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Structural Features of the Phosphorus Heterocumulene Ylides (*sp*-Ylides)

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Abstract — The features in phosphorus heterocumulene yilides Ph_3PCCX [X = NPh, NC(O)Ph, C(CN)CO·(OMe), O, S] with the ylide carbon geometry close to *sp*-hybridization are studied using ab initio methods. Estimation of structural parameters of a new member in the $Ph_3PC^{\alpha}=C^{\beta}=NC(O)Ph$ series on the B3LYP/6-31G(*d,p*) level and together with experimental data for related ylide (X = NPh) gave the following values: $r(PC^{\alpha})$ 1.665 Å, $r(C^{\alpha}=C^{\beta})$ 1.237 Å, $\omega(PC^{\alpha}C^{\beta})$ 145.2°. Nonvalent interactions of sp^{λ} orbital of the ylide carbon atom bearing extra negative charge with coplanar π-electrons of the nearest $C^{\beta}=N$ bond are found close to those of nitrogen lone pair with the $C^{\alpha}=C^{\beta}$ bond and leading to up to 10° nonlinearity of $C^{\alpha}–C^{\beta}=N$ triad of the phosphorus iminoketene ylides. Chemical nonequivalence of the PC^{ipso} bonds in the triphenylphosphonium fragment, relation of $^1J_{PC^{\alpha}}$ spin–spin coupling and antisymmetric bonding vibration ν^{as}(C=C=X) to the structure of the carbanion, and inductive hyperconjugative influence of atom (or group) X on the ylide carbon geometry are discussed.
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Interpretation on the basis of D_{2d} dot group of IR and Raman spectra of allene [1], the simplest representative of a special class of compounds containing cumulate double bonds, has confirmed presumed by valence theory linearity of the allene triad and orthogonality of the π systems of its neighboring double bonds. Typical features of allenes appear as extremely strong deshielding of central carbon atom of the triad, to 200 ppm [2], and presence in its IR spectrum of the strongest (contrary to the theory) absorption band near 2000 cm^{-1} [1]. The relation between the triad properties modified by introducing a heteroatom, by asymmetric influence of polar terminal groups, and deviation from linearity and other structural characteristics of such heterocumulene system is of considerable interest. In this respect special attention has been paid to phosphaheterocumulenes which include C=C=X triad polarized by phosphonium group which promotes their reactivity in the addition reaction, the Wittig reaction and other [3]. In distinct to phosphorus sp^2-ylides $R_3P–CXY$, structure of *sp*-ylides $R_3P=C=C=X$ starting with their first representatives (X = O, S) [4, 5] groundlessly attracted much less attention, despite their unique geometry which includes unusual mediate value of the angle at the ylide carbon atom and very low bond lengths in the cumulene chain.

In continuation of the study of phosphorus ylides [6–8], in this work we performed quantum-chemical investigation by nonempirical RHF/3-21G(*d,p*), RHF/3-31G(*d,p*) and B3LYP/6-21G(*d,p*) methods of electronic structure of triphenylphosphonium phenyliminoketeneylide (**I**), triphenylphosphonium bezoliminoketeneylide (**II**), triphenylphosphonium 3-methoxycarbonyl-3-cyanocumuleneylide (**III**), triphenylphosphonium keteneylide (**IV**), triphenylphosphonium thioketeneylide (**V**), and reference compound allene (**VI**), and compared their calculated structural, electronic and spectral characteristics with published and our own experimental data. For the ylide **I** some of torsion angle were obtained from X-ray structural data [9] by transformation of oblique to Cartesian coordinates. The ylide **II** was first prepared by us as a solution in methylene chloride in a NaCl cell of IR spectrometer at the spontaneous transformation of the corresponding azlactone and detected by its absorption bands at 2062 and 1673 cm^{-1} (the details will be reported elsewhere). More recently it was isolated as an amorphous substance [10] [the paper text contains an error, the correct value is 2062 (C=C=N) cm^{-1}], therefore no structural data are available). The ylide **III** was obtained in a solution [11] and is included to the study because it practically adequately simulates ylide **II**: the =C–C≡N fragment is similar to the imine nitrogen =N– by inductive component and methoxy-

Table 1. Calculated by the methods RHF/6-31(*d,p*), B3LYP/6-31(*d,p*) and experimental [9] structural characteristics of iminoketeneylide $Ph_3PC^{\alpha}=C^{\beta}=NPh$ (**I**)

Parameters [a]	6-31G(*d,p*)	B3LYP/6-31G(*d,p*)	Experiment	$\Delta^{calc.-exp.}$ [b]
$-E$, au	1391.35337	1398.13964	–	–
μ, D	7.8	6.8	–	–
$r(PC^{\alpha})$, Å	1.675	1.676	1.677	–0.001
$r(C^{\alpha}=C^{\beta})$, Å	1.263	1.281	1.248	0.033
$r(C^{\beta}=N)$, Å	1.231	1.244	1.252	–0.008
$\omega(PC^{\alpha}C^{\beta})$, deg	135.6	137.3	134.0	3.3
$\omega(C^{\alpha}C^{\beta}N)$, deg	175.7	173.5	172.5	1.0
$\omega(C^{\beta}NC^{i}C^{o})$, deg	7.9	5.4	1.9 [c]	3.5
q(P), au	0.966	0.848	–	–

[a] Hereinafter the charges are given in a Lewdin approximation. [b] The difference between calculated on B3LYP/6-31G(*d,p*) level and experimental parameters. [c] Determined for C^{β}=N–Ph from atomic coordinates [9].

carbonyl group simulates –C(O)Ph group by conjugation component. It is also helpful that IR spectrum of ylide **III** contains three experimental charactersistic absorption bands [12] allowing conclusive comparison with calculated values. The calculations were performed with complete geometry optimization by the PC GAMESS [13] program from the GAMESS (US) QC [14] package. The optimization accuracy was predetermined by two criterions simultaneously: the mean squire gradient 0.004 kcal $Å^{-1}$ and the maximum gradient 0.012 kcal $Å^{-1}$. In the BLYP calculations the original Vosko–Wilk–Nusair correlation potential (VWN#5, Eq. 5 in [15]) was applied. The accuracy in calculation of vibration frequency of compounds **II**, **III**, and **VI** is restricted by positive only shifts in atomic Cartesian coordinates.

The results of calculations for ylide **I** with 6-31G(*d,p*) basis functions are listed in Table 1. As a whole, they satisfactorily reproduce basic experimental structural parameters of central fragment of the molecule [9]. Accounting for the electron correlation leads to some overestimation of the angle at the imine carbon atom C^{α} and does not improves the situation with underestimation of interactions of $C^{\alpha}=C^{\beta}$ double bond. On the other hand, there is a tendency to better representation of P–C^{α} bond length, $\omega C^{\alpha}C^{\beta}N$ bond angle and $\tau C^{\beta}NC^{i}C^{o}$ torsion angle (*i* and *o* correspond to *ipso* and *ortho* positions in phenyl ring), the latter defines a degree of conjugation in the C^{β}=NPh fagment. Juging from experimental (1.9°) and calculated (5.4°) values of the torsion angle, almost complete coplanarity of C^{β}=N bond and benzene ring plane is observed, indicating maximum overlap of their π-subsystems. The terminal triphenylphosphonium and phenyl substituents together with the nitrogen n_N and ylide carbon $n_{C^{\alpha}}$ lone pairs (for convenience and due to certain analogy, the 2*p* orbital of ylide carbon atom with extra electron density is denoted as $n_{C^{\alpha}}$ [8]) occupy orthogonal planes ($\tau PC^{\alpha}NC^{i}$ = 89.4°). The ylide **I** is a polar thermodynamically stable compouns. Accounting for electron correlation decreases separation in the ylide bond. Stabilization of ylide charge from the side of the cumulene chain is restricted practically by the $C^{\alpha}=C^{\beta}$=N triad, due to low acceptor ability of phenyl (Fig. 1).

Earlier calculations of model heterocumulene ylides H_3P=C=C=X (X = NH, O, S) performed on the STO-3G level [16] has showed restriction of the minimal basis in prediction of bended structure of the cumulene chain. Calculation for the ylide **II** on the higher level RHF/3-21G(*d,p*) (Table 2) does not allow to overcome this restriction leaving the $PC^{\alpha}C^{\beta}$ fragment of the cumulene chain close to linear (177.9°) and predicting existence of *cis–trans* isomers with higher stability of the former. Further extension of basis to 6-31G(*d,p*) and then application of hybrid exchange-correlation functional on the B3LYP/6-31(*d,p*) level lead to bending the $PC^{\alpha}C^{\beta}$ fragment to 143.2° and 148.5°, respectively, and define a gauche isomer of **II** as the only stable structure in the both approximations (Table 2). If the differences of calculated on the B3LYP/6-31G(*d,p*) level and experimental parameters Δc-e structural parameters in the ylide **I** (Table 1, col. 5) are taken as true for the ylide **II** taking into account similarity of C=C=N triads in their structures, then predicted value of $PC^{\alpha}C^{\beta}$ angle for **II** is 145.2° and of C=C bond length 1.237 Å. The former value is higher by 10° than experimental value for ylide **I** and corresponds to that for ketenylide Ph_3PCCO (**IV**) (145.5°) [4]. Assuming similarity in parameters of the cumulated carbonyl in

Table 2. Calculated by the methods RHF/3-21(*d,p*), RHF/6-31(*d,p*), B3LYP/6-31(*d,p*) and predicted experimental structural characteristics of iminoketeneylide $Ph_3PC^{\alpha}=C^{\beta}=NPh$ (**II**) and its analogous cumuleneylide $PH_3PC^{\alpha}=C^{\beta}=C^{\gamma}(CN)C(O)OMe$ (**III**)

Parameters [a]	**II**				**III**
	3-21G(*d,p*)	6-31G(*d,p*)	B3LYP/6-31G(*d,p*)	Experiment [b]	B3LYP/6-31G(*d,p*)
$-E$, au	1496.10284	1504.09775	1511.42375	–	1471.13932
ν, D	9.5	11.9	10.7	–	13.9
$r(PC^{\alpha})$, Å	1.639	1.669	1.664	1.665	1.705
$r(C^{\alpha}=C^{\alpha})$, Å	1.231	1.251	1.270	1.237	1.257
$r(C^{\alpha}=N)$, Å	1.244	1.238	1.248	1.256	1.372
r(C=O), Å	1.222	1.193	1.221	–	1.215
$\omega(PC^{\alpha}C^{\beta})$, deg	177.9	143.2	148.5	145.2	137.6
$\omega(C^{\alpha}C^{\beta}N)$, deg	177.1	174.0	171.2	170.2	176.6
$\tau(C^{\beta}NCC)$, deg	–179.6	43.8	29.5	–	0.0
$\tau(PC^{\alpha}C^{\beta}N)$, deg	–126.1	137.8	148.8	–	170.5
$\tau(C^{\alpha}C^{\beta}C{=}O)$, deg	0.4 (*cis*) [c]	–112.0 (*gauche*)	–125.2 (*gauche*)	–	–173.6 (*trans*)
q(P), au	0.788	0.970	0.859	–	0.865

[a] The data for ylide **II**; for ylide **III** N should be replaced by C^{γ} and $\tau C^{\beta}NCC$ by $\tau C^{\beta}C^{\gamma}CO$, where O relates to methoxy group. [b] For the calculation the $\Delta^{calc.-exp.}$ value from Table 1 is used. [c] The *cis*-isomer is by 6.3 kcal mol^{-1} more stable than *trans*-isomer.

ketenylide **IV** and iminobenzyl group in ylide **II** by π-electron-acceptor characteristics, it can be suggested, in correspondence with $n_{C^{\alpha}} \rightarrow \pi_O$ mechanism, equal $PC^{\alpha}C^{\beta}$ bending for the both ylides **II** and **IV**. Inclusion of $n_{C^{\alpha}} \rightarrow \pi_O$ mechanism in going from iminophenyl derivative **I** to iminobenzyl compound **II** leads to deeper charge and bond order alternation along the $C^{\alpha}+\cdots O^{-}$ chain (Fig. 1). On the other hand, the PC^{α} bond length is probably reciprocal of electronegativity of the X substituent in the series of Ph_3CCX ylides **I**–**IV**: 1.648 (O) [4], 1.665 (NCOPh), 1.677 (NPh, S) [5, 9], 1.705 Å [C(CN)C(O)OMe]. It is interesting to note that value and direction of deviation of C=C=N triad from linearity in the ylides **I** and **II** are similar, 7.5° and 9.2°, respectively, pointing to similarity in interactions for these systems (see below).

According to the calculation, compound **III** (Table 2) is thermodynamically stable ylide with high polarity (13.9 D), which probably causes problems at its isolation as individual compound [11]. Its conformation corresponds to almostorthogonal location of the substituents at C^{α} and C^{β} atoms (85.7°). The ylide bond length 1.705 Å is maximal in the series of ylides **I**–**V** but falls to the range 1.68–1.75 Å characteristic of sp^2-ylides $Ph_3P{=}CXY$ [17]. In the cumulene ylide **III** occurs further extension in charge alternation and bond lenths along the cumulene chain (Fig. 1), so for the ylides **II** and **III** is possible to claim increasing contribution of the P^{+}–C≡C–N– resonance structure to the hybride.

Insofar as complete geometry optimization for ylides **II** and **III** on the B3LYP/6-31G(*d,p*) leads to unsatisfactory results on the $C^{\alpha}=C^{\beta}$ bond length and the bond angle at C^{α} (the $\Delta^{calc.-exp.}$ value is over 0.05 Å and 10°, respectively), we performed calculation of ylides **IV** and **V** on the same level but with partial geometry optimization, fixing experimental geometry of $C^{i}_{3}P{=}C{=}C{=}X$ (X = O, S) fragment as is given by X-ray structural data [4,5]. The calculated bond orders and atomic charges of ylides **IV** and **V** and those for the reference allene **VI** are listed in Table 3. It is seen that correction of the ylide geometry by the experimental data minimally affects calculated parameters of the cumulene chain, so that

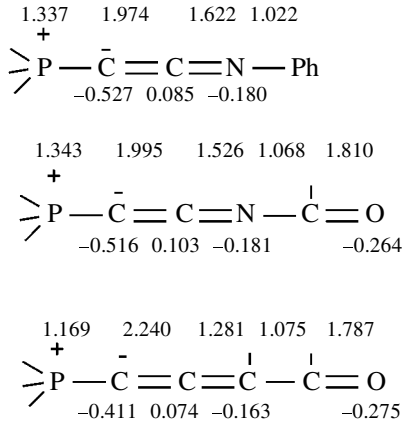


Fig. 1. Molecular diagrams for ylides **I**–**III**, B3LYP/6-31G(*d,p*) calculations.

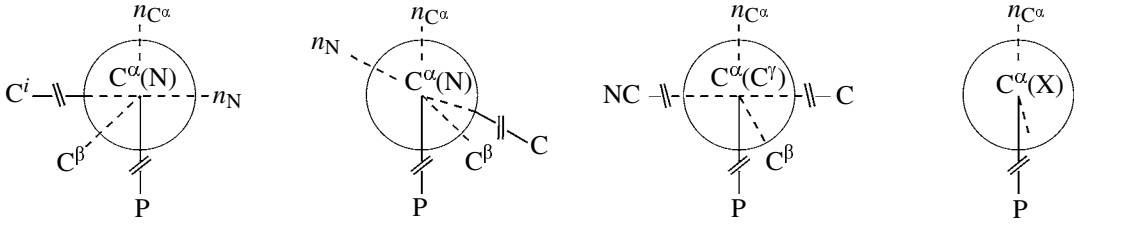
Table 3. Calculated by B3LYP/6-31(*d,p*) method bond orders and atomic charges in ylides **IV** and **V** and allene **VI**

Comp. no.	X	Optimization	$W_{PC^{\alpha}}$	$W_{C^{\alpha}C^{\beta}}$	$W_{C^{\beta}X}$	q_P, au	$q_{C^{\alpha}}$, au	$q_{C^{\beta}}$, au	q_X, au
IV	O	Complete	1.442	1.769	1.899	0.856	–0.586	0.144	–0.199
		Partial [a]	1.385	1.913	1.890	0.865	–0.565	0.116	–0.218
V	S	Complete	1.391	1.753	1.671	0.855	–0.489	–0.085	–0.122
		Partial [a]	1.340	1.815	1.653	0.868	–0.477	–0.096	–0.154
VI [b]	C^{γ}	Complete	–	1.973	1.973	–	–0.273	0.017	–0.273

[a] See the text. [b] Calculated structural parameters: *r*(C=C) 1.307 (1.309) Å, *r*(CH) 1.088 (1.080) Å, ω(HCH) 117.1° (119.0°); in parentheses data of gas electronography [1].

the tendency in variation of the latter in going from oxygen **IV** to sulfur **V** derivative remains the same for the both cases of optimization. It is characteristic of ylides **IV** and **V** as compared to allene **VI** the lower bond orders in the C^{α}=C^{β}=X triad despite a noticeable shortening of C^{α}=C^{β} bond to 1.210 [4] and 1.209 Å, respectively. Approximate equality of their lengths under the influence of either strong π- and σ-acceptor in **IV** or of ever stronger, but only π-acceptor in **V** that increases angle at C^{α} by more than by 20° indicates predominance of conjugation mechanism in the effect of substituent X on the redistribution of electron density in the C^{α}=C^{β}=X triad. If the residual charge on the ylide carbon atom (expressed as $\delta^{13}C$ shift) is taken as a measure of the ylide stabilization, then the stabilization of the ylides grows in the series **IV** < **I** < **V** < **III** = –0.586 (–10.47 [16]) < –0.527 (27.90 [16]) < –0.516 (41.83 [10]) < – 0.489 (36.31 [16]) < –0.411 au (ppm).

Nonvalent interactions of lone pair (LP) with coplanar π-electrons versus deviations of the cumulene chain from linearity. In distinct to allenes, the presence of LP at the X heteroatom and ylide carbon atom in the series of ylides **I**–**V** leads to their nonvalent interactions not only with each other but also with coplanar π-systems of neighboring C^{α}=C^{β} and C^{β}=X bonds. In our opinion, these interactions cause deviation of C^{α}=C^{β}=X triad from linearity Scheme 1 shows Newman projections (scaled by × 50) of ylides **I**–**V** [in parentheses are given values of bond angles ω($C^{\alpha}C^{\beta}$X)].

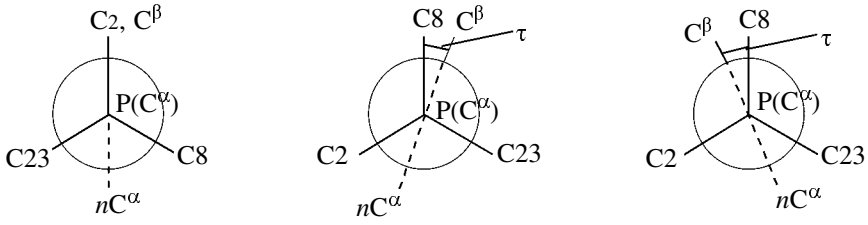


I (175.5°) **II** (170.2°) **III** (176.6°) **IV, V** (175.6°, 178.3°) (1)

As seen, the direction of deviation of the apex of C^{β} angle from the line joining the X heteroatom and the ylide carbon of the triad is opposite to the vector sum of the LPs at these atoms. The projection of C^{β} apex on the horizontal axis is proportional to the interaction with the LP of the heteroatom, that on the vertical axis is proportional to the interaction with the LP of ylide carbon. In the ylides **I** and **II** the shifts of C^{β} axis are maximal and occurs approximately along the bisector of the angles formed by PC^{α} and NC^{i} bonds which are 90° and 68° respectively. The close values of the projections indicates approximately equal contributions (ca. 4.4°, the difference 180°-ω) from each LP of nitrogen and ylide carbon to the triad nonlinearity. In the ylides **III**–**V** either due to the absence of LP at C^{7} (**III**) or owing to local symmetry C_{3v} of three LPs at the X heteroatom (**IV**, **V**) the projection of the shift of C^{β} apex on the horizontal axis is absent, and the shift value (the projection on the vertical axis) is determined by the LP of ylide carbon only and therefore it falls down by the factor of two for the ylide **III** and continues to decrease for

the ylides **IV** and **V** in proportion to the population of the LP of ylide carbon atom included to the electron density transfer by $n_{C^{\alpha+}} \rightarrow \pi(X^-)$ mechanism.

The negative hyperconjugation mechanism and chemical nonequivalency of phosphorus-carbon bonds in the triphenylphosphonium group. Mutual location of the ylide carbon LP and the triphenylphosphonium fragment PC^i bonds in the ylides **I**–**III** obtained by B3LYP/6-31G(*d,p*) are shown on the Newman projections relatively to PC^α bond in the Scheme 2.



$\tau C^\beta C^\alpha PC2 = 4.9°$ **I**

$\tau C^\beta C^\alpha PC8 = -23.0°$ **II**

$\tau C^\beta C^\alpha PC8 = -19.6°$ **III**

(2)

It is clearly seen eclipsed (or close to it) location of one of PC^i bond (i = 2, 8, 23) and C^α=C^β bond of the cumulene triad. Hence, the *sp*-ylides **I**–**III** (as well as ylides **IV** and **V**, as follows from our calculations and experiments [4,5]) are in a transoid conformation, like the sp^2-ylides [18]. In correspondence with the earlier results for trichlorophosphonium ylides [8], such location should respond to maximum electron density transfer from the ylide carbon LP to the antibonding σ*-orbital of the eclipsed PC^i bond by the mechanism of negative hyperconjugaqtion $\pi(PC^\alpha) \rightarrow \sigma^*(PC^i)$, with a noticeable elongation of the latter. Actually, our calculation points to chemical nonequivalency of PC^i bonds with elongation of eclipsed (first position) bond: 1.843, 1.834, 1.833 (**I**), 1.840, 1.835, 1.831 (**II**) and 1.833, 1.824, 1.823 Å (**III**), in accordance with the experimental data: 1.804, 1.800, 1.796 (**I**) [9], 1.815, 1.808, 1.784 (**IV**) [4] and 1.804, 1.799, 1.783 Å (**V**) [5]. As a criterion of the chemical nonequivalence of the bonds of phosphonium group can be taken the average difference between the eclipsed bond length and a half sum of two other bond lengths. For the studied triphenylphosphonium ylides **I**–**V** this criterion equals: 0.009 (**I**–**III**), calculation, and 0.011 Å (**I**, **IV**, **V**) experiment, and for trichlorophosphonium ylides it is 0.062 Å (calculation) [8], and falls down in correspondence with electronegativity of the partner atoms at the phosphorus.

Interrelation between the ylide I–V structure and $^1J_{PC^\alpha}$ spin–spin coupling constants and antisymmetric bond vibration $\nu^{as}(C^\alpha{=}C^\beta{=}X)$ of the carbanion. Despite the closeness in the values of bond angle at the ylide carbon C^α in the ylides **II** and **IV**, inspiring equal contributions of the *s*-part of C^α hybrid orbital of the P–C^α bond to the $^1J_{PC^\alpha}$ spin–spin coupling constant, their experimental values differ significantly: 119.3 [10] and 187.8 Hz [16], respectively. Thus, the known symbatic dependence of $^1J_{PC^\alpha}$ on the value of the angle at C^α [16] in the series of cumulene ylides $Ph_3P{=}C{=}C{=}X$ is distorted when the value 119.2 Hz for the ylide **II** is included. The difference in the $^1J_{PC^\alpha}$ value for ylides **II** and **IV** can be connected with the difference in *s*-hybridization of the phosphorus orbital in the P–C^α bond, with the bond length and with the inductive effect of X substituent. We have no reasons to expect a significant difference in structure of the triphenylphosphonium fragment of ylides **II** and **IV**, hence, in the *s*-hybridization of phosphorus atom (the charge on the phosphorus atoms differ by 0.003 au only, see Tables 2 and 3). The difference in contribution due to different P–C^α bond lengths is also probably negligible, because the theoretical estimation of $^1J(^{13}C{-}^1H)$ spin–spin coupling constant in methane with the comparable value 125 Hz is 2 Hz per 0.01 Å only [19]. Inductive effect of the substituent X in going from ylide **II** to **IV** probably can contribute significantly: change in $^1J_{P-C^\alpha}$ due to this factor can achieve 100Hz, e.g., for a pair of compounds with tetracoordinated phosphorus H_3C–P(S)Me ($^1J_{P-C^\alpha}$ = 56.1 Hz) and H_2ClC–$P(O)F_2$ ($^1J_{P-C^\alpha}$ = 166 Hz) [20].

For details, we considered s-orbital populations of the partner atoms P and C^α and their bonding orbital, which is characterized by the value of bond order W_{P-C^α}. The data obtained for the ylides **I**–**V** on the

Table 4. Calculated by B3LYP/6-31(*d,p*) method populations (au) of phosphorus and ylide carbon *s*-orbitals, P=C$^{\alpha}$ bond orders ($WW_{PC^{\alpha}}$) and experimental spin–spin coupling constants $^{1}J_{PC^{\alpha}}$ (Hz) in phosphorus heterocumuleneylides **I**–**V**

Comp. no.	Atom	1*s*	2*s*	3*s*	4*s*	Σ [a]	∏ [b]	$W_{PC^{\alpha}}$	∏ W	$^{1}J_{PC^{\alpha}}$ [c]
I	P	1.998	1.990	1.214	0.079	1.293	1.610	1.337	2.152	147.3
	C$^{\alpha}$	1.992	0.675	0.570	–	1.245				
II	P	1.998	1.990	1.212	0.083	1.295	1.599	1.343	2.148	119.3
	C$^{\alpha}$	1.992	0.664	0.571	–	1.235				
III	P	1.998	1.990	1.221	0.072	1.293	1.792	1.169	2.095	(~80)
	C$^{\alpha}$	1.992	0.687	0.699	–	1.386				
IV	P	1.998	1.990	1.210	0.094	1.304	1.571	1.442	2.266	187.7
	C$^{\alpha}$	1.992	0.644	0.561	–	1.205				
V	P	1.998	1.990	1.214	0.097	1.311	1.774	1.391	2.467	216.6
	C$^{\alpha}$	1.992	0.656	0.698	–	1.354				

[a] Total population of valent ant polarizational *s*-orbitals P(3*s* + 4*s*), C$^{\alpha}$(2*s* + 3*s*) for phosphorus and ylide carbon atoms. [b] Dot of total populations P(3*s* + 4*s*)C$^{\alpha}$(2*s* + 3*s*) ≡ $s_P s_{C^{\alpha}}$. [c] Data from [8,16]; the constant in parentheses is estimated graphically from the plot $^{1}J_{PC^{a}} \sim s_P s_{C^{\alpha}} W_{PC^{\alpha}}$ in Fig. 2 and data in the table for ylide **III**.

B3LYP/6-31G(*d,p*) level are comprised in Table 4. The populations of core 1*s* and 2*s* phosphorus orbitals and of ylide carbon 1*s* orbital are the same over whole series of ylides **I**–**V** and are close to 2 au. As far as the core electrons do not involved (or involved inderectly) to the mutual interaction, their contribution to $^{1}J_{P-C^{\alpha}}$ spin–spin couplind should be assumed to be a certain not varied small value. Change in population of valent *s*-orbitals on ylide carbon in the series of ylides **I**–**V** several times (up to sixfold) extend that on the phosphorus atom. Similar variations are found also for the polarized *s*-electrons. For accounting these changes we summated populations of valent and polarized *s*-electrons on each atom separately and calculated their dot value ∏ (Table 4, column 8). As the contact spin–spin coupling of the phosphorus nuclei with neighboring ylide carbon atom is performed via population of the PC$^{\alpha}$ bond, we took this into account

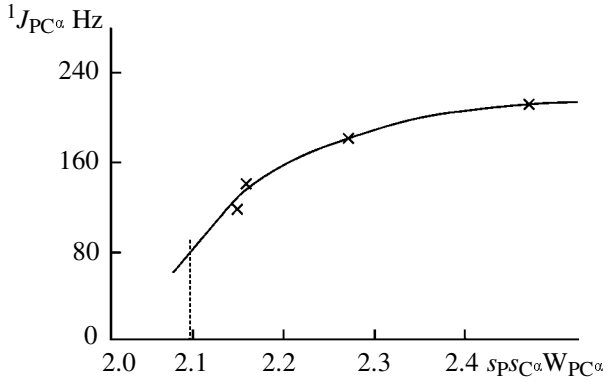


Fig. 2. The plots of $^{1}J_{PC^{\alpha}}$ spin–spin coupling constants on the dot of *s*-orbital populations and bond order $s_P s_{C^{\alpha}} W_{PC^{\alpha}}$ in the ylides **I**–**V**.

by multiplication of the ∏ value by the bond order $W_{PC^{\alpha}}$. The series of ∏($W_{PC^{\alpha}}$) values obtained (column 10 in Table 4) is monotonous, and is shown in Fig. 2 as a plot of $^{1}J_{PC^{\alpha}}$ on ∏$W_{PC^{\alpha}}$. Now the value of $^{1}J_{PC^{\alpha}}$ constant does not fall out the plot, in contrast to the analogous $^{1}J_{PC^{\alpha}}$ plot on the angle ω(PC$^{\alpha}$C$^{\beta}$) [16]. Extrapolation of the $^{1}J_{PC^{\alpha}}$–∏$W_{PC^{\alpha}}$ plot gives for ylide **III** the $^{1}J_{PC^{\alpha}}$ value approximately 80 Hz, in correspondence with low enough bond order of the PC$^{\alpha}$ bond in this compound (Table 4).

In Table 5 we compare the data obtained in calculation and experiment for some characteristic frequencies of ylides **II** and **III** and allene **VI**. The scaling factor was determined from the condition $\Sigma\delta_i = 0$ on the characterstic frequencies in Table 5. The largest deviations of the calculated frequencies from experimental ones occurs in ylide **III**, while data for ylide **II** is in good agreement with experiment. It is seen from the shape of asymmetric bonding vibration ν^{as}(C$^{\alpha}$=C$^{\beta}$=X) that contribution of C$^{\beta}$=X bond to the vibration falls down in going from allene to ylides **II** and **III** with simultaneous increase in vibration intensity. The intensity ratio **II**:**III**:**VI** = 1230:182:1 indicates a sharp increase in derivative of dipole moment proportional to $\sqrt{1/2}$. which is probably connected with polarization of C$^{\alpha}$=C$^{\beta}$ bond due to certain asymmetry of C=C=C triad in **III** and its significant grow at inclusion of heteroatom to C=C=N triad in **II**. In this series also shortening of C$^{\alpha}$=C$^{\beta}$ bond is proportional to the cahnge in shape, **II**:**III**:**VI** = 1.309:1.257:1.237, therefore we attempted to correlate experimental frequencies ν^{as}(C$^{\alpha}$=C$^{\beta}$=X) with experimental C$^{\alpha}$=C$^{\beta}$ bond lengths suplemented with either predicted bond length for ylide **II**, or calculated

Table 5. Calculated by B3LYP/6-31(*d,p*) method and experimental characteristic frequencies, intensities and vibration modes for ylides **II** and **III** and allene **VI**

Parameters	**II** (X=N)			**III** (X=N)			**VI** (X=C$^{\gamma}$)		
	calc. [a]	exp. [b]	δ, cm^{-1}	calc. [a]	exp. [c]	δ, cm^{-1}	calc. [d]	exp. [d]	δ, cm^{-1}
$\nu^{as}(C^{\alpha}=C^{\beta}=X)$, cm^{-1}	2056	2062	–6	1993	2060	–67	1975	1957	+18
I, D^2/au mass-Å^2	1597.4	av.	–	237.3	–	–	1.3	br.s	–
ΔC^{α}, Å	–0.128	–	–	–0.169	–	–	–0.111	–	–
ΔC^{β}, Å	0.204	–	–	0.211	–	–	0.237	–	–
ΔX, Å	–0.074	–	–	–0.057	–	–	–0.111	–	–
ν(C=O), cm^{-1}	1669	1673	–4	1713	1666	+43	–	–	–
ΔC, Å	0.133	–	–	0.228	–	–	–	–	–
Δ, Å	–0.087	–	–	–0.140	–	–	–	–	–
ν(C≡N), cm^{-1}	–	–	–	2221	2200	+21	–	–	–
ΔC, Å	–	–	–	0.222	–	–	–	–	–
ΔN, Å	–	–	–	–0.157	–	–	–	–	–

[a] Scaling factor is taken 0.955 (see the text). [b] Our data for the IR spectrum of solution in CH_2Cl_2, concentration 0.1 mol l^{-1}. [c] Data for IR spectrum of powder in KBr [12]. [d] IR spectrum of gas.

bond length of ylide **III**, for the series of ylides **I**–**IV** and allene **VI** (Fig. 3). The plot obtained is close to linear and attest the fact that the force constant of C^{α}=C βond not only defines predominantly the value of frequency $\nu^{as}(C^{\alpha}=C^{\beta}=X)$ but also, in turn, depends on both electronegativity and π-elctronacceptor properties of atom X. Actually, for the case of maximal charge on the ylide carbon atom (–0.585 au) and $C^{\alpha}=C^{\beta}$ bond length (1.210 Å) the ylide **IV** absorbs in the region of highest frequencies 2110 cm^{-1} [16], while in the ylide **III** the frequency falls down to 2060 cm^{-1} [12]with increase in $C^{\alpha}=C^{\beta}$ bond length to 1.257 Å despite the decrease in charge on C^{α} to –0.486 au and increase in bond length to 2.2 (2.0 in ylide **IV**).

Thus, the performed study shows that mechanism of disclosing the $\omega(PC^{\alpha}C^{\beta})$ angle in phosphorus *sp*-ylides (Fig. 4) is probably analogous to the mechanism of flattening of nitrogen pyramid in anilines: the energy gain at delocalization of lone pair is spent for compensation of the energy loss at rehybridization of the atom bearing LP. The rehybridization leads to linearization of $PC^{\alpha}C^{\beta}$ triad in ylides **I**–**V**, or to the pyramid flattening in anilines. The structure of phos0 phathioketenylide **V** $\omega(PC^{\alpha}C^{\beta})$ = 168° includes the shortest $C^{\alpha}=C^{\beta}$ bond (1.209 Å) and is the most close to linear, inspiring maximum contribution of betaine $Ph_3P^+–C^{\alpha}\equiv C^{\beta}–S^-$ to its structure. The characteristic feature of ylides **I**–**V** is difference in ability of two π_1- and π_2-subsystems to delocalization of electron density: in the first subsystem the delocalization is

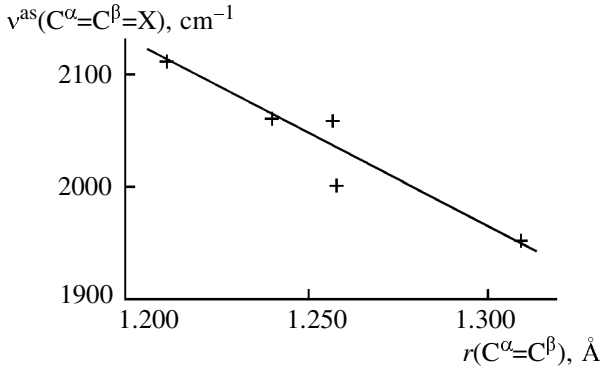


Fig. 3. Plot of frequency $\nu^{as}(C^{\alpha}=C^{\beta}=X)$ on the $C^{\alpha}=C^{\beta}$ bond length in the ylides **I**–**V** and allene **VI**.

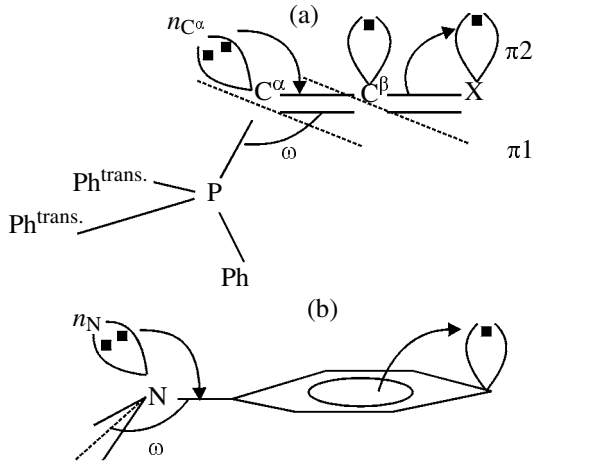


Fig. 4. Transoid conformation of ylides **I**–**V**. Mechanism of linearization of (a) triad $PC^{\alpha}C^{\beta}$ and flattening of the nitrogen pyramid and (b) in *sp*-ylides and anilines.

restricted by $C^{\alpha}=C^{\beta}$ bond, while in the second the extra negative charge is delocalized over whole carbanion residue and defines degre of linearization of central $PC^{\alpha}C^{\beta}$ triad (Fig. 4).

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