beta H}$ was also measured to give the value of 155.0 Hz (the ^1H-undecoupled ^{13}C spectrum, rigorously acid-free conditions). This spectral parameter can be used as an indicator of the ylidic β-carbon hybridisation;[54,56] the value of $^1J_{C\beta H}$ obtained for **1** let us evaluate the approximate $sp^{2.22}$ hybridisation state of this atom. Above spectral data determined for the mixed P-ylide **1** correspond well with the $^1J_{C\beta H}$ and $^1J_{PC\beta}$ values of 144–161 and 195–242 Hz, respectively, reported for the γ,δ-stabilised α-phosphono ylides of the geometry close to planar at β-carbon.[40,53] For example, C_β of the phosphono ylide **9** (G=CN, $M^+=K^+$) resonates at similar frequency as for **1**; δ_C 3.6, $^1J_{CH}=161.3$ Hz and $^1J_{PC}=235.5$ Hz (DMSO-d_6).[53] Thus, the best representation of phosphonate moiety (and its nearest local electronic environment) in the molecular system **1** is again given by formula **13** (Ref. 7).

For the phosphonium ylides that are not stabilised by resonance, a much higher deviation from the planarity of β-carbon was reported.[14,21,26b,c,57] Indeed, in the case of unsubstituted at C_β simple ylide **10**, the PC_β bond is bent in crystal by about 30.8° from the methylene group plane;[58]

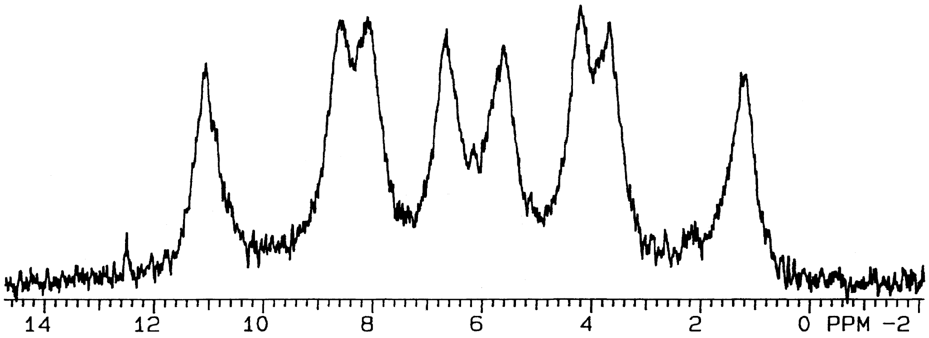


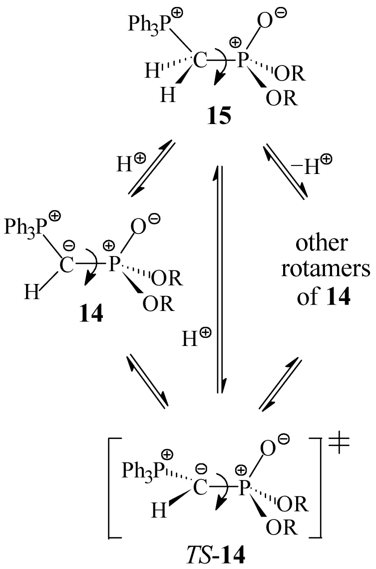
Figure 4. The ylidic carbon part of the ^1H-coupled 50 MHz ^{13}C NMR spectrum of **1** in $CDCl_3$ solution recorded under H^+-exchange conditions (gated proton decoupling at ca. 21°C, 25803 scans). The 1.0 Hz line broadening was applied in processing the spectrum.

see also Table 2. The coupling constant $^1J_{C\beta H}$ determined from its ^{13}C NMR spectra (152.6–153 Hz),[26b,c,56] was found to be similar to that measured by us for **1**. On contrary, $^1J_{PC\beta}$ was found considerably lower, 98.6–101,[26b,c,51,54–56] indicating a higher order of the PC bond and the 'flat pyramidal' shape[26b] of the ylidic centre.

Our ^{13}C NMR analysis of ylide **1** needs additional comment. In fact, an extremely broad signal of C_β was observed initially in the routine ^{1}H-coupled ^{13}C NMR spectrum, which appeared as a double doublet of broad doublets of very weak intensity (Fig. 4). Accordingly, the $^1J_{CH}$ of 151.2 Hz was calculated taking to some extent $^1J_{CP}$ values derived from the $^{13}C\{^1H\}$ spectrum into account. A dynamic character of the $C_\beta{-}H_\beta$ bond in **1** was clearly visualised in related ^{1}H and ^{31}P NMR spectra as well (vide supra). However, under anhydrous and acid-free conditions C_β was easily observed as a sharp multiplet.

Undoubtedly, in the sample solution (prepared initially from the commercial untreated $CDCl_3$, usually[27f] containing traces of DCl and air-moisture) a rapid equilibration between species **14** and **15** (R=Ph) occurred, influencing the observed spectral parameters (Scheme 3). Indeed, an approximate $sp^{2.31}$ hybridisation upon C_β was found from $^1J_{CH\beta}$ (151.2 Hz) measured under such H^+-exchange conditions, indicating for some participation of sp^3-hybridised species in the analysed mixture. Analogously, an extensive broadening of the C_β signal in the ^{1}H-coupled ^{13}C NMR spectrum was reported for the proton-catalysed interconversion between isomers *Z* and *E* of ylide **3** (R=Ph, G=OMe).[27f] Thus, we now propose, that the $^1J_{CH}$ value measured for P-ylides can be used, in general, as a convenient probe of their carbanionic (ylidic) purity; the related quaternary phosphonium salts usually exhibit substantially smaller values of $^1J_{CH}$.[2,54,56]

So, from all the NMR spectroscopic data collected above for ylide **1**, it appears that a rapid reversible inversion of nonplanar geometry at its β-carbon occurs at room temperature, and most likely it is the reason for an absence of observable geminal coupling $^2J_{P\alpha H\beta}$ in its NMR spectra. The published variable-temperature ^{1}H NMR spectra of **10**[27a] strongly suggest such a possibility. A fast (on the NMR timescale) pyramidalisation of C_β in **1** can be easily rationalised by its carbanionic character. Indeed, a rapid inversion of pyramidal geometry of the ylidic centre in nonstabilised triphenylphosphonium cyclopropylide was observed in solution, within the temperature range −110 to 30°C.[22,57] However, an internal rotation[19a,25c] about axes $P_\alpha{-}C_\beta$ and/or $C_\beta{-}P_\gamma$ in a *cisoid*-conformation of ylides **14**, giving rise to some other high-energy rotational forms (Scheme 3), cannot be ruled out as an origin of the observed spectral phenomena, at this stage. Undoubtedly, this problem requires further investigations.



Scheme 3. The proposed equilibrium comprising ylides **14** (R=alkyl, aryl).[7]

On the whole, the ^{13}C NMR image of the Ph_3PC moiety in ylide **1** is very similar to that reported for the oxo ylide **3** (R=Ph, G=OMe).[27g] However, using the $^1J_{PC}$ value as a measure of the ylidic β-carbon pyramidality,[20b,26b] a slightly more pronounced planarity of C_β in the latter molecule seems to occur, as $^1J_{PC\beta}$ of 127[27g] or 131[50] Hz were determined for it at room temperature, comparing to 123.0 Hz measured by us for **1**. Hence, all NMR spectroscopic findings fully support our earlier conclusion derived from the X-ray results, that close structural similarity exists between phosphonium ylides stabilised either by the phosphonate or carboxylate group. Indeed, a predominant contribution of the charge-separated **B**-type (ylide) form in the resonance hybrid of ylide **3** was suggested previously.[50] However in a reappraisal of earlier NMR work, such γ,δ-oxo stabilised ylides were considered to exist in solution as ca. 1:1 mixture of **B**- and **D**-type (enolate) ionic forms, with no participation of **A**-type (ylene) forms,[26b] although other authors questioned such a simple description.[27g] On the other hand, a high importance of the **D**-type 1,4-dipolar form in the overall resonance hybrid was suggested for C-ester ylides **3** (R=Ph, G=H, R, OR), on the basis of NMR and IR solution data.[59]

It is noteworthy that fully-charged structure **C**, proposed in this work (based on general considerations reinforced by computational results) as the best description of true molecule of the P-ester ylide **1**, is a resonance midway between traditional forms **B** and **D**. Undoubtedly, these two last canonical structures are appropriate as forms really participating in the nonhypervalent **B**–**D** type resonance hybrid of the carbonyl-stabilised ylides; e.g. the conformationally rigid **D**-type form contribution easily explains a *Z*/*E* isomerism observed for several such systems. In the light of foregoing results, a resonance hybrid of the γ,δ-oxo stabilised ylides is dominated, presumably, by a double zwitterionic structure of the type **C** as well.

3. Conclusions

X-Ray crystallographic, solution NMR studies, and gas-phase theoretical calculations indicated that the title molecule (**1**) adopts various *cisoid* conformations with a near planar, slightly pyramidal shape at the ylidic β-carbon. An extensive π-electron delocalisation involving all heavy atoms of its ylidic backbone was found, with substantial (if not exclusive) contribution of a double zwitterionic resonance form **C** in real molecular entity. In general, this phosphono-stabilised phosphonium ylide can be considered as intermediate, both geometrically and electronically, between unsubstituted nonstabilised ylide **10** (with a pyramidal C_β atom) and such C_β-planar γ,δ-oxo stabilised system **3** (R=Ph, G=OMe), i.e. the C-ester analogue of **1**. Furthermore, the $CHP(O)(OPh)_2$ moiety in **1** appears very similar both structurally and spectroscopically to that in γ,δ-oxo stabilised phosphono ylides, e.g. in an almost perfectly planar P-ester anion **9** ($G=CO_2Me$). It suggests the possibility of parallel considering **1** also as the phosphonium-stabilised phosphono ylide. Such idea of the mixed ylide is strongly supported by the X-ray determined P–C distances, which are both equal to the 'best P-ylidic' distance.

As the crystal structure and NMR spectroscopic data obtained for ylide **1** were also compared with those reported for the other resonance stabilised Wittig-type reagents and structurally related phosphorus-based anionic species, it was concluded that an almost identical overall electronic situation of the P-ylidic bonding characterises the whole family of these highly reactive, nonhypervalent molecular systems. Most likely, it is governed by strong electrostatic interactions represented mainly by structures of the type **C**, with only small participation of the π back-donation from corresponding carbanionic centres (negative hyperconjugation). These results lend support to a growing realisation that ylidic systems are describable in ionic terms;[14,18,21,25,26,46,60] see e.g. formula **13**.

4. Experimental

4.1. General

NMR spectra were recorded at ambient temperatures with a Bruker 200 AC (or Varian Gemini 200 BB) instruments, operating at 200.11 (199.98), 50.33 (50.29) and 81.01 (80.95) MHz for ^1H, ^{13}C and ^{31}P nuclei, respectively. Chloroform-*d* (Dr Glaser AG, Basel; 99.8% D, stabilised with silver flakes) from the freshly opened bottle (or stored over activated 4 Å molecular sieves) was used as solvent, unless specified otherwise. For some experiments with ylide **1** carried out under strictly anhydrous and acid-free conditions, $CDCl_3$ was passed through a freshly activated basic alumina (Al_2O_3) column prior to measurement. In addition, a small quantity of basic Al_2O_3[27d] or CaH_2[27g] were introduced into the NMR sample tubes, to give fine suspensions of these solid reagents in $CDCl_3$. Proton and carbon chemical shifts are δ-values, in ppm, referenced relative to internal TMS, while δ_Ps are positive in the direction of increasing frequency from an external 85% aqueous H_3PO_4 (no bulk susceptibility correction). $^1J_{CH}$ values for **1** were measured from ^1H-coupled ^{13}C NMR spectra obtained with the gated proton decoupling[54] (spectral width 9000 Hz with a time domain of 32K, zero-filling to 64K data points; internal standard: CH_2Cl_2). Scalar spin-spin coupling constants (*J*) are given in Hz. Low-resolution chemical ionisation mass spectra (CI-MS) were taken on a Finnigan MAT 95 spectrometer. Melting point (uncorrected) was determined on a Boëtius apparatus.

4.1.1. *O*,*O*-Diphenyl (triphenylphosphanylidene)methylphosphonate (1). Ylide **1** was prepared under 'salt-free' conditions following the modified methodology described by Jones et al.[4a] *O*,*O*-diphenyl (chloromethyl)phosphonate (24 g, 85 mmol) was mixed with triphenylphosphine (24 g, 91 mmol) and heated at 180–190°C for 4 h. The reaction mixture was extracted with warm water (1 L), filtered, and filtrate was alkalised with stirring, with 10% KOH aq. solution till pH 12. A gummy precipitate was decanted and dissolved in $CHCl_3$ (100 mL), and the resulting solution was dried (Na_2SO_4) and evaporated in vacuo. The residue was crystallised twice from ethyl acetate (previously filtered through freshly activated basic alumina) to yield 35 g (81%) of product as colourless crystals, mp 146.5–147.0°C (lit.,[4a] 149–150°C; lit.,[9] 143–145°C). NMR: ^1H, δ 1.49 (s, 1H, H_β) [or (d, $^2J_{P\gamma H\beta}=5.2$ Hz, 1H, H_β), acid-free medium], 6.95–7.55 (m, 25H, H-C_{ar}) [lit.,[4a] 1.50 (br s, 1H, H_β)]; $^{13}C\{^1H\}$, δ 6.55 (dd, $^1J_{CP\gamma}=221.3$ Hz and $^1J_{CP\alpha}=123.0$ Hz, C_β), 121.14 (d, $J_{CP}=4.7$ Hz, C2′), 123.47 (d, $J_{CP}=1.1$ Hz, C4′), 128.40 (d, $J_{CP}=12.3$ Hz, C3), 128.78 (dd, $^1J_{CP\alpha}=92.2$ Hz and $^3J_{CP\gamma}=3.9$ Hz, *ipso*-C1–P_α), 128.96 (d, $J_{CP}=0.8$ Hz, C3′), 131.72 (d, $J_{CP}=2.9$ Hz, C4), 132.76 (d, $J_{CP}=10.3$ Hz, C2), and 152.09 (d, $J_{CP}=6.9$ Hz, *ipso*-C1′–O); ^{13}C (partly), δ 6.55 (ddd, $^1J_{CP\gamma}=221.3$ Hz, $^1J_{CH}=151.2$ Hz, and $^1J_{CP\alpha}=123.0$ Hz, C_β) [or (ddd, $^1J_{CP\gamma}=221.3$ Hz, $^1J_{CH}=155.0$ Hz, and $^1J_{CP\alpha}=123.0$ Hz, C_β), acid-free medium]; $^{31}P\{^1H\}$, δ 20.41 (d, $^2J_{PP}=45.5$ Hz), 27.08 (d, $^2J_{PP}=45.5$ Hz); ^{31}P, δ 20.41 (br dsept, $^2J_{PP}=45.5$ Hz and $^3J_{PHar}\approx 12$ Hz, P_α–Ph), 27.08 (br d, $^2J_{PP}=45.5$ Hz, P_γ–OPh). MS (CI, isobutane) *m*/*z* 509 (100%) $[M+1]^{+\cdot}$ {lit.,[4a, 10] (EI) *m*/*z* 508 $[M]^{+\cdot}$, 352 (100%)}.

4.1.2. *O*,*O*-Diphenyl (chloromethyl)phosphonate [$ClCH_2P(O)(OPh)_2$]. Compound was obtained by treating (chloromethyl)phosphonic dichloride with excess of phenol at 230°C, as described by Vaghefi et al.;[61] yield 97%. Colourless liquid, bp 170°C/1 mm Hg (lit.,[4a] 150–152°C/0.05 mm Hg, lit.,[61] 145–147°C/0.15 mm Hg) which solidified after standing in a refrigerator. NMR: ^1H, δ 3.79 (d, $^2J_{PH}=10.1$ Hz, 2H, CH_2Cl), 7.1–7.4 (m, 10H, H–C_{ar}); $^{13}C\{^1H\}$, δ 32.47 (d, $J_{CP}=160.9$ Hz, CH_2Cl), 120.45 (d, $J_{CP}=4.4$ Hz, C2), 125.62 (d, $J_{CP}=1.4$ Hz, C4), 129.82 (d, $J_{CP}=1.1$ Hz, C3), and 149.71_5 (d, $J_{CP}=8.4$ Hz, *ipso*-C1); $^{31}P\{^1H\}$, δ 11.25 (br s); ^{31}P, δ 11.25 (br t, $^3J_{PH}=10.1$ Hz).

4.1.3. (Chloromethyl)phosphonic dichloride [$ClCH_2P(O)Cl_2$]. Compound was prepared from CH_2Cl_2 and PCl_3 in presence of $AlCl_3$, following the method of Kinnear and Perren;[62] yield 32%. Colourless liquid, bp 55°C/1 mm Hg (lit.,[62] 50°C/0.5 mm Hg). NMR: $^{31}P\{^1H\}$, δ 37.1 (C_6D_6).

4.2. Calculation details

Fixed geometry single-point computations on **1** were made at a restricted Hartree-Fock level of theory with the Pentium III optimised PC GAMESS version 6.2[63] of the GAMESS (US) QC software package,[64] using structure found in crystal. Medium (6-31G) and larger (6-311G) split-valence Pople's basis sets, supplemented by one or two sets of polarisation functions were applied for all atoms. No extra virtual d-orbitals were added in these calculations according to recommendations[14] of the noninvolvement of such orbitals in phosphorus compounds, as the most important role for d-type functions of the P atom is to polarise a charge density in the molecule.[22,26b,32,60] Moreover, some calculations were performed (with the full relaxation of geometry) for several other conformations of **1**, at the RHF or Becke3-LYP (B3LYP) hybrid density functional level of theory; the standard double-split 6-31G(d,p) basis set within the Gaussian 98W suite of programs[48] was applied. These low-energy forms were initially modelled with the MM+ force field[65] code implemented in the HyperChem program.[66] Net atomic charges were obtained from total Mulliken and Löwdin atomic populations (GAMESS). All calculations were carried out on free molecules in the gaseous phase at 0 K, with no solvent effects included. The 1.5 GHz Pentium 4 class PC running Windows XP was used.

5. X-Ray crystallography

5.1. Data collection

Relatively stable, colourless crystals of **1** were grown from solutions in ethyl acetate. Data were collected with a Rigaku AFC5S diffractometer[67] using graphite-monochromated Cu Kα radiation (λ=1.54178 Å) and ω scan mode. Crystal size 0.5×0.3×0.2 mm^3; θ range 2.37–36.31°, index range $0<h<22$, $0<k<39$, $0<l<10$; reflection collected/independent/observed $[I>2\sigma(I)]$ 5592:4976:3445. A dataset was reduced with TEXSAN;[68] and intensities were corrected analytically for absorption[69] with $T_{\min}$=0.44375 and $T_{\max}$=0.72701, and for the Lorentz and polarisation effects.

5.2. Structure solution and refinement

The structure was solved by direct methods using SHELXS-86[70] which revealed the positions of nonH atoms, and refined by full-matrix least-squares methods against F_o^2 with the SHELXL-97.[71] All heavy atoms were allowed to refine with anisotropic displacement parameters. The H atoms were placed in calculated positions and allowed to ride on their parent atoms $[U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})]$ with the exception of the ylidic H(101) atom, which was located in a difference Fourier synthesis and then refined isotropically. Geometrical calculations and molecular plots were performed with programs PARST97,[72] ORTEX[73] and PLATON.[74] Detailed crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (reference number CCDC 190415).[75]

5.3. Crystal data

$C_{31}H_{26}O_3P_2$, M_r=508.46, T=293(2) K, orthorhombic, space group *Pbca* (No. 61), a=18.653(3) Å, b=31.833(3) Å, c=8.873(3) Å, $\alpha=\beta=\gamma=90°$, V=5269(2) Å^3, Z=8, d_{calc}=1.282 g cm^{-3}, μ(Cu Kα)=1.743 mm^{-1}, F(000)=2128; unique data/restraints/parameters 4976:0:330; goodness-of-fit (on F^2) 1.002; R_1(all data)=0.0711, wR_2(all data)=0.1559, $R_1[I>2\sigma(I)]$=0.0488, $wR_2[I>2\sigma(I)]$=0.1444, where $R_1=\sum(|F_o-F_c|)/\sum|F_o|$, $wR_2=[\sum w(|F_o-F_c|)^2/\sum|F_o|^2]^{1/2}$, $w=1/[\sigma^2(F_o^2)+(0.1003P)^2]$, $P=[(F_o^2+2F_c^2)]/3$; largest diff. peak and hole 0.451 and −0.333 e Å^{-3}.

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