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Peculiarities of p_π–p_π Conjugation in Aminosubstituted Phosphaalkenes

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ABSTRACT

Effects of p_π–p_π *conjugation in phosphaalkenes have been considered by taking into account the results of X-ray structural studies and ab initio quantum-chemical calculations. The structural consequences of the conjugation depend to a certain extent on the character of the substituent and the place of its attachment to the double P═C bond. Depending on the location of the substituent, bond polarization may strengthen or weaken (compensate for) the conjugation effects. A high contribution of the s-character of the lone electron pair of the P atom is an essential feature of the electron structure of a phosphaalkene.*

INTRODUCTION

It is known [1] that two main factors control stabilization of the two-coordinated state of the phosphorus atom in a phosphaalkene: spatial shielding of the double P═C bond by bulky substituents (kinetic stabilization), and delocalization of the π-electron charge density of the double bond due to its conjugation with the neighboring groups (thermodynamic stabilization). On consideration of the latter effect in more detail and taking into account the considerable polarization of the P═C bond, it may be supposed that, in a phosphaalkene, the character of conjugation would to some extent depend on the side of the double bond to which a donor (acceptor) group is attached.

The object of the present study is to find out how and to what extent the n–π conjugation influences the spatial and electronic structure of C-amino- and P-aminosubstituted phosphaalkenes.

STRUCTURAL DATA

C-Aminosubstituted Phosphaalkenes

According to extensive structural data (see [2] and references therein) on phosphaalkenes containing the $R_2N\text{–}\overset{|}{C}\text{═}P\text{–}X$ group, the P═C double bond is usually elongated to 1.70–1.76 Å in comparison with the standard value of 1.65–1.67 Å [2a], whereas the C–N bond is, on the contrary, significantly shortened to 1.35–1.39 Å in comparison with the value of 1.45 Å, characteristic of the single $C(sp^2)$–$N(sp^2)$ bond [3]. It is noteworthy that the

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This paper is dedicated to Professor Dr. Rolf Appel on the occasion of his 70th birthday.

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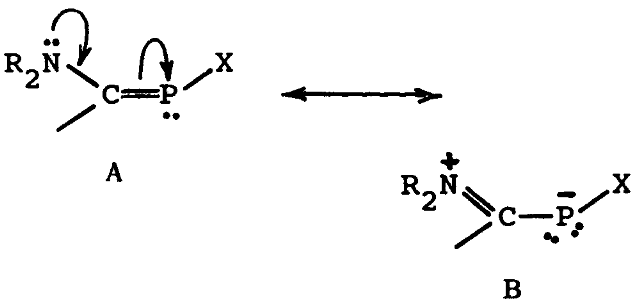
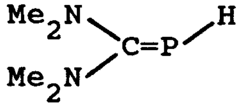
extent of the double P=C bond elongation and the symbiotic shortening of the single N–C bond depend significantly on the orientation of the amino group relative to the double bond. This effect is the greatest in the case of their coplanarity and decreases with the rotation of the amino group relative to the double bond [2a]. The bond lengths distribution observed in the C-aminosubstituted phosphaalkenes may be interpreted in terms of the conjugation between the π-system of the double P=C bond and the lone electron pair of the N atom (LP(N)) (Scheme 1).



SCHEME 1

In the present work, the experimental deformation electron density (DED) maps in the region of the P=C bond of the *C*,*C*-bis(dimethylamino)methylenephosphine [1] was calculated in order to elucidate the qualitative peculiarities of the electronic distribution in C-aminosubstituted phosphaalkenes. An X-ray structural study of compound **1** was carried out by us earlier [2a]. The general view of the molecule **1** is shown in Figure 1.



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A total of 820 low angle reflections with sin $\theta/\lambda \leq 0.65$ Å^{-1} were used for the map calculation, whereas 712 "high" angle reflections with sin $\theta/\lambda \geq 0.5$ Å^{-1} were used for refinement of the structure (R = 0.028, R_w = 0.030, GOF = 2.36). Figure 2a represents the DED map in the C^{1}PH plane (deviation of the N^1 and N^2 atoms from the plane are equal to 0.39 and 0.36 Å). Two features of this map should be noted: the DED maximum with the height of 0.39 e/Å^3 on the P=C bond and the maximum 0.18 e/Å^3 located behind the P atom nucleus. The same maxima are also seen in the DED section normal to the PC^{1}N^{1}N^2 plane and passing through the P and C^1 atoms, i.e. in the plane of the π-bond (Figure 2b). The maximum A on the DED maps, which may be associated with the localization of the lone pair of the P atom (LP(P)), is situated at 0.65 Å from the nucleus of this atom. The location and shape of this maximum differ considerably in the DED maps of the $>C=P<$ group in the molecule **1** and in the molecules with the isovalent $>C=N<$ group, wherein the LP(N) occupies the sp^2-hybrid orbital [4]. Thus, contrary to the maximum of the LP(N), which is located approximately on the extension of the bisector of the N atom bond angle, the corresponding maximum of the LP(P) is located in fact on the extension of the C=P bond (i.e. the latter maximum is shifted in the direction characteristic of the sp-hybridization). This result indicates that the LP(P) in **1** is likely to have an increased s-character.

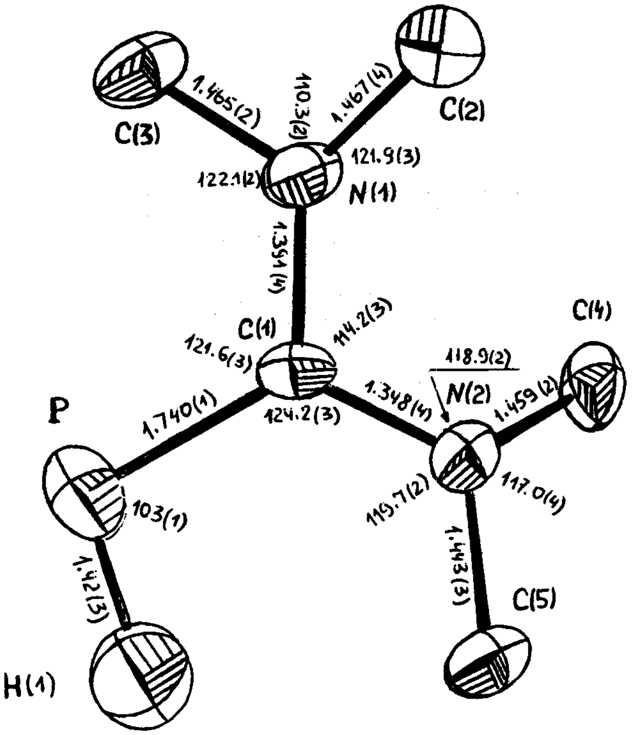


FIGURE 1 General view of the molecule **1** and its main geometrical parameters.

P-Aminosubstituted Phosphaalkenes

Hitherto the compound **2** has been the only structurally investigated representative of P-aminosubstituted phosphaalkenes [5]. The molecular structure of **2** has an interesting feature [6]: despite the conformation favorable for the $n_N{-}\pi_{P=C}$ conjugation (the dihedral angle between the planes of the double bond and amino group does not exceed 5°) no structural evidence of the conjugation described by Scheme 2 is observed. Indeed, the P=C bond in **2** (1.641(7) Å in both crystallographically inde-

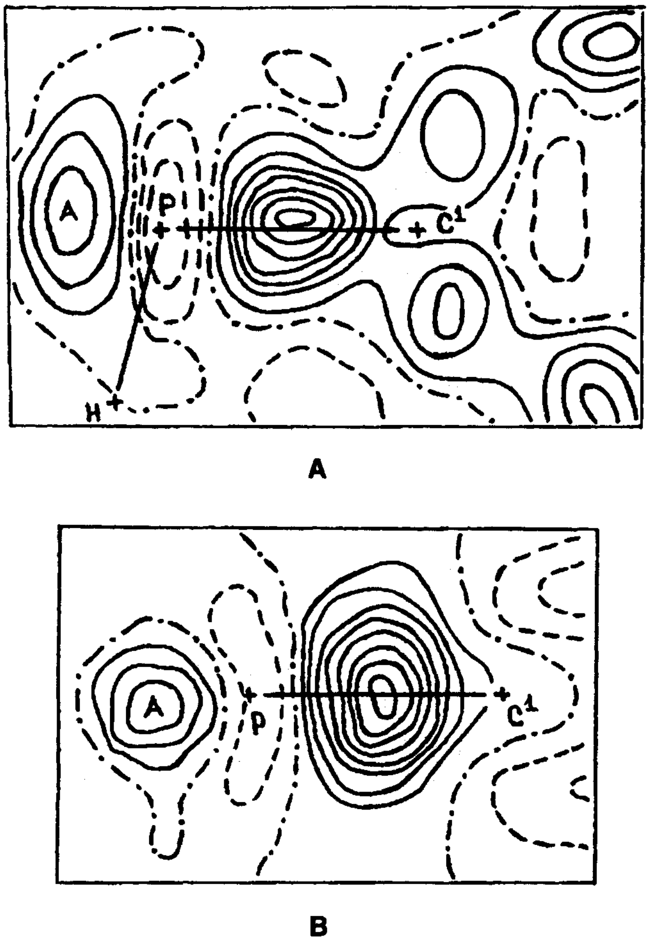
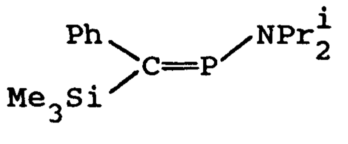


FIGURE 2 DED maps of the molecule 1: a) in the HPC^1 plane (isolines are drawn at 0.05 e/Å^3 intervals); b) in the π-bond plane, i.e. in the plane orthogonal to the PC^{1}N^{1}N^2 plane and passing through the P=C^1 bond (isolines are drawn at 0.05 e/Å^3 intervals).

pendent molecules) is not elongated in comparison with the corresponding value of 1.657(5) Å in the η^1-complex **3** [7], wherein the NSi$_2$ and PCSi$_2$ planes are, in fact, orthogonal and the lengths of the single P–N bonds in **2** (1.673(6) and 1.676(6) Å) and **3** (1.681(4) Å) coincide within 2σ. Structural changes observed on going from **2** to **3** do not agree with Scheme 2. To a certain extent such disagreement could be related to the validity of a correct comparison of these structures. The formation of an η^1-complex may, in principle, change considerably the electronic structure of the initial phosphaalkene (though analysis of the structures of phosphaalkenes and their η^1-complexes with transition metals testifies indirectly that, as a rule, such changes are not great [2a]). However, the P=C bond in **2** is not elongated in comparison with the values found in other phosphaalkenes. Moreover, it is one of the shortest among P=C double bonds observed in all structurally studied phosphaalkenes. The above-mentioned structural features of **2** may be interpreted in terms of two models: a) owing to whatever reasons, the n_N–$\pi_{P=C}$ conjugation in P-aminosubstituted phosphaalkenes is inefficient; b) the conjugation is significant (which is supported by the spectral data [8]). However, its structural manifestations do not agree with the "classical" scheme. If the first assumption is true and coplanarity of the amino group and the double P=C bond gives no or only a slight energy gain due to their conjugation, it may be anticipated that an increase of bulkiness of substituents R at the N atom will readily cause rotation of the amino group (i.e. transformation from A to B conformation) as a result of the steric repulsion X· · ·R and C· · ·R.



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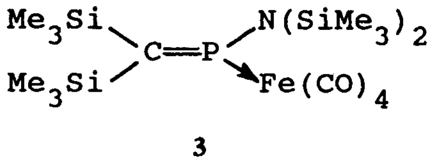

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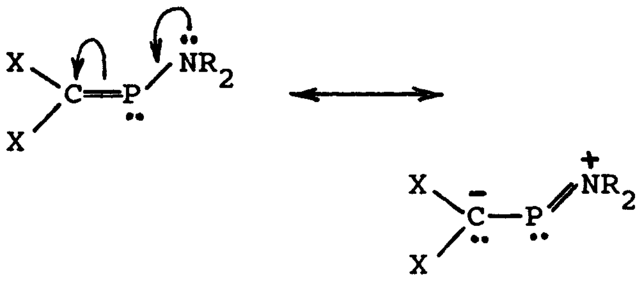
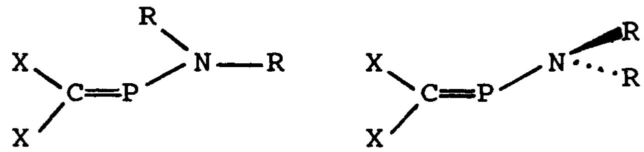


SCHEME 2



A B

In order to test this assumption experimentally, we prepared the P-aminosubstituted phosphaalkene with the most bulky substituents at the N atom among the known compounds of this class, viz. *N*-trimethylsilyl-2,4,6-tri(*tert*-butyl)-phenylamino-*C*,*C*-bis(trimethylsilyl)methylenephosphine **4**, and carried out its X-ray structural study. The general view of the molecule **4** is represented in Figure 3; bond lengths and angles are given in Table 1.

An X-ray structural study has shown that the dihedral angle between the amino group and the

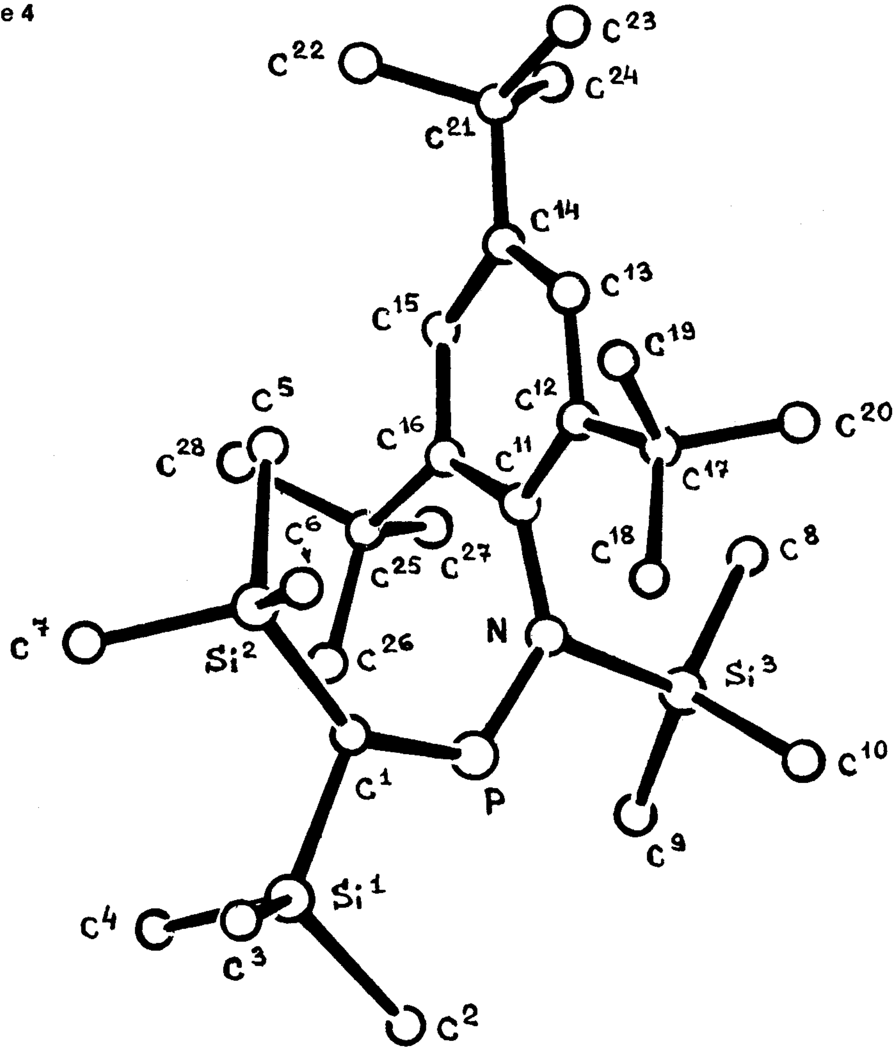
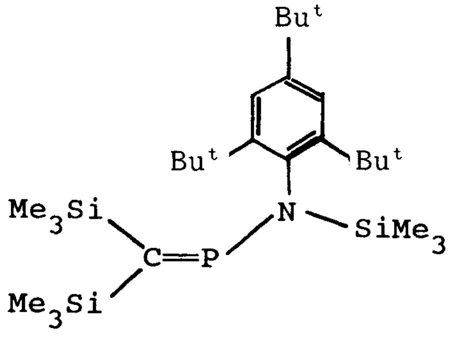


FIGURE 3 General view of the molecule **4**

TABLE 1 Selected Bond Lengths d (Å) and Bond Angles ω (°) in Molecule **4**

P–N	1.687(1)	NPC^1	121.38(6)
P–C^1	1.652(1)	PNSi^3	110.67(5)
Si^1–C^1	1.898(1)	PNC^{11}	132.58(8)
Si^2–C^1	1.877(1)	Si^{3}NC^{11}	116.72(7)
Si^3–N	1.797(2)	PC^{1}Si^1	104.67(8)
N–C^{11}	1.455(1)	PC^{1}Si^2	140.64(8)
C^{11}–C^{12}	1.412(2)	Si^{1}C^{1}Si^2	114.70(7)
C^{11}–C^{16}	1.429(2)	NC^{11}C^{12}	120.4(1)
C^{12}–C^{13}	1.396(2)	NC^{11}C^{16}	119.5(1)
C^{13}–C^{14}	1.375(2)	C^{12}C^{11}C^{16}	119.8(2)
C^{14}–C^{15}	1.376(2)	C^{11}C^{12}C^{13}	118.1(2)
C^{15}–C^{16}	1.391(2)	C^{12}C^{13}C^{14}	123.8(1)
		C^{13}C^{14}C^{15}	116.4(2)
		C^{14}C^{15}C^{16}	124.7(1)
		C^{11}C^{16}C^{15}	117.1(2)

nodal plane Si^{1}Si^{2}C^{1}P of the double bond in the molecule **4** is only slightly increased in comparison with the corresponding value in **2**. It is equal to 11.2(2)°. Thus, despite a considerable increase of the bulkiness of substituents at the N atom, the coplanar orientation of the amino group and the double P=C bond remains preferable to the orthogonal



4

conformation; the increased steric crowding is overcome by deformation of the bond angles rather than by rotation of the amino group: a) the bond angle at the two-coordinated P atom is increased to the value of 121.38(6)°, which is unusually large for phosphaalkenes; b) a planar trigonal configuration of the N atom (the bond angles sum, 360.0(2)°) is distorted considerably—the PNC^{11} bond angle is increased to 132.58(8)°, while the $PNSi^3$ and Si^3NC^{11} bond angles are decreased to 110.67(5) and 116.72(7)°; c) the PC^1Si^2 bond angle, 140.64(8)°, is increased considerably in comparison with the angles PC^1Si^1, 104.67(8), and $Si^1C^1Si^2$, 114.70(7)°; d) a nonbonded interaction (repulsion), $C^5\cdots C^{11}$ (the corresponding interatomic distance, 3.293(2) Å, is considerably shorter than the doubled van der Waals radii, 3.40 Å, of the C atom [9]), results in considerable distortion of the tetrahedral coordination of the Si^2 atom (the $C^1Si^2C^5$ bond angle is increased to 118.14(7)°, while the $C^5Si^2C^6$ and $C^5Si^2C^7$ bond angles are decreased to 105.5(2) and 104.7(1)°. In addition, steric hindrance in **4** decreases the planarity of the central group considerably. Thus, while in the two independent molecules, **2**, the deviation of the N atom from the C(Si)C=P plane is only 0.003(6) and 0.024(5) Å, in **4** the N atom is displaced from the $Si^1Si^2C^1P$ plane by 0.266(1) Å (the Si^2C^1PN torsion angle is equal to 9.8(3)°). Thus, according to an X-ray study, the sterically strongly crowded A rather than B conformation is realized in the molecule **4**. This is an indirect evidence for considerable contribution of the $n_N-\pi_{P=C}$ conjugation.

Other structural features of the molecule **4** should also be noted. The P=C and P–N bond lengths, 1.652(1) and 1.687(1) Å, coincide with the values found in **2** (P=C, 1.641(7) and 1.641(7) Å; P–N, 1.673(6) and 1.676(6) Å) within 2σ. The orthogonal orientation of the $C^{11}\cdots C^{16}$ benzene ring and the plane of the N atom bonds (the corresponding dihedral angle is 89.37(4)°) practically excludes any possibility of the $n_N-\pi_{Ph}$ conjugation, whereas the $N-C^{11}$ distance, 1.455(1) Å, corresponds to the length of a purely single $N(sp^2)-C(sp^2)$ bond [3]. The geometry of the $C^{11}\cdots C^{16}$ benzene ring is unexceptional for the 2,4,6-tri(Bu^t-)phenyl substituent [10]: due to the electron-donor character of the Bu^t-groups, $C^{11}C^{12}C^{13}$, $C^{13}C^{14}C^{15}$, and $C^{11}C^{16}C^{15}$, the bond angles are decreased to the values of 118.1(2), 116.4(2), and 117.1(2)°, whereas the $C^{12}C^{13}C^{14}$ and $C^{14}C^{15}C^{16}$ bond angles are increased to 123.8(1) and 124.7(1)°.

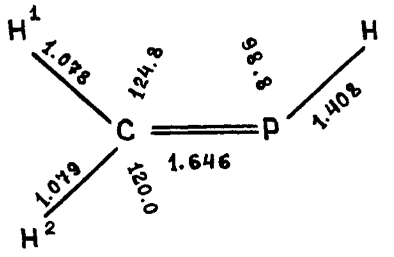


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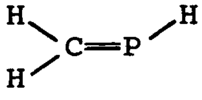
FIGURE 4 Geometrical parameters of the model molecule **5**.

QUANTUM-CHEMICAL CALCULATIONS

The X-ray structural data gives rise to the following questions related to peculiarities of the electronic structure of phosphaalkenes: a) the unusually high s-character of the LP(P) (according to the experimental DED maps of the molecule **1**); b) the considerable difference in the structural manifestation of the $n_N-\pi_{P=C}$ conjugation in the cases of C- and P-aminosubstituted phosphaalkenes.

In order to analyse these features in full detail we have performed calculations of the model structures **5–7** (by use of the 3-21G* basis set) with ge-



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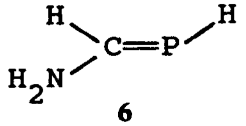

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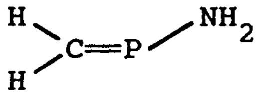

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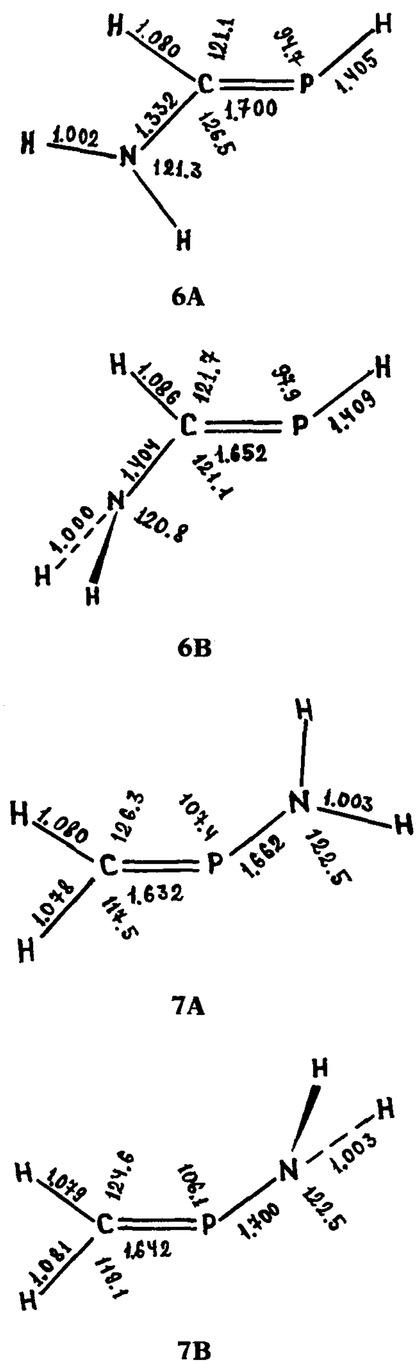
TABLE 2 Mulliken Charges q(e) and Total Energy E_{tot}(a.u.) in Molecules **5–9**

		Charges				Sum of π-Charges	Total Energy
Molecule	Conformation	q_P	q_C	$q_{N\,(B)}$	$q_{NH_2\,(BH_2)}$	$q^\pi_{PC} = q^\pi_P + q^\pi_C$	E_{tot}
5	—	0.278	−0.747	—	—	2.015	−378.39960
6	A	0.020	−0.144	−0.848	−0.087	2.255	−433.15585
	B	0.249	−0.231	−0.905	−0.189	2.027	−433.12594
7	A	0.732	−0.894	−1.023	−0.300	2.132	−433.16634
	B	0.641	−0.784	−1.048	0.342	2.022	−433.15232
8	A	0.366	−0.840	0.320	0.262	1.891	−403.52741
	B	0.244	−0.810	0.365	0.337	2.012	−403.51658
9	A	0.235	−0.711	−0.031	−0.047	1.933	−403.51127
	B	0.296	−0.771	−0.044	−0.024	2.001	−403.50758



6A

6B

7A

7B

FIGURE 5 Geometrical parameters of the model molecules **6** and **7** for the two extreme conformations: A—the molecule is completely planar; B—the NH_2 group is perpendicular to the double bond plane.

ometry optimization. As found in structurally studied phosphaalkenes, the bond angle at the two-coordinate P atom varies in the wide range of 100–120°, depending on the bulkiness of the substituents. For the molecule **5**, calculations of the localized molecular orbitals (LMO) for the structures with the fixed values of the CPH bond angle 90° (structure **5a**), 109.5° (structure **5b**), and 120° (structure **5c**) were also carried out. Two conformations were considered for the molecules **6** and **7**: the completely planar conformation A and the conformation B with the NH_2 group being orthogonal to the double bond plane. The results of these calculations are presented in Figures 4 and 5 and in Table 2.

Methylenephosphine 5

The calculated geometry of the molecule **5** is found to be in good agreement with the experimental structural data: the P=C bond length, 1.646 Å, lies within the interval 1.64–1.67 Å, characteristic of phosphaalkenes having a localized double bond [2a]; the CPH bond angle, 98.8°, is close to the corresponding experimental value of 97.4°, which has been observed by microwave spectroscopy in the unstable phosphaalkene $H_2C{=}PH$ [11], and to the value of 103(1)° in the molecule **1**. As in the structurally studied phosphaalkenes, the C atom bond configuration is distorted [2b]: the PCH^1 bond angle is increased to 124.8° in comparison with the PCH^2 angle of 120.0°.

The double bond, P=C, is considerably polarized with the atomic charges $q_P = +0.278$ e and $q_C = -0.747$ e. It should be noted also that the data obtained in the present study for molecule **5** are in qualitative agreement with the calculations carried out earlier by other authors with different sets of basis functions [12].

Figure 6 represents schematically the results of calculations of the LMO according to Boys. In the double bond region, localization results in the appearance of the two symmetrical "banana" bonds, linking the P and C atoms. This result corresponds to the well-known tendency of localization according to the Boys method, which in the double bond region gives two equivalent bent bonds symmetrically situated relative to the line connecting the atoms instead of σ- and π-components. The centroids of these LMO's are arranged along the C=P bond above and under the molecular plane by 0.362 Å and are somewhat shifted toward the C atom (by 0.083 Å from the bond midpoint). The LMO centroid corresponding to the LP(P) lies in the molecular plane at a distance of 0.616 Å from the P atom and is somewhat shifted from the CPH angle bisector in the direction of the extention of the P=C bond line: $\alpha = 44.7°$, while the corresponding value for the bisector is 49.4°.

The interesting result of calculation is a rather high (more than 70%) s-character of the LP(P): the ratio of contributions of p- and s-orbitals (s/p) in the LMO of LP(P) is 2.51. It should also be mentioned that, in the ab initio calculations of the molecule $H_2C{=}PH$ [13], the LP(P) wave function has a spherical shape that corresponds to its increased s-character. This result is also in good agreement

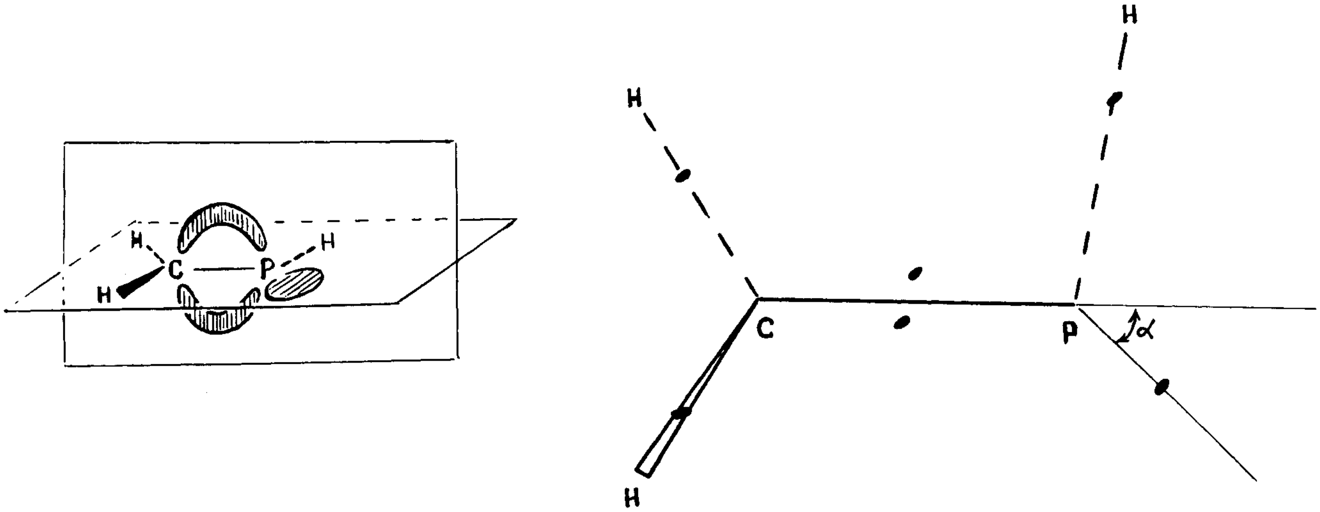


FIGURE 6 Scheme of the localized MO centroids of the molecule **5**.

with the data of semiempirical calculations of $Me_2N(Et_2N)C{=}PR$ (R = H, $SiMe_3$) [14]. Using the well-known relation between the bond angle and the degree of hybridization (see [15] and the references therein), it could be anticipated that the increase of the CPH bond angle would be accompanied by a considerable decrease in the s-character of LP(P). However, our calculations have shown that, on increasing the CPH bond angle from 90.0° in **5a** to 109.5° in **5b** and 120.0° in **5c** (a situation that models increasing steric hindrance in the molecule), the s/p ratio remains rather high, viz. 2.73, 2.26, and 2.01 (i.e. the LP(P) has ~73, 69, and 67% of the s-character). This result may be explained in terms of ideas developed by Kutzelnigg [16]. According to this author the concept of orthogonal hybrid AO's is applicable only to the elements of period II (first of all for carbon), whereas nonorthogonality of the hybrid AO's in compounds of the elements of the following periods (including period III) results in the significantly different types of correlation between the bond angle and the degree of hybridization. It is quite possible that the abovementioned high s-character of the LP(P) in phosphaalkenes is responsible for their much lower activity in comparison with phosphines in oxidative addition reactions [1c]. (In accord with the ab initio calculations performed in the same basis as in the present study, the s/p ratio for phosphines PH_3, H_2PNH_2, and H_2PPH_2 is equal to 1.28, 1.35, and 1.44, respectively [17].) It is interesting that a rather high s-character of the LP(P) is characteristic not only for phosphaalkenes but also for λ^3-iminophosphines. Thus, in accordance with the ab initio calculations of the H–N=P–H molecule [18], the LP(P) (the NPH bond angle being 100.4°) is localized mainly (by ~80%) at the s-orbital, while the LP(N) (the PNH bond angle is 110.8°) has predominantly (by ~60%) p-character.

In conclusion, it should be emphasized that calculations performed for the model molecule **5**, with localization of the MO's, adequately reproduce main features of the electronic structure of the molecule **1**, as observed in the experimental DED maps.

C-Aminomethylenephosphine 6

Let us at first analyze the results of calculations of the conformation B, where, due to the orthogonal orientation of the double bond and the amino group, the effect of the $n_N - \pi_{P=C}$ interaction is offset. As is evident from Table 2, in comparison with the methylenephosphine **5**, redistribution of charges takes place in the molecule **6B**: the shift of electron density from the C atom in the direction of the more electronegative N atom results not only in a drastic decrease of the negative charge at the C atom (by 0.516 e) but also in a certain decrease of the positive charge at the P atom (by 0.029 e). This also causes a significant decrease of the P=C bond polarity. For quantitative estimation of the change in electrostatic interaction between two atoms, it is convenient to use the product of charges at these atoms [19] ("+" sign corresponding to repulsion, "−" sign to attraction). In the case under consideration, on going from **5** to **6B**, the product $q_P \cdot q_C$ decreases significantly (by $-0.150\ e^2$). Therefore, despite the slight (by 0.022) increase of the overlap population of the P=C bond, the latter is even somewhat elongated (by 0.006 Å).

The following changes due to the effect of the $n_N - \pi_{P=C}$ interaction are observed in the planar A conformation of the molecule **6** as compared to the B conformation: electron density transfer of the

LP(N) in the direction of the double bond (the negative charge at the NH_2-group is diminished by 0.102 e) is accompanied also by an additional shift of electron density from the C atom (by 0.087 e). This total charge shift towards the P atom leads to a considerable decrease of the positive charge at this atom (by 0.229 e) to the resulting value of only 0.020 e. Thus, the polarity of the P=C bond is still further decreased, and the $q_P \cdot q_C$ value approaches zero (-0.0003 e^2). On the contrary, the polarity of the N–C bond in the conformation A increases (product $q_N \cdot q_C$ decreasing by $+0.087$ e^2, i.e. repulsion between the charges of the same sign being weakened). Consequently, the $n_N-\pi_{P=C}$ conjugation effect itself (increase of the sum of π-charges $q^{\pi}_{PC} = q^{\pi}_{P} + q^{\pi}_{C}$ up to 2.255 e in comparison with the value of 2.0 e indicating a transfer of the π-electron density from the NH_2-group to the antibonding π^*-orbital of the double P=C bond) and the corresponding change of bond polarities act in the same direction, and as a result the N–C bond is shortened by 0.072 Å, and the P=C bond is elongated by 0.048 Å.

Thus, results of the calculations for the model systems as well as experimental X-ray structural data confirm that, in C-aminosubstituted phosphaalkenes, structural manifestations of the $n_N-\pi_{P=C}$ conjugation are adequately described by Scheme 1.

In conclusion of this section, it should be noted that, for molecule **6**, the conjugated conformation A is more favorable than the conformation B by 18.77 Kcal/mol (according to the SFC/3-21G* calculation).

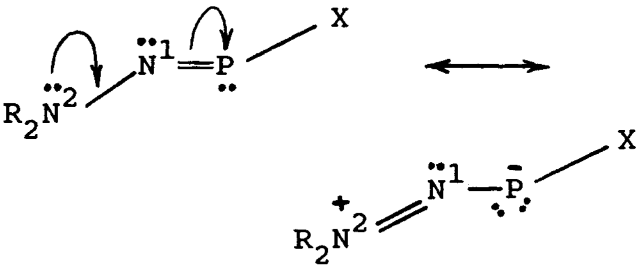
P-Aminomethylenephosphine 7

At first, let us consider the results of calculations for the orthogonal configuration **7B**. Introduction of the amino group to the P atom and shift of electron density from this atom in the direction of the more electronegative N atom result in the change of charge distribution, opposite to that observed in **6B**: the positive charge at the P atom is increased by 0.363 e, while the negative charge is increased at the C atom (by -0.037 e), i.e. the P=C bond polarity in the molecule **7B** increases ($q_P \cdot q_C$ increases by -0.294 e^2) in comparison with **5** (whereas in **6B** *it decreases*). In accordance with these changes, the P=C bond is shortened from 1.646 Å in **5** to 1.642 Å in **7B**, despite decreasing of its population by 0.106.

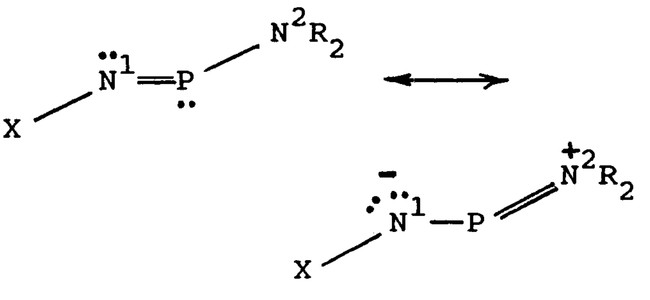
The transition from the conformation B to the planar conformation A of the molecule **7** is accompanied by the transfer of 0.042 e from the amino group in the C atom direction and the further (in comparison with **7B**) increase of both the positive charge at the P atom (by 0.091 e) and the negative charge at the C atom (by 0.110 e). As a result, the polarities of both P–N ($q_P \cdot q_N$ increasing by -0.078 e^2) and P=C bonds ($q_P \cdot q_C$ increasing by -0.152 e^2) are increased. However, the conjugation effect for the P–N bond (increase of the π-component of this bond) and the resulting effect of bond polarization act in one direction. They cause a shortening of the P–N distance in the conformation A by 0.038 Å. For the P=C bond, these effects are opposing each other; increase of polarity of the bond causes shortening, while conjugation (loosening of the π-system) leads to elongation. Because in **7** the first effect obviously prevails, the double P=C bond is shortened by 0.010 Å. Thus, on going from the orthogonal (B) to the planar (A) conformation, simultaneous shortening of the P–N and P=C bonds is observed; i.e., the structural manifestation of the $n_N-\pi_{P=C}$ interaction in the model molecule **7** does not correspond to the generally accepted conjugation pattern depicted in Scheme 2.

It is to be emphasized that (just as it has been anticipated on the basis of analysis of X-ray structural data) the $n_N-\pi_{P=C}$ conjugation effect markedly stabilizes the planar conformation—the energy of the **7A** conformer is 8.80 Kcal/mol lower than that of conformer **7B**.

It should be particularly emphasized that, according to ab initio calculations, a quite analogous interaction of the amino group with the double bond has also been observed in the case of λ^3-iminophosphines: in N-aminosubstituted compounds of this class, structural manifestations of the $n_N-\pi_{N=P}$ conjugation correspond to Scheme 3, whereas, in the case of P-aminosubstituted iminophosphines, structural consequences of conjugation do not agree with the generally accepted Scheme 4 (just as in the case of P-aminosubstituted phosphaalkenes, in the planar conformation A a simultaneous short-



SCHEME 3



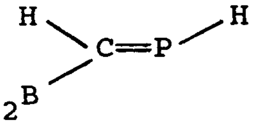
SCHEME 4

ening of the ordinary P–N^2 and double P–N^1 bond being observed).

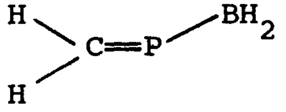
The substitution effects on the double P=N bond in λ^3-iminophosphines are considered in more detail in several papers published quite recently [20].

Boryl Substituted Phosphaalkenes **8** *and* **9**

In order to obtain a more general notion about features of the conjugation effects in phosphaalkenes, it seemed of interest to consider not only the case of the double P=C bond interaction with π-donor substituents (molecules **6** and **7**), but with π-acceptors as well. Therefore we carried out the calculations of the model molecules **8** and **9** in two conformations A and B. The results obtained are represented in Figure 7 and Table 2.

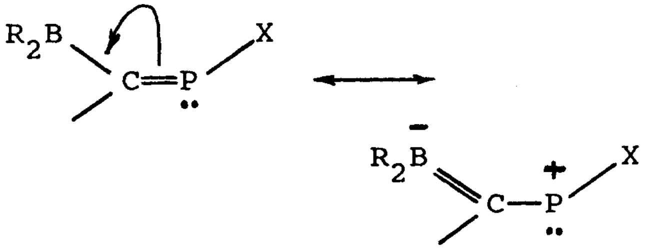


8

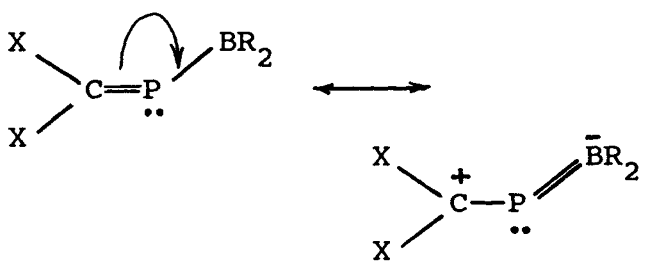


9

The calculations revealed that, in both molecules, the planar conformation A is characterized by increasing the charge at the BH$_2$ group in comparison with the orthogonal conformation B (by −0.075 e in **8** and 0.023 e in **9**) and concomitant lowering of the sum of π-charge at the double P=C bond. These changes indicate the p_{BH_2}–$\pi_{P=C}$ conjugation in the molecules **8A** and **9A**, which should result in elongation of the P=C bond and shortening of the B–C (B–P) bond (Schemes 5 and 6).

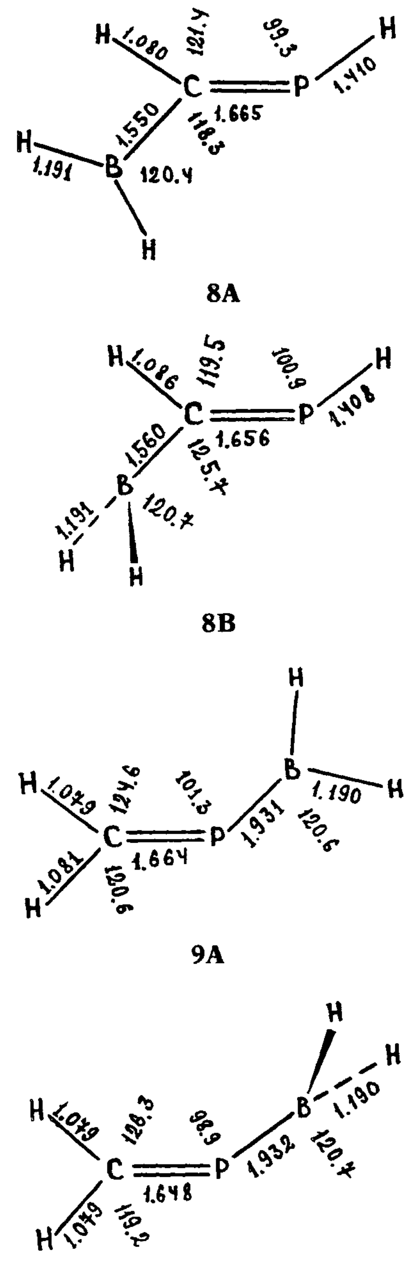


SCHEME 5



SCHEME 6

However, this effect is superimposed by the change of the bond polarization, which is related to the charge redistribution (with an electron density transfer toward the BH$_2$ group). Thus, in the molecule **8A**, the $q_P \cdot q_C$ value increases by −0.109 e^2 (i.e. polarization effect acting in the direction opposite to conjugation), while the $q_C \cdot q_B$ value diminishes by −0.027 e^2; effects of polarization and conjugation for this bond act in the same direction. As a result of the total effect, the C–B bond is shortened by 0.010 Å, while the P=C bond length remains practically unchanged. On the contrary, in the molecule **9A**, the effects of conjugation and po-



8A

8B

9A

9B

FIGURE 7 Geometrical parameters for the model molecules **8** and **9** for the two extreme conformations: A—the molecule is completely planar; B—the BH$_2$ group is perpendicular to the double bond plane.

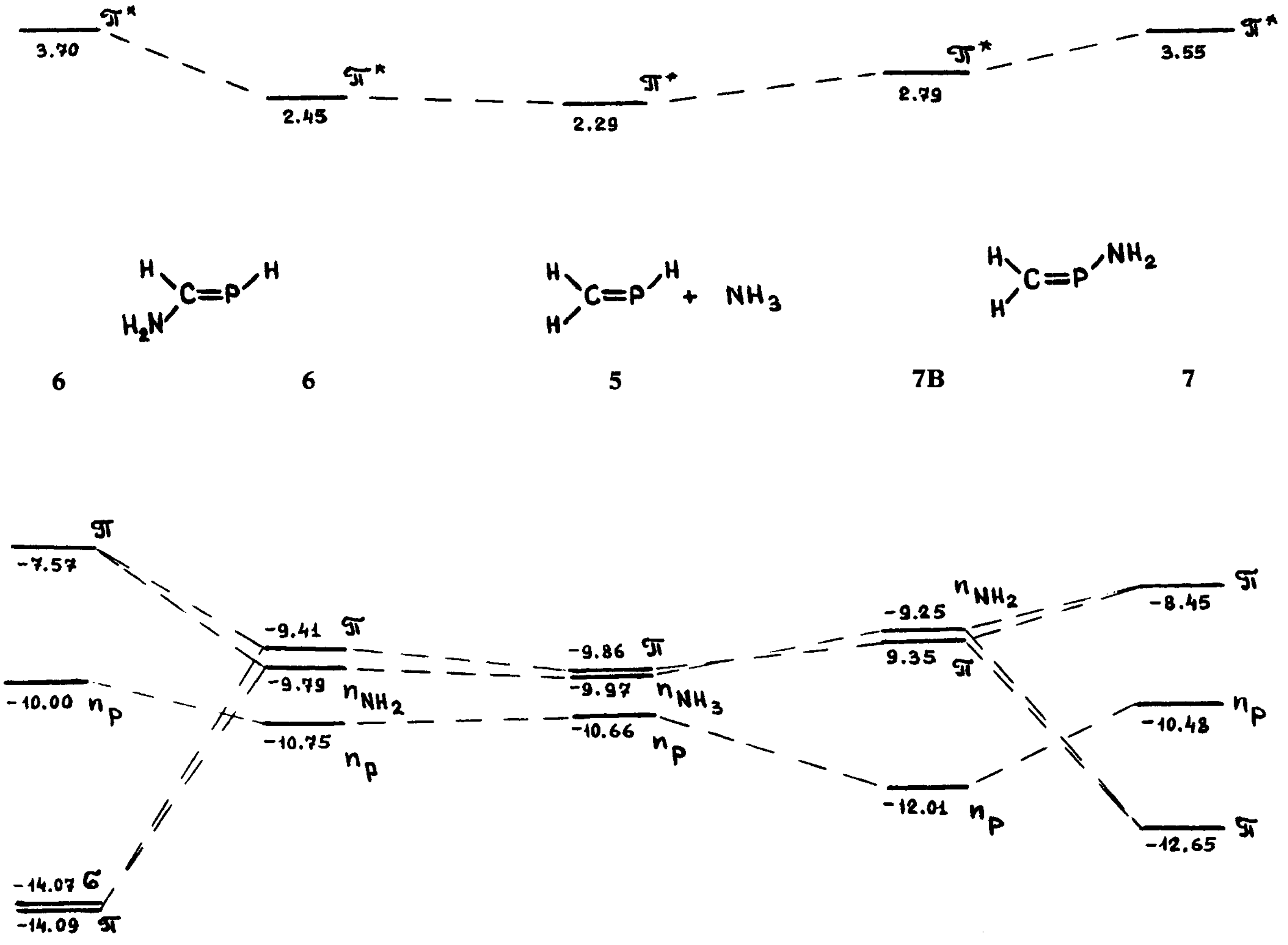
larization ($q_P \cdot q_C$ being increased by -0.061 e^2) act in the same direction. As a result, this bond is elongated by 0.016 Å, while for the P–B bond these effects compensate each other ($q_P \cdot q_B$ being decreased by 0.006 e^2) and its length remains practically unchanged.

Thus, structural aspects of conjugation effects in phosphaalkenes depend greatly on to which of the two atoms of the P=C double bond the π-donor (π-acceptor) group is bonded. Presumably, this dependence is defined by a considerable decrease of the p_π–p_π conjugation on going from the II to the III (and the following periods) elements. At the same time, the effects of the change of bonds polarization induced by the charge transfer become, on the contrary, more pronounced for the elements of period III due to a longer distance of the valence electrons from the nucleus [21]. As a result, these two effects become of the same order and their combined structural manifestation depends on whether they act in the same or opposite directions.

Frontier Molecular Orbitals of the Molecules **5–9**

The diagrams of energy levels of the frontier molecular orbitals of the model phosphaalkenes are presented in Figures 8 and 9. The main conclusion from these diagrams is that energy changes of molecular orbitals, on going from the orthogonal to the planar conformation, are more significant when the substituent (NH_2 or BH_2) is bonded to the carbon atom. This result is in good agreement with the concept of weakening of the p_π–p_π interaction when passing from the atoms of the second period to the atoms of the third and following periods [21]. The molecule **6A** has the lowest ionization potential ($-E_{\text{Homo}}$). The closeness of energy levels of the orbitals n_P and $\pi_{P=C}$ of the molecule **5** and n_{NH_3} (Figure 8) means that the character of the HOMO depends significantly on the molecular conformation and the attachment site of the amino group (to C or P atom). Change in the sequence of the frontier

FIGURE 8 Scheme of molecular orbitals in **5–7** (energy values in eV).



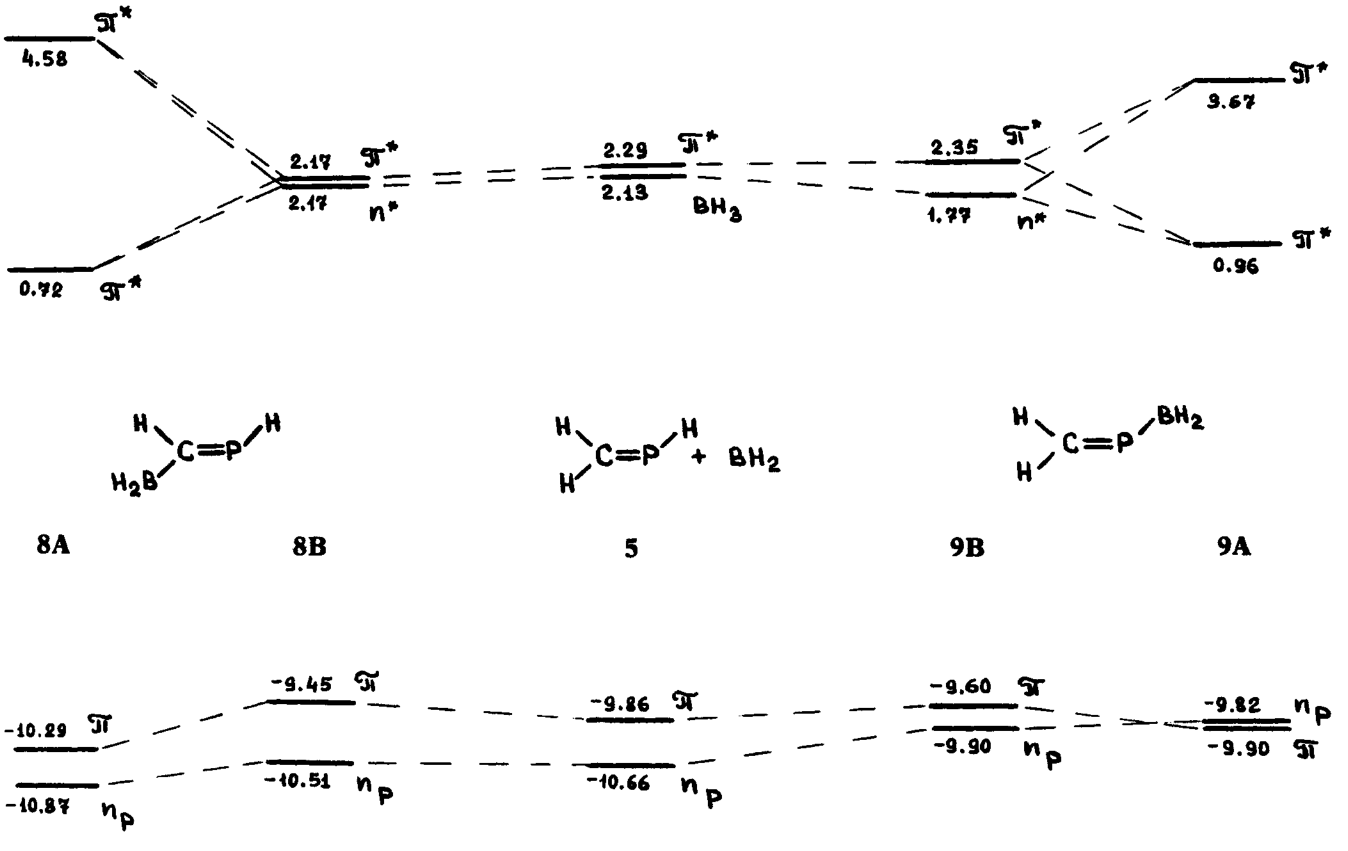


FIGURE 9 Scheme of molecular orbitals in 8 and 9 (energy values in eV): n—orbitals localized in the C=P group plane; π—in the plane perpendicular to the latter; n*—a vacant orbital of the BH_2 group in the conformation B.

molecular orbitals in **9A** in comparison with **5** (Figure 9) is caused by lowering of the π-orbital due to interaction with the BH_2 group vacant orbital.

Conclusion

The results of the X-ray structural studies and quantum-chemical calculations discussed in the present paper allow us to make the following conclusions:

1) The characteristic feature of the electronic structure of phosphaalkenes is the high s-character of the P atom lone electron pair.

2) The structural consequence of the p_π–p_π conjugation in phosphaalkenes depends greatly on the character of the substituent and its attachment site. Depending on the substituent position conjugation effects may be markedly reinforced or weakened (compensated) by changes in the bond polarization.

EXPERIMENTAL

All calculations of DED maps for the molecule **1** have been carried out with an Eclipse S/200 computer using the INEXTL program package [22].

An X-ray structural study of the compound **4** has been performed with a CAD-4 ENRAF-NONIUS diffractometer (λCuK_α, graphite monochromator, the ratio of the scanning rates $\omega/\theta = 1.2$, $\theta_{max} = 66°$, 5847 independent reflections). Crystals **4** are monoclinic, at 20°C $a = 10.171(3)$, $b = 32.382(7)$, $c = 11.452(3)$ Å, $\beta = 114.67(2)°$, $V = 3427.3$ Å^3, $Z = 4$, $d_{calc} = 1.01$ g/cm^3, space group $P2_1/c$. The structure was solved using the MULTAN program and refined by the least-squares technique in full-matrix anisotropic approximation. All hydrogen atoms were located in a difference Fourier synthesis and refined isotropically. In refinement, 4907 reflections with $F_{obs} > 5\sigma$ were used. The final discrepancy factors are $R = 0.042$ and $R_W = 0.064$. Coordinates and equivalent isotropic temperature factors of nonhydrogen atoms and coordinates of H atoms are deposited at the Cambridge Crystallographic Data Centre [23]. All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package [24].

The ab initio MO LCAO SCF calculations of the molecules **5–9** were carried out with the GAUSSIAN 80 [25] and MONSTERGAUSS 81 [26] programs with the standard (internal) 32-1G* basis set, containing five d-orbitals at each nonhydrogen atom. Geometry optimization was performed according to the BERNY procedure [27]. In the molecules **6–9** bond lengths and bond angles were optimized for two conformations—the planar conformation A (completely planar molecule) and the orthogonal conformation B (the EH_2 group ($E = N, B$) being orthogonal to the molecular plane). In addition, the following restrictions were imposed: the EH_2 group is planar, and the E–H bonds and C(P)EH bond angles for both H atoms in this group are equivalent. For the molecule **5**, calculations with the values of the CPH bond angle 90.0° (**5a**), 109.5° (**5b**), and 120.0° (**5c**) and fixed other geometrical parameters obtained by optimization of Scheme 5 were also performed. Calculations of the localized MO according to Boys were also carried out for the molecules **5**, **5a**, **5b**, and **5c** [28].

N-*Trimethylsilyl*-N-(*2,4,6-tri*-tert-*butylphenyl)amino*-C,C-*bis*-(*trimethylsilyl)methylenephosphine* 4

The equimolar quantity of lithium *N*-trimethylsilyl-2,4,6-tri-*tert*-butylphenylamide in 20 mL of THF was added on cooling to −40°C to the solution of 0.01 mole of *P*-chloro-*C*,*C*-bis(trimethylsilyl)methylenephosphine in 30 mL of THF. The mixture was stirred for 3 h at room temperature, then the solvent was removed in vacuo. Hexane (60 mL) was added to the residue, an LiCl precipitate was removed and the filtrate was repeatedly concentrated in vacuo. The product obtained was purified by crystallization from glyme. Yield 2.74 g (54%), mp 114–117°C, yellow crystals readily soluble in organic solvents. Found: Anal. Calc. for $C_{28}H_{56}NPSi_3$: C, 64.43; H, 10.81; P, 5.93; Si, 16.14. Found: C, 64.56; H, 10.80; P, 6.15; Si, 16.07.

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