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A DIPOLE MOMENT STUDY OF ALKYLIDENETRIPHENYLPHOSPHORANES, HEXAPHENYLCARBODIPHOSPHORANE, PHOSPHACUMULENE YLIDES AND TRIPHENYLPHOSPHAZINE

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Summary

Analysis of the electric dipole moments in benzene of (dichloromethylene)-triphenylphosphorane, hexaphenylcarbodiphosphorane, (2,2-diethoxyvinylidene)-triphenylphosphorane and of benzoylmethylene- and *p*-nitrobenzoylmethylene-triphenylphosphoranes enables the $Ph_3P{=}CH_2$ dipole moment to be estimated. The best value (4.5 ± 0.5 D) is derived from the dipole moments of (dichloromethylene)triphenylphosphorane and benzoylmethylenetriphenylphosphorane, which do not involve a hybridization moment of the ylidic carbon atom. This value corresponds approximately to the π-bond moment of the phosphorus—carbon bond of phosphorus ylides, and indicates that this π-bond has 55% ionic character. The mesomeric moments of the (P=C=C=X) chain in triphenylphosphoranylideneketenes ($Ph_3P{=}C{=}C{=}X$, with X = O, S or NPh) were derived and the values are briefly discussed. The dipole moment of triphenylphosphazine supports an *E*-conformation.

Introduction

In the last decade several experimental and theoretical studies have been devoted towards establishing the nature of the phosphorus—carbon bond in alkylidenephosphoranes $R_3P{=}CR'_2$ [1—4].

The electronic structure of alkylidenephosphoranes (phosphorus ylides) is

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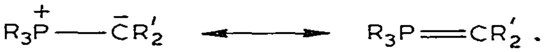
usually described as a resonance hybrid between structures A and B:



$$R_3\overset{+}{P}-\overset{-}{C}R'_2 \longleftrightarrow R_3P{=}CR'_2 .$$

(A) (B)

The infrared spectra of unstabilized ylides Me_3PCH_2 and Ph_3PCH_2 suggest P^VC bond orders of 1.65 and 1.3, respectively [5,6]. Abnormally short P^VC distances in $Me_3P{=}CH_2$ [7], $Me_3P{=}C{=}PMe_3$ [8], $Ph_3P{=}CH_2$ [9], $Ph_3P{=}C{=}C(OEt)_2$ [10], $Ph_3P{=}C{=}PPh_3$ [11], $Ph_3P{=}C{=}C{=}NPh$ [12], $Ph_3P{=}C{=}C{=}O$ [13], $Ph_3P{=}C{=}C{=}S$ [14], $Ph_3P{=}C(CO_2Me)C(CO_2Me){=}CHPh$ [15], $Ph_3P{=}C(Cl)COPh$ [16] $Ph_3P{=}C(I)COPh$ [17], $p\text{-}MeC_6H_4SO_2CH{=}PPh_3$ [18], favour the $d\pi$—$p\pi$ double bond formulation B *. Whereas the values of the coupling constants ^1J(CH)-(methylene) in trialkyl(methylene)phosphoranes are consistent with the ylene form B, the low frequency chemical shift favours the ylide form A [19]. A substantial π-interaction between the phosphonium and carbonium groups in a series of stabilized and unstabilized phosphorus—carbon ylides is indicated by CNDO/2 and MINDO/3 calculations, and by ^{13}C and ^{31}P NMR data [20]. Phot electron spectra of trimethyl(methylene)phosphorane, $Me_3P{=}CH_2$, seem to rev a carbanionic nature for the carbon atom [21]. In addition to these studies, semi-empirical calculations [21—25] and ab initio SCF investigations [26,27] have been performed on hypothetical methylenephosphorane $H_3P{=}CH_2$.

Analysis of the dipole moments of benzoylmethylenetriphenylphosphorane [28] and benzoylmethylenetriphenylarsenane [29] in benzene showed these two derivatives to exist in the *syn* conformation, and gave for $\mu(Ph_3P{=}CH_2)$ an $\mu(Ph_3As{=}CH_2)$ 5.4 and 5.0 D, respectively, whence a substantial ionic characte (~60%) can be deduced for the π-bonding between P^V or As^V and the adjacent carbon atom in phosphorus or arsenic ylides (vide infra).

In view of these results, it is clear that an examination of the dipole moments of simple, unstabilized phosphorus—carbon ylides would be of value. Unfortunately, unstabilized phosphorus—carbon and arsenic—carbon ylides, such as $R_3P{=}CH_2$ and $R_3As{=}CH_2$, recently synthesized by Schmidbaur and coworkers [30,31], are too unstable to be examined, but a careful study of (dichloromethylene)triphenylphosphorane $Ph_3P{=}CCl_2$ (recently prepared by Appel and Morbach [32]) and hexaphenylcarbodiphosphorane, $Ph_3P{=}C{=}CPPh$ has led to sufficiently accurate values of their dipole moments.

Also of interest are the dipole moments, studied in the present work, of (2,2-ethoxyvinylidene)triphenylphosphorane $Ph_3P{=}C{=}C(OEt)_2$, phosphacumulene ylides $Ph_3P{=}C{=}C{=}X$ (X = NPh, O or S) [4], and of triphenylphosphazine $Ph_3P{=}N{-}N{=}CH_2$.

In this study an attempt has been made to define the nature of the P^VC bon in phosphorus ylides and to elucidate problems concerning the mesomeric inte action in phosphacumulene ylides and the preferred conformation of triphenyl phosphazine in solution.

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* Throughout this paper the ylidic phosphorus—carbon bond is for convenience written as P=C, though it is better described as a resonance hybrid between $\overset{+}{P}{-}\overset{-}{C}$ and P=C.

Experimental

Materials

Cryoscopic R.P. benzene (from "Prolabo", Paris) was recrystallized and dried over metallic sodium: at 25°C, d_4 0.8737, n_D 1.4982, ϵ 2.2741 (assumed).

Pure samples of (chloromethylene)triphenylphosphorane and (dichloromethylene)triphenylphosphorane were kindly supplied by R. Appel (see [32]).

(2,2-Diethoxyvinylidene)triphenylphosphorane, hexaphenylcarbodiphosphorane, triphenylphosphoranylketen and related compounds ($Ph_3P{=}C{=}C{=}X$, with X = O, S or NPh) were prepared by Bestmann and coworkers (cf. [4] and the bibliography cited therein).

Aroylmethylenetriphenylphosphoranes (p-$XC_6H_4COCH{=}PPh_3$, X = H, Cl or NO_2), previously prepared by Arcoria and Scarlata [28], were recrystallised and their melting points checked. New samples of aroylmethylenetriphenylarsenanes (p-$XC_6H_4COCH{=}AsPh_3$, X = H, F or NO_2), described in references 29 and 33, were also examined.

Physical measurements

The dipole moments were measured in benzene at 27.0°C, since the laboratory temperature is normally 22—24°C. To avoid the effects of air, especially detrimental for unstabilized phosphorus ylides, solutions were prepared under nitrogen in a dry box.

The total polarization of the solute, extrapolated to infinite dilution, was calculated from the ratios [34]:

$$\alpha_0 = \lim_{(w\,=\,0)} \left(\frac{\epsilon - \epsilon_1}{w}\right) \text{ and } \beta = \frac{\Sigma(v - v_1)}{\Sigma w} ,$$

where w is the weight fraction of the solute, ϵ and v are, respectively, the dielectric constant and specific volume of the solutions; subscript one refers to the pure solvent as used, i.e. prepared in the same way as the solutions. The α_0 value has been determined by least-square analysis of the $\epsilon(w)$ polynomial function (linear or, in some cases, quadratic). A microbalance was used in making up the solutions. Specific volumes were accurately measured with a Digital Microdensimeter DMA 02C (from "Anton Paar KG", Graz, Austria). The distortion polarization ${}_EP + {}_AP$ was assumed to equal the molecular refraction of the solute (R_D), as calculated from $\gamma = \Delta n^2/w$ and β, using an equation similar to that of Halverstadt and Kumler [34]. Differences between the refractive indices of solutions and pure solvent were measured using a thermostatted "VEB Carl Zeiss" interferometer. The technique for the measurement of dielectric constants has been described elsewhere [35].

For each solute examined, values of w_{max} (reported to only three decimal points. though it is known with at least five), α_0, β (in ml g^{-1}), $P_{2\infty}$ and R_D (both in ml mol^{-1}), and μ (in Debye units) are listed in Table 1.

From the accurately measured molecular refractions of phosphacumulene ylides $Ph_3P{=}C{=}C{=}X$ (X = O, S or NPh) and of p-chlorobenzoylmethylenetriphenylphosphorane (130.3 ml mol^{-1}), a value for $R_D(Ph_3P{=}C)$ of 93 ± 2 ml mol^{-1} can be derived from the bond additivity scheme of Vogel et al. [36]. Similarly, the molecular refractions of aroylmethylenetriphenylarsenanes

TABLE 1

PHYSICAL DATA FROM DIPOLE MOMENT DETERMINATIONS IN BENZENE

Solute	T (°C)	w_{max}	α_0	$-\beta$ (ml g^{-1})	$P_{2\infty}$ (ml mol^{-1})	R_D (ml mol^{-1})	μ (D)
$Ph_3P{=}CHCl$	27	0.002	6.6	0.334	462.2	101.2	4.21 ± 0.05
$Ph_3P{=}CCl_2$	27	0.004	8.5	0.371	633.5	106.0	5.09 ± 0.10
$Ph_3P{=}C{=}C(OEt)_2$	28	0.054	3.35	0.264	337.1	125.5	3.23 ± 0.02
$Ph_3P{=}C{=}PPh_3$	28	0.014	5.0	0.325	635.3	186.0	4.69 ± 0.05
$Ph_3P{=}C{=}C{=}NPh$	28	0.025	13.1	0.340	1024.5	127.0	6.66 ± 0.03
$Ph_3P{=}C{=}C{=}O$	25	0.009	16.9	0.339	1034.0	100.5	6.77 ± 0.03
$Ph_3P{=}C{=}C{=}S$	28	0.012	24.95	0.352	1575.2	108.0	8.51 ± 0.02
$Ph_3P{=}N{-}N{=}CH_2$	30	0.066	5.80	0.317	410.3	98.9	3.94 ± 0.02

p-$XC_6H_4CH{=}AsPh_3$, 130, 140 and 136 (±2) ml mol^{-1} for X = H, F or NO_2, afford $R_D(Ph_3As{=}C)$ 97 ± 2 ml mol^{-1}, a value close to that (97.5 ± 2 ml mol^{-1}) deduced from $R_D(Ph_3P{=}C)$ by adding five times the difference (equal to 4.52 — 3.63 = 0.89 ml mol^{-1} [37]) between R_D(As—C) and R_D(P—C). These values serve to provide more accurate measures of the molecular refractions of the phosphorus and arsenic ylides previously studied [28,29]. The molecular refractions so derived are given in Table 2, they are so close to those previously given that the conclusions in references 28 and 29 need not to be changed.

Results and discussion

Table 3 lists the dipole moments of the ylides examined in the present work.

The electric dipole moment of (dichloromethylene)triphenylphosphorane

^{13}C and ^{31}P NMR data, as well as CNDO/2 and MINDO/3 calculations, indicate that the carbon adjacent to phosphorus is trigonally hybridized in alkylidene phosphoranes $H_3P{=}CH_2$, $H_3P{=}CHMe$, $H_3P{=}CMe_2$, $Ph_3P{=}CHMe$ and $Ph_3P{=}CMe_2$ [20]. Consequently, the dipole moment of (dichloromethylene)triphenylphosphorane $Ph_3P{=}CCl_2$ can be expressed as

$$\begin{aligned}\mu(\mathrm{I}) &= \mu(\mathrm{Ph_3P{=}CH_2}) + \mu(\mathrm{H_2C{=}CCl_2}) + \Delta m,\\ &= Y_0 \qquad\qquad + 1.28\ [38] \qquad + \Delta m,\end{aligned}$$

where Δm measures the change in mesomeric moment of the two chlorine atoms on passing from $Cl_2C{=}C$ to $Cl_2C{=}P$.

$m(Cl_2C{=}P)$ is certainly greater than is $m(Cl_2C{=}C)$ because of the following. Contribution of $Cl^+{=}C(Cl){-}\bar{X}$(X = C or P) ionic structures depends on the energy needed in passing from C=X to C—$\bar{X}$, which is $E_\pi(C{=}X) - A(X)$ (see [39,40]). Now $E_\pi(C{=}P)$ is likely to be very small, in $H_3P{=}CH_2$ [22,26] and $Me_3P{=}C{=}PMe_3$ [8], whereas $E_\pi(C{=}C)$ can be as high as 40 kcal mol^{-1} [41]. This large difference cannot be balanced out by the smaller electron affinity of phosphorus than of carbon: A(P) 0.72 eV [42] (other values between 0.57 and 1.33 eV [43]), A(C) 1.37 eV [41]. HMO calculations show that the m value is much increased by reducing the resonance integral $k(C{=}X)$ [44], in (Z—C = X) systems. As $m(Cl_2C{=}C)$

TABLE 2

RECALCULATED DIPOLE MOMENTS OF PHOSPHORUS AND ARSENIC YLIDES PREVIOUSLY EXAMINED (Debye units)

Phosphorus ylide	$P_{2\infty}$ (ml mol^{-1})	R_D (ml mol^{-1})	μ^a (D)	Arsenic ylide	$P_{2\infty}$ (ml mol^{-1})	R_D (ml mol^{-1})	μ^a (D)
$Ph_3P{=}CHCHO$	953	102	6.45	$Ph_3As{=}CHCOMe$	796	112	5.78
$Ph_3P{=}CHCOMe$	751	108	5.57	$Ph_3As{=}CHCOPh$	756	130	5.53 [b]
$Ph_3P{=}CHCOPh$	752	126	5.53	p-$PhC_6H_4COCH{=}AsPh_3$	807	155	5.65
p-$MeC_6H_4CH{=}PPh_3$	689	131	5.53	p-$MeC_6H_4COCH{=}AsPh_3$	731	135	5.40
p-$ClC_6H_4CH{=}PPh_3$	1075	131	6.80	p-$FC_6H_4COCH{=}AsPh_3$	1076	130	6.82 [c]
p-$NO_2C_6H_4CH{=}PPh_3$	1910	132	9.33	p-$BrC_6H_4COCH{=}AsPh_3$	1097	140	6.84 [d]
$(p$-$ClC_6H_4)_3P{=}CHCOPh$	510	141	4.25	p-$NO_2C_6H_4COCH{=}AsPh_3$	1924	136	9.35 [b]
p-$ClC_6H_4COCH{=}P(p$-$ClC_6H_4)_3$	699	146	5.20	$MeO_2CCH{=}AsPh_3$	901	114	6.20
$EtO_2CCH{=}PPh_3$	631	114	5.02	p-$NO_2C_6H_4N{=}AsPh_3$	1622	115	8.59
$EtO_2CC(Me){=}PPh_3$	717	119	5.41				

[a] In benzene at 25°C, if not specified, and for ${}_EP + {}_AP = R_D$. [b] G.C. Pappalardo and G. Scarlata (personal communication) have found 5.55 and 9.24 D, respectively. [c] At 25°C (H. Lumbroso and P. Fröyen, unpublished). [d] At 27°C (H. Lumbroso and P. Fröyen, unpublished).

TABLE 3

DIPOLE MOMENTS OF VARIOUS UNSTABILIZED AND STABILIZED YLIDES (Debye units)

No.	Compound	μ(benzene) (D)
	(Chloromethylene)triphenylphosphorane	4.21 ± 0.05
I	(Dichloromethylene)triphenylphosphorane	5.09 ± 0.10
II	Hexaphenylcarbodiphosphorane	4.69 ± 0.05
III	(2,2-Diethoxyvinylidene)triphenylphosphorane	3.23 ± 0.02
IV	Benzoylmethylenetriphenylphosphorane	5.53 ± 0.02
V	Benzoylmethylenetriphenylarsenane	5.53 ± 0.03
	para-Nitrobenzoylmethylenetriphenylphosphorane	9.33 ± 0.02
	para-Nitrobenzoylmethylenetriphenylarsenane	9.35 ± 0.02
VI	Triphenylphosphoranylideneketen	6.77 ± 0.03
VII	Triphenylphosphoranylidenethioketen	8.51 ± 0.02
VIII	Triphenylphosphoranylidene-*N*-phenylketeneimine	6.66 ± 0.03
IX	Triphenylphosphazine	3.94 ± 0.02

is $\mu(H_2C{=}CCl_2) - \mu(H_2CCl_2) = 1.28 - 1.59 = -0.31$ D [45], $m(Cl_2C{=}P)$ may attain —0.6 D. If so, one calculates

$$Y_0 = 5.09 - 1.28 + 0.31 = 4.11\ (\pm 0.1\ \text{D}).$$

The electric dipole moment of hexaphenylcarbodiphosphorane

Some difficulties arise in interpreting the dipole moment of hexaphenylcarb diphosphorane (II); these are associated with the value of its PCP angle and of the hybridization moment of the central carbon atom.

In the solid phase allene ylide II has a disordered structure which consists of two assemblies of molecules, equally populated, with PCP angles of 143.8 and 130.1° [11]. The structure in solution is not known, but it is likely that all the molecules have the same nonlinear structure (say with angle PCP 137°). There is also a possibility that the isolated molecule has, like hexamethylcarbo diphosphorane in the gas phase [8], an average linear structure with shrinkage caused by a low frequency bending vibration giving rise to the apparent nonlin rity and, consequently, to the observed dipole moment (4.69 D, for $_{E}P + {}_{A}P = R_D$).

For rigid angular models the dipole moment can be expressed as

$$\mu = 2\ Y^*\cos\alpha = 2\ Y_0^*\cos\alpha + \mu_h$$

where Y_0^* is the intrinsic dipole moment of ($Ph_3P{=}C$) groups and μ_h the hybrid zation moment of the carbon atom (as defined by Gibbs [46]). It can be show (see [47]) that the hybridization moment for the model seen in Fig. 1 is $\mu_h = 2e(1 - a^2) \cdot F_{VI}(\alpha) \cdot G(C)$ [46], where a is the contribution of the carbon σ-bonding orbital to the σ-bond wave function $\psi(C{-}P) = a\varphi_C + (1 - a)\varphi_P$, $F_{VI}(\alpha)$ a known function of the PCP angle (2α) and $G(C) = \int x \cdot (2s) \cdot (2p) \cdot d\tau$ 0.468 Å [48]. In the present case, the electronegativity difference $x(C) - x(P)$, which is normally 0.4, is markedly decreased by π-charges on the atoms (~0.5 and —0.5 e) and becomes 0.13 only; hence a^2 is nearly 0.5, and $\mu_h(C) = F_{VI}(\alpha)$ (2.25) in Debye units.

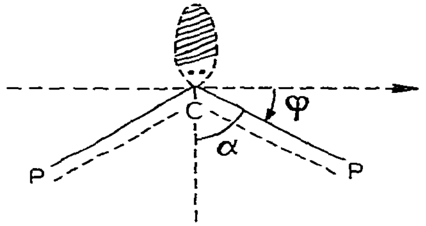


Fig. 1. Angular hybridization model for Ph_3PCPPh_3.

The first model for II leads to a mean quadratic dipole moment:

$$\overline{\mu_{(II)}^2} = \frac{(2\ Y^*\cos 71.9)^2 + (2\ Y^*\cos 65.0^\circ)^2}{2},$$

whence $Y^* = 6.3$ D. The second rigid model is consistent with a dipole moment equal to $\mu_{(II)} = 2\ Y^*\cos(68.5^\circ)$, giving $Y^* = 6.4$ D and, for $\mu_h(C) = 1.6$ D, $Y_0^* = 4.2$ D.

Calculation of the dipole moment of the third (flexible) model needs knowledge of the "average amplitude" of the $\phi = (\pi - 2\alpha)/2$ angle. Taking $\phi_m \sim 35^\circ$, as a trial, leads to:

$$\overline{\mu_{(II)}^2} = \frac{4\ Y^{*2}\int_0^{\phi_m} \sin^2\phi \cdot d\phi}{\phi_m} = 2\ Y^{*2}\left(1 - \frac{\sin 2\phi_m}{2\phi_m}\right)$$

whence $Y^* \sim 7$ D.

From these results it appears that the best value for Y^* is 6.4 D, whence $Y_0^* = 4.2$ D. By subtracting the ($H—C_{sp^2}$) bond moment, 0.6 D [49], one obtains 3.6 D, in fair accord with the value of $Y_0 = 4.1$ D deduced from the dipole moment of (dichloromethylene)triphenylphosphorane.

A dipole analysis of (2,2-diethoxyvinylidene)triphenylphosphorane

In the crystalline phase (2,2-diethoxyvinylidene)triphenylphosphorane (III) has the following structure [10]: angle PCC 125.6°, angle CCO′ 127.6°, angle CCO″ 123.0°, and geometry for $C(OEt)_2$ is shown in Fig. 2.

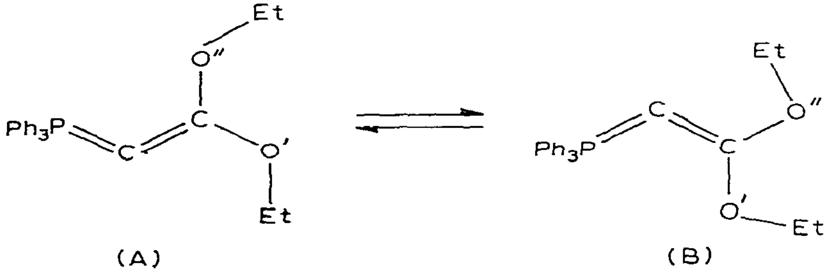
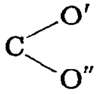


Fig. 2. Structures of planar conformers of (2,2-diethoxyvinylidene)triphenylphosphorane (diagrammatic).

In solution in toluene, facile inversion through the ylidic (central) carbon atom is observed [50]. However, since the relaxation time in dielectric polarization phenomena is small on the NMR time scale, the observed moment (3.23 D) corresponds to that of A or B, (Fig. 2), identical planar conformers. Some flexibility of these models is probable, and should be taken into account.

The dipole moment of ylide III can be regarded as the vector sum

$$\mu(\mathrm{III}) = \mu(\mathrm{Ph_3P{=}C}) + \mu_h(\mathrm{C}) + \mu(s\text{-}cis\text{-methoxyvinyl}) + \mu(s\text{-}trans\text{-methoxyvinyl}) - \mu(\mathrm{H_2C}_{sp^2})$$

where $\mu_h(\mathrm{C}) = 2.0$ D, $\mu(\mathrm{H_2C}_{sp^2}) = 0.6$ D. The dipole moment of *s-cis*-methoxyvinyl (0.96 D) acts at 60° to the C—O′ bond axis [51], whence $m(\mathrm{O{-}C{=}C}) = 0.35$ D; that of *s-trans*-methoxyvinyl is obtained by adding the vector $\boldsymbol{m}$ to $\mu(\mathrm{Me_2O''}) = 1.25$ D [45]. With these rather rough assumptions, one derives $Y = \mu(\mathrm{Ph_3P{=}C}) = 3.1$ D and, thereby, $Y_0 = \mu(\mathrm{Ph_3P{=}CH_2}) = 2.5$ D. Because of the approximate nature of the treatment, these values are only indicative, and probably much too low. They would be increased by ~0.5 D by taking into account of the flexibility of the system, and slightly augmented (by 0.2 D) if allowance were made for the geminal effect lowering the dipole moment of the  group *. Reduction in $\mu_h(\mathrm{C})$ also strongly increases the derived Y value, which would reach 4.4 D for $\mu_h(\mathrm{C}) = 0$. There is also a possibility that $m(\mathrm{O{-}C{=}C})$ is greater than 0.35 D and attains m(anisole) = 0.9 D [44], since only absolute μ_a and μ_b values are given by microwave spectroscopy [51] **. It follows, therefore, that a value for Y_0 much greater than 2.5 D could be derived from the dipole moment of (2,2-diethoxyvinylidene)triphenylphosphorane.

The dipole moments of benzoylmethylenetriphenylphosphorane and benzoylmethylenetriphenylarsenane

Attempts to rationalise the electric dipole moments of benzoylmethylenetriphenylphosphorane and -triphenylarsenane, IV and V, have already been made [28,29]. The dipole moments in benzene, both equal to 5.53 D (recalculated, see experimental part), show that these compounds exist in the planar *syn*-conformation (Fig. 3). The angles (θ) that μ(IV) and μ(V) make with the C—Ph bond axis are calculated by solving the vectorial equations:

$$\mu(p\text{-}\mathrm{NO_2C_6H_4CH{=}ZPh_3}) = \mu(\mathrm{IV\ or\ V}) + \mu^*(\mathrm{Ph{-}NO_2}),$$

$$\mu(p\text{-}\mathrm{NO_2C_6H_4CHO}) = \mu(\mathrm{Ph{-}CHO}) + \mu^*(\mathrm{Ph{-}NO_2}).$$

Taking $\mu(p\text{-}\mathrm{NO_2C_6H_4CHO}) = 2.49$ D (see [28 and 53]), $\mu(\mathrm{PhCHO}) = 2.99$ D acting at 34° to the Ph—CO bond axis [54], one obtains $\mu^*(\mathrm{Ph{-}NO_2}) = 4.32$ D and, putting this value in the first vectorial equation gives $\theta(\mathrm{IV}) = 38°$, $\theta(\mathrm{V}) = 37°$, from $\mu(p\text{-}\mathrm{NO_2C_6H_4CH{=}ZPh_3}) = 9.33$ and 9.35 D (Z = P or As).

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* Owing to the mutual inductive effect of both C—Cl bonds, the dipole moment of dichloromethylene (1.59 D) is 0.4 D smaller than that calculated using methyl chloride (1.8 D). See [52].

** The sign of μ_b is beyond doubt; for $\mu_b = 0.915$ D and $\mu_a = +0.294$ or -0.294 D, m can be estimated at 0.3 and 0.8 D respectively.

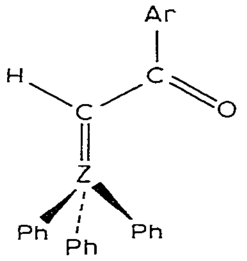


Fig. 3. *syn*-Conformation for aroylbenzoylmethylene-triphenylphosphoranes and -triphenylarsenanes (Z = P or As, Ar = Ph or p-$NO_2C_6H_4$).

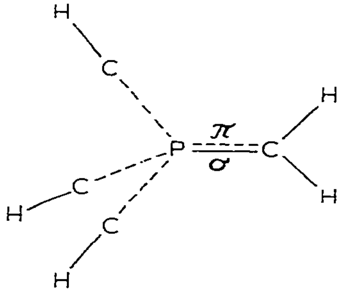


Fig. 4. Bond dipole moments in $Y_0 = \mu(Ph_3P{=}CH_2)$ (diagrammatic) ($Y_0 \sim \mu_\pi(P{=}C) = \mu(P...C)$).

Now μ(IV and V) can be regarded as equal to the resultants:

μ(IV and V) = $\mu(Ph_3Z{=}CH_2) + \mu(Ph{-}CHO) + m$

where $\mu(Ph_3Z{=}CH_2) = Y_0$, as the molecules have no hybridization moment of their ylidic carbon atom, and m is the mesomeric moment of the (Z = CH—C=O) group. Solving these equations gives

$\mu(Ph_3P{=}CH_2)$ = 4.8 D, m(P=C—C=O) = 2.8 D;

$\mu(Ph_3As{=}CH_2)$ = 4.7 D, m(As=C—C=O) = 2.9 D

(cf. [28] and [29] for more details).

The (Z=C—C=O) mesomeric moments are much greater than that of (C=C—C=O), which is only 0.8 D in *trans*-acrolein ($m = \mu(\text{acrolein}) - \mu(H_2C{=}O) = (3.11) \cdot u - (2.34) \cdot x$ [45]). This is certainly due to the weakness of the π-bonding in P=C (see Table 4). Great importance of the ($\overset{+}{P}{-}C = C{-}\overset{-}{O}$) canonical form in the resonance hybrid for keto-stabilized phosphorus ylides has been suggested on other grounds [55].

The significance of the results on $Y_o = \mu(Ph_3P{=}CH_2)$

The best value for $\mu(Ph_3P{=}CH_2)$ is that derived from the dipole moments of (dichloromethylene)triphenylphosphorane (Y_o = 4.1 D) and benzoylmethylene-triphenylphosphorane (Y_o = 4.8 D) since for these derivatives the analysis does

TABLE 4

HMO CALCULATED π-ELECTRON DENSITIES IN (X—C′=C″=O) SYSTEMS (Z-shaped).

System	q(C or X)	q(C′)	q(C″)	q(O)	m
(C″=O) [a]	—	—	0.745	1.255	2.4
(C=C′—C″=O) [b]	0.859	1.036	0.739	1.367	1.6
(X=C′—C″=O) [c]	0.744	1.085	0.769	1.402	2.9

[a, b] $h(\dot{O}) = 1.0$, $k(C{=}O) = 1.5$ [$\alpha(A) = \alpha(C) + h\beta$, $k(C{=}O) = \beta(C{=}O)/\beta(C{=}C)$]. [c] $h(X) = 0$, $h(\dot{O}) = 1.0$, $k(C{=}X) = 0.6$, $k(C{=}O) = 1.5$.

not need knowledge of the hybridization moment of the carbon atom joined to phosphorus. In the following a value of $Y_o = 4.5 \pm 0.5$ has been used.

Since in phosphorus ylides the phosphorus is nearly tetrahedral [7—18] and the ylidic carbon atom trigonally hybridized [20], the five H—C_{sp^2} bond moments nearly cancel as do the four P—C_{sp^2} ones (Fig. 4). Consequently, as a first approximation, Y_o equals the π-bond moment of the P=C link, which can be divided into two parts, a ionic term μ_i and an overlap component μ_r [46,56]. As μ_r depends little on the hybridization state of the atoms (μ_r(C—H) = 1.15, 1.06 and 0.89 D for C_{sp^3}, C_{sp^2} or C_{sp}, μ_r(P—H) = 1.60 and 1.85 D for P_{sp^3} or not hybridized [56]), one can assume $\mu_r(P \cdots C) \sim \mu_r(P_{sp^3}—C_{sp^3}) = 0.44$ D [46], and derives $\mu_i(P \cdots C) = 4.0 \pm 0.5$ D.

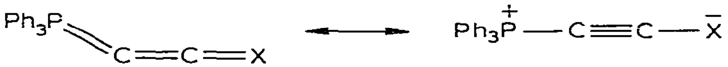
Now the bond moment calculated for a pure ionic bond $\overset{+}{P}—\overset{-}{C}$ is $k \cdot eR$, with $k \leqslant 1$ and $R = 1.7$ Å, that is $k \cdot (8.15)$. If $k = 1$, this leads to a ionic character of 50 ± 5% for the π-bond of the ylidic P^VC link, but there is a possibility that k be somewhat smaller than unity. Analysis of the dipole moment of *N*-trimethylammoniobenzamidate (5.27 D) led to $\mu(\overset{+}{N}—\overset{-}{N}) = 6.5$ D [53], whence $k = 0.9$. If so the ionic character becomes 55 ± 5%. This result, though approximate, is consistent with infrared and Raman spectroscopic studies on methylenetrimethylphosphorane and -triphenylphosphorane which indicate bond orders for P^VC bonds of 1.65 [5] and 1.35 [6], respectively, and also with conclusions drawn from ^{13}C and ^{31}P NMR data, as well as from CNDO/2 and MINDO/3 calculations, for some unstabilized and stabilized phosphorus ylides [20]. The theoretical results depend markedly upon whether or not *d* orbitals on the phosphorus atom are included (see [22,23,26]); this is precisely the problem to be resolved. For methylenetriphenylphosphorane, a theoretical moment of ca. 2.2 D has been found [24]. Such high π-bond moments for ylidic P=C and As=C links are due to relative weakness of the energy of these π-bonds ($nd\pi$ — $2p\pi$) [28,29]. Taking $h(\dot{Z}) = -0.5$, and $k(P{=}C) = k(As{=}C) = 1.0$, 0.8, 0.5 and 0.3, leads to $\mu_\pi(P{=}C) = 2.15$, 2.48, 3.72 or 5.28 D; $\mu_\pi(As{=}C) = 2.35$, 2.71, 4.07 or 5.77 D, to be compared with $\mu_\pi(Z{=}C) \sim 4.5$ D.

The mesomeric effect in phosphacumulene ylides

Phosphacumulene ylides ($Ph_3P{=}C{=}C{=}X$, X = O, S or NPh, VI—VIII) are compounds showing remarkable features in their structure (see [4]): VI (X = O), angle PCC 145.5° [13]; VII (X = S), angle PCC 168.0° [14], VIII (X = NPh), angle PCC 134.0° [12]. They all exhibit high dipole moments of 6.77, 8.51 and 6.66 D, respectively, which can be expressed as:

$$\boldsymbol{\mu}(\text{VI—VIII}) = \boldsymbol{\mu}(Ph_3P{=}C) + \boldsymbol{\mu}_h(C) + \boldsymbol{\mu}(H_2C{=}C{=}X) - \boldsymbol{\mu}(H_2C) + \boldsymbol{m}$$

where $\mu_h(C) = 1.3$, 0.45 and 1.7 D respectively, and m stands for the mesomeric moment of the P=C=C=X group as a result of resonance



Only the dipole moment of ketene is known (1.43 D [45]). That of thioketene was assumed to equal $[\mu(H_2C{=}S) - \mu(H_2C{=}O)] + 1.43 = (1.65 - 2.34) + 1.43 = -0.69$ [45] + 1.43 = 0.74 D. The dipole moment vector $\boldsymbol{\mu}(H_2C{=}C{=}N{-}Ph)$ has been equated to $\boldsymbol{\mu}(H_2C{=}C{=}N) + \boldsymbol{\mu}(Ph{-}N_{sp^2})$, with $[\mu(H_2C{=}C{=}N) = \mu(H_2C{=}N) -$

$\mu(H_2C{=}O)] + 1.43 = 1.8$ [57] $- 2.34$ [45] $+ 1.43 = 0.89$ D and $\mu(Ph{-}N_{sp^2}) = \mu(\text{mesityl}{-}N) + \mu_h(N_{sp^2}) - \mu_h(N_{sp^3}) = 1.24$ D (from [58]) $+ 0.14$ D [46,59] $= 1.38$ D. With these assumptions, $m(\text{VI}) = 0.7$ D, $m(\text{VII}) = 3.3$ D, $m(\text{VIII}) = 2.2$ D, for $\mu(Ph_3P{=}C) = 5.1$ D.

The (P=C=C=O) mesomeric moment appears to be much smaller than that in benzoylmethylenetriphenylphosphorane (2.8 D). Unexpectedly since the latter much exceeds m(*s-trans*-acrolein), it is equal to that of methylene ketene, $m = 2.14$ D [60] $- \mu(H_2C{=}C{=}O) = 2.14 - 1.43 = 0.71$ D.

The results clearly show that the thiocarbonyl bond conjugates much more with a double bond (here P=C) than do carbonyl and keteneimine bonds. This parallels the mesomeric moments found for the (C=C—C=S) and (C=C—C=O) conjugated systems, which have values of 1.5 and 0.7 D, respectively [40].

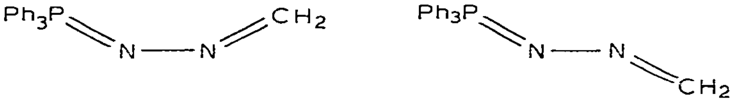
As the magnitude of the mesomeric moment m reflects contribution of the linear ionic structure, the greater it is the larger should be the PCC angle. This is observed for the compound pairs VI and VII, and VIII and VII, but not for VIII and VI. In the latter case the unexpected trend may be due to the electronegativity of the carbon increasing with the PCC angle (C_{sp^2} 2.75, C_{sp} 3.29 [61]), with the result that $\mu(Ph_3P{=}C)$ should be somewhat greater in VIII than in VI; such an effect cannot account, of course, for the large differences $m(\text{VII}) - m(\text{VI})$ and $m(\text{VII}) - m(\text{VIII})$.

The preferred conformation of triphenylphosphazine

Triphenylphosphazine ($Ph_3P{=}N{-}N{=}CH_2$, IX) can exist in a number of forms among which more stable are the planar *Z*- and *E*-conformers which benefit from full (P=N—N=C) conjugation energy (Fig. 5).

The dipole moments of *Z*- and *E*-conformers are $\mu(Z \text{ or } E) = \mu(Ph_3P{=}N) + \mu(H_2C{=}N) + m(P{=}N{-}N{=}CH_2)$, where $\mu(Ph_3P{=}N) = 4.7$ D from $\mu(Ph_3P{=}NH) = 4.21$ D [45] and $\mu(H{-}N_{sp^2}) = 1.25$ [as deduced from $\mu(NH_3)$] $+ 0.14 = 1.39$ D, and $\mu(H_2C{=}N) = 1.8$ D [57] if angle PNH = 120°. As $\mu(Z)$ exceeds the value 6.0 ± 0.2 D (for angle CNN = PNN = 115 ± 5°) calculated ignoring m, and $\mu(E)$ can be lower than $\mu(Ph_3P{=}N) = 4.7$ since $\mu(H_2C{=}N)$ acts in an opposite direction, the experimental moment (3.94 D) clearly shows that the compound exists as *E*.

Analysis of the dipole moment suggests $m(E) = 1.1$ D, assuming there is no *Z*-contributor. ^{13}C and ^{31}P NMR spectroscopy imply that interconversion of the *E* and *Z* conformers is rapid or that one conformer is strongly preferred over the other [62]; the observed dipole moment supports the latter model, further indicating that the prevailing conformer is *E*-shaped. In the gaseous state formaldazine prefers the *E* conformation [63,64], and so does acetaldazine in the liquid phase [65,66]. The small moment of the latter (1.17 D in heptane for ${}_EP + {}_AP = R_D$ [67]) may be due to presence of some polar conformer (see



Z-conformer *E*-conformer

Fig. 5. Planar *Z*- and *E*-conformers of triphenylphosphazine.

[68]). In the crystal, 4,4′-dibromocinnamaldazine [69] and 4,4′-dimethoxybenzaldazine [70] have a planar centrosymmetric structure.

Conclusion

Analysis of the dipole moments of (dichloromethylene)triphenylphosphoran (I), hexaphenylcarbodiphosphorane (II), (2,2-diethoxyvinylidene)triphenylphosphorane (III) and benzoylmethylene-triphenylphosphorane (IV) enables an estimate to be made of the ($Ph_3P{=}CH_2$) dipole moment, which cannot be measured directly. The best value (4.5 ± 0.5 D) is that drawn from the moment of I and IV which, in contrast to those of II and III, do not contain a term due to hybridization of the ylidic carbon atom. This value is consistent with a high ionic character (~55%) for the π-bond of P=C in phosphorus ylides.

The group mesomeric interaction is weaker in triphenylphosphoranylideneke than in benzoylmethylene-triphenylphosphorane. The mesomeric moment of triphenylphosphoranylidenethioketene (3.3 D) is much higher than those of triphenylphosphoranylideneketene and triphenylphosphoranylidene-*N*-phenylketeneimine (0.7 and 2.2 D) and this is consistent with the PCC angles in the series (168.0, 145.4 and 134.0°).

In solution in benzene triphenylphosphazine exists mainly in the *E*-conformation.

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