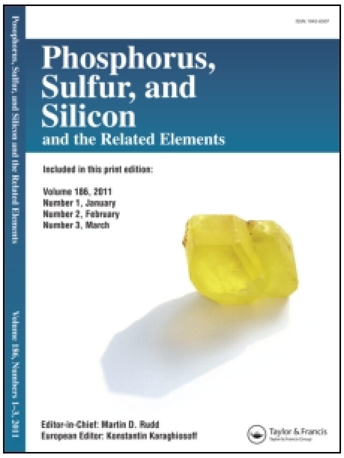

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MOLECULAR AND CRYSTAL STRUCTURE AND ELECTRON DENSITY DISTRIBUTION IN P-BIS(TRIMETHYLSILYL)AMINO-C,C-DICHLOROMETHYLENEPHOSPHINE

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MOLECULAR AND CRYSTAL STRUCTURE AND ELECTRON DENSITY DISTRIBUTION IN P-BIS(TRIMETHYLSILYL)AMINO-C,C-DICHLOROMETHYLENEPHOSPHINE

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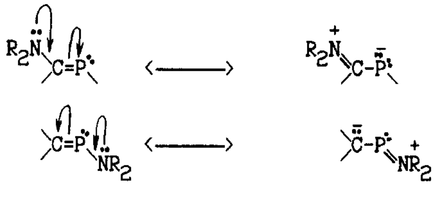
Molecular and crystal structure of P-bis(trimethylsilyl)amino-C,C-dichloromethylenephosphine which is a liquid at ambient temperature (m.p. ~ −9°C) was determined at −120°C by the low-temperature X-ray diffraction method and deformation electron density maps were calculated. Experimental evidence is obtained for the conclusion that in P-aminosubstituted phosphaalkenes the n_N-$\pi_{P=C}$ conjugation causes not only shortening of the single P—N bond through which this conjugation is transferred but also shortening of the P=C double bond. Comparison of peculiarities of electron density distribution is given for both highly conjugated and double-bond localized phosphaalkenes.

Key words: Phospaalkenes; X-ray; conjugation; electron-density distribution.

INTRODUCTION

Recently we have considered structural and energetical consequences of the n_N-$\pi_{P=C}$ conjugation in P- and C-aminosubstituted phosphaalkenes on the basis of the results of X-ray structural studies and *ab initio* quantum-chemical calculations.[1] In particular, both experimental and theoretical data have shown that this conjugation in C-aminosubstituted phosphaalkenes may be well described by the "classical" Scheme (1):


(1)
(2)

On the other hand, the results of our *ab initio* calculations[1] are in contradiction with the Scheme (2) for P-aminosubstituted phosphaalkenes: transition of a completely planar molecule into a conformation where the amino group is orthogonal to the double bond plane is accompanied by a simultaneous elongation of both the P=C and the P—N bonds. Undoubtedly, an experimental verification of these results is of interest. For this purpose structural data for P-aminosubstituted phos-

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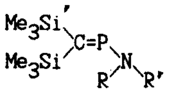
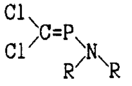
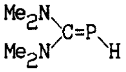
phaalkenes with the amino group turned out of conjugation have to be obtained (for planar molecules such data are available[1,2]). However, our attempts to prepare a crystalline compound of the type (A) with the orthogonal amino group, suitable for an X-ray study, were unsuccessful.[1]



(A)

The n_N-$\pi_{P=C}$ conjugation has been found to stabilize the planar conformation of (A) quite sufficiently. Hence, steric hindrances arising from the bulky R and R′ substituents do not primarily lead to the rotation of the amino group around the P—N bond; instead they cause a considerable increase of the CPN, PNR and PCSi bond angles as well as displacement of the N atom out of the double bond plane (the Si(1)CPN torsion angle reaches ca. 10°). On the basis of steric consideration we have assumed that phosphaalkenes **1** (which are a liquid at the ambient temperature) may be suitable for solving of the above mentioned problem due to their orthogonal conformation of the amino group.





1: R = Bu^t (a), SiMe$_3$ (b)

2

Earlier we have obtained[1] experimental deformation electron density maps for the phosphaalkene **2** with a high degree of the π-electron density delocalization from the double P=C bond due to the n_N-$\pi_{P=C}$ conjugation. We believed that the similar data for a phosphaalkene with a localized double P=C bond and the comparison of the electron density distribution in these two types of compounds **1** and **2** would be rather interesting.

Therefore we have carried out a precision X-ray structural investigation of the compound **1b** first prepared by the authors.[3]

RESULTS AND DISCUSSION

1. Molecular and Crystal Structure

The general view of the molecule **1b** and its relevant geometric parameters are given in Figure 1, molecular packing in crystal is shown in Figure 2. The Cl(1)Cl(2)C(1)PN double bond system is essentially planar (atom deviations from the mean-square plane do not exceed 0.022(1) Å). The N atom has a planar trigonal bond configuration—the bond angles sum being 358.9(3)°. As expected, the nitrogen lone pair [LP(N)] is not conjugated with the P=C double bond due to steric hindrances, as the dihedral angle between the Cl(1)Cl(2)C(1)P and NSi(1)Si(2) planes is equal to 76.55(7)°.

The comparison of geometric parameters of **1b** and planar P-aminosubstituted phosphaalkenes investigated previously[1,2] shows that in the latter the single P—N

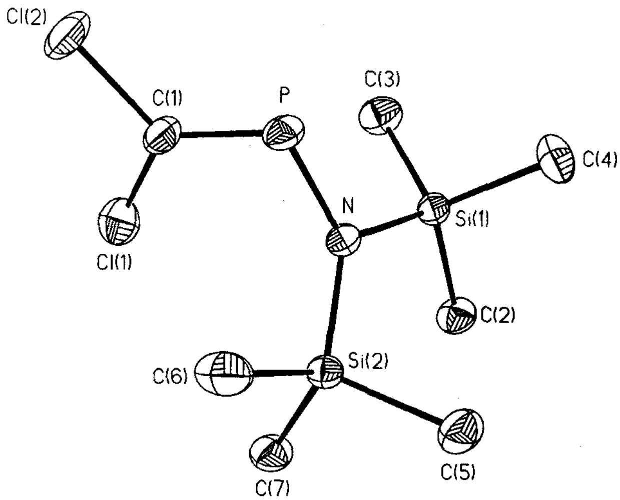


FIGURE 1 General view of the molecule **1b** (H atoms omitted for clarity). The main geometrical parameters: P—N 1.697(1), P—C(1) 1.685(2), Cl(1)—C(1) 1.726(2), Cl(2)—C(1) 1.736(1), Si(1)—N 1.770(1), Si(2)—N 1.771(1), Si—$C_{av.}$ 1.865(2) Å, NPC(1) 105.3(1), PNSi(1) 115.0(1), PNSi(2) 120.0(1), Si(1)NSi(2) 123.9(1), Cl(1)C(1)Cl(2) 114.0(1), Cl(1)C(1)P 127.8(1), Cl(2)C(1)P 118.2(1)°.

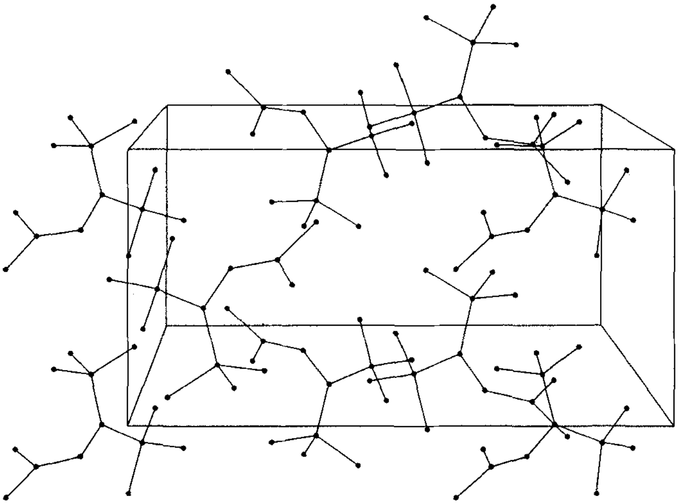


FIGURE 2 Molecular packing in crystal **1b**.

bond is shortened by ca. 0.01–0.02 Å (from 1.697(1) in 1b to 1.673(6)–1.687(1) Å) due to the n_N-$\pi_{P=C}$ conjugation. However, the P=C double bond is not elongated as may be expected from the traditional conjugation Scheme (2). On the contrary, this bond is even shortened by 0.03–0.04 Å (from 1.685(2) in **1b** to 1.641(7)–1.652(1) Å). Thus, experimental data obtained in the present investigation completely support the previous conclusions about the character of conjugation in the P-aminosubstituted phosphaalkenes based on the *ab initio* calculations.[1] These rather unusual structural consequences of the n_N-$\pi_{P=C}$ conjugation are caused by the fact that the n-π conjugation leads, in general, not only to the weakening of the double P═C bond and to the increase in the π-component of a "single" P—N bond but also to changes in the polarization of these bonds due to the LP(N) electron density transfer towards the double P═C bond. In particular, as *ab initio* calculations revealed, in P-aminosubstituted phosphaalkenes the polarity of both P—N and P═C bonds is increased due to this electron density transfer. The increased polarity of the P—N bond leads to its further shortening whereas the polarity of the P═C bond not only compensates its elongation caused by weakening of its π-component but leads even to some shortening of this bond.

Other geometric parameters of the molecule **1b** are unexceptional for phosphaalkenes.[4] The effect of C- and P-halogenosubstitution on the molecular and electronic structure of phosphaalkenes including the compound **1b** have been discussed elsewhere.[5] One may only note the elongation of the Cl(1)—C(1) bond in comparison with the Cl(2)—C(1) bond by 0.010(2) Å caused evidently by distortion of the planar trigonal bond configuration of the C(1) atom. Indeed, the Cl(1)C(1)P bond angle is increased to 127.8(1)°, due to the Cl(1) . . . N steric repulsion, while the Cl(2)C(1)P bond angle is decreased to 118.2(1)° (which causes increasing in the *s*-character of the C(1) AO forming the C(1)—Cl(1) bond and, respectively, to increasing in the *p*-character of the C(1) AO in the C(1)—Cl(2) bond). This non-equivalence of the C(1)—Cl bond lengths may be also caused, to some extent, by hyperconjugative effects.[6]

Molecules **1b** are kept within crystal by common Van der Waals interactions. Molecular packing is shown in Figure 2. No shortened intermolecular contacts are observed. Amongst the intermolecular distances shorter than 4.00 Å the shortest Cl . . . P, Cl . . . C, C . . . C and C . . . H contacts are 3.969(1), 3.793(2), 3.624(3) and 3.10(2) Å, respectively (corresponding sums of Van der Waals radii are 3.70, 3.50, 3.40 and 2.90 Å[7]).

2. *Deformation Electron Density Distribution*

Experimental maps of the distribution of deformation electron density (DED) are shown in Figures 3 and 4. In Figure 3 the DED section through the nodal P═C double bond plane is given (section (a)). In Figure 4 the section orthogonal to the first one and also passing through this bond, is presented (section (b)).

In connection with problems considered in this paper, the most interesting characteristics of the maps shown are DED distributions in the region of the P═C double bond and the P atom lone pair [LP(P)]. In section (a) (Figure 3) on the P═C double bond the strong peak with the height of 0.43 e/Å^3 is observed; its maximum is shifted by ~0.15 Å from the bond center towards the P atom. This result is in agreement with the localised character of the P═C double bond in **1b** and corresponds to its polarity direction $\overset{\delta+}{\mathrm{P}}\text{—}\overset{\delta-}{\mathrm{C}}$ (according the *ab initio* HF/6-31G* calculations[5] such a charge distribution is the feature both of P- and C-halogenosubstituted phosphaalkenes). It is important to note that in compound **2** with the π-system delocalized due to n_{N}-$\pi_{\mathrm{P=C}}$ conjugation, the peak on the double bond in the corresponding section (0.39 e/Å^3) is shifted from the bond center in the opposite direction by 0.08 Å. This result is in accordance with the opposite $\left(\overset{\delta-}{\mathrm{P}}\text{—}\overset{\delta+}{\mathrm{C}}\right)$ polarity of the P═C double bond in conjugated phosphaalkenes. It

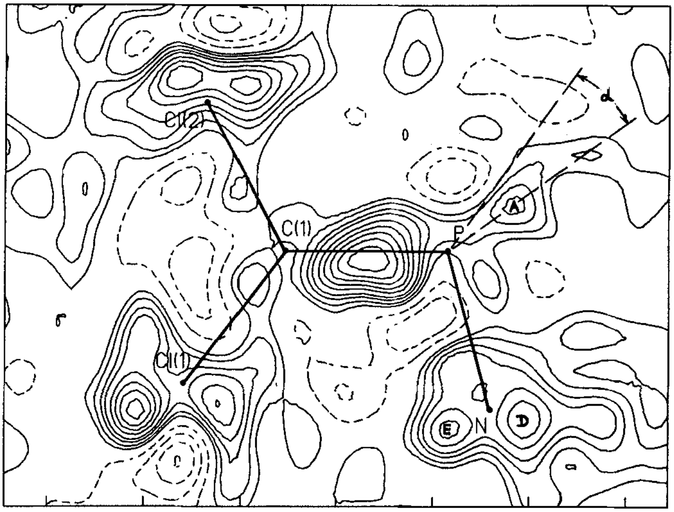


FIGURE 3 DED map of the molecule **1b** in the Cl(1)Cl(2)C(1)P plane (section (a)); isolines are drawn through 0.1 $e/\text{Å}^3$ for negative DED value and 0.05 $e/\text{Å}^3$ for positive one.

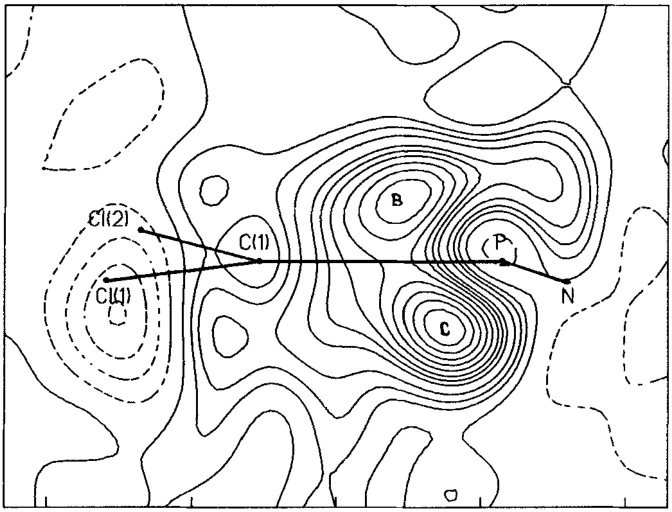


FIGURE 4 DED map of the molecule **1b** in the π-bond plane, i.e. in the plane orthogonal to the Cl(1)Cl(2)C(1)P plane and passing through the P═C(1) bond (section (b)); isolines are drawn as in Figure 3.

is worthwhile to mention that in section (b) for the compound **1b** (Figure 4) the DED peak of the double bond has a pronounced saddle-like shape with two local maxima B and C (with heights of 0.48 and 0.57 $e/\text{Å}^3$) situated at ca. 0.41 Å above and 0.46 Å below the P . . . C(1) line with the saddle point of 0.39 $e/\text{Å}^3$ in height located approximately on this line. The maxima B and C probably correspond to a strong and localised π-component of the double P═C bond.

On the other hand, the peak A in the section (a) (Figure 3) corresponding to LP(P), is being at 0.84 Å from the P atom nucleus and is slightly lower (0.18 $e/\text{Å}^3$) than P═C bond peaks. Similar to **2**, as a consequence of an essential LP(P) *s*-character, the peak A in the section (a) is not located exactly on the C(1)PN angle outer bisector but is shifted toward the prolongation of the P=C bond. However, this shift is considerably lesser for **1b**. Thus, for **2** the α angle characterizing the peak A shift from the C(1)PN angle bissector is ~40°, while for **1b** it is ~20° only. This difference in the LP(P) orientation relative to the P=C bond is probably caused by the repulsion of LP(P) and LP(N) which are almost parallel in **1b**. This conclusion is supported by the fact that the angle between the P—N bond and the line connecting the D and E peaks in section (a) is increased up to ~100° as compared with an ideal value of 90°. One may note that the D and E peaks in section (a) corresponding to the LP(N) are quite distinctly pronounced, their heights being 0.25 e/Å^3, and these peaks are located at 0.32 and 0.46 Å from the internuclear P . . . N line, respectively. The DED map in the region of the LP(N) is in accordance with the conception about its localized character and the sp^2 hybrid state of the nitrogen atom (that is, of an essentially pure *p*-character of the LP(N)). It should be specially emphasized that the features of DED distribution in the corresponding section for **2** is markedly different from these for **1b**. Due to the n_N-$\pi_{P=C}$ conjugation in **2**, DED of the LP(N) is uniformly distributed above and under the N—C bond line and practically coalesces with the DED maximum on this bond, testifying the appearance of the π component for this formally single bond.

TABLE I

Coordinates of non-hydrogen atoms and their equivalent isotropic temperature factors U_{eq}

Atom	x	y	z	U_{eq}
Cl(1)	0.6015(1)	0.2979(1)	0.3443(1)	46(1)
Cl(2)	0.3051(1)	0.3451(1)	0.1634(1)	57(1)
P	0.4704(1)	0.1833(1)	0.1323(1)	28(1)
Si(1)	0.5961(1)	0.0341(1)	0.2725(1)	21(1)
Si(2)	0.8529(1)	0.1551(1)	0.1848(1)	21(1)
N	0.6443(1)	0.1281(1)	0.2038(1)	21(1)
C(1)	0.4636(2)	0.2703(1)	0.2144(2)	33(1)
C(2)	0.7902(2)	-0.0032(1)	0.3809(1)	30(1)
C(3)	0.4211(2)	0.0570(1)	0.3522(1)	33(1)
C(4)	0.5202(2)	-0.0484(1)	0.1587(1)	36(1)
C(5)	0.9450(2)	0.0656(1)	0.1141(2)	36(1)
C(6)	0.8352(2)	0.2486(1)	0.0859(2)	40(1)
C(7)	1.0009(2)	0.1829(1)	0.3264(1)	31(1)

Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalised U(i,j) tensor

EXPERIMENTAL

The monocrystal of liquid under normal conditions compound **1b** suitable for X-ray diffraction study was grown from the melt in the thin-walled capillary (ca. 0.4 mm diameter) by very slow cooling of its melt near the m.p. ca. −9°C. The resulting crystal was slowly cooled to −120°C and at this temperature an X-ray experiment was carried out.

Crystal data for **1b**: $C_7H_{18}Cl_2NPSi_2$, $M = 274.3$, monoclinic, $a = 7.947(1)$, $b = 15.831(2)$, $c = 11.650(2)$ Å, $\beta = 102.30(2)°$, $V = 1432.0(7)$ Å^3, $Z = 4$, $d_c = 1.27$ g cm^{-3}, space group $P2_1/n$, $\mu = 6.95$ cm^{-1}, F(000) = 797.

Crystallographic measurements were made using the Syntex $P2_1$ diffractometer operating in the $\theta/2\theta$ scan mode (MoK$_\alpha$-radiation, graphite monochromator, $1 \leq 2\theta \leq 100°$). From the total number 15074 measured reflections 5390 independent ones with $I \geq 4\sigma(I)$ were used in the structure solution and refinement. In the interval $2\theta \leq 44°$ all reflections in the full sphere of the reciprocal space were collected and their intensities were averaged with the $R_{int} = 0.016$. The structure was solved by direct methods (all hydrogen atoms were located in the difference Fourier maps) and refined by full-matrix least squares technique in the anisotropic-isotropic (for H atoms) approximation. In the final quasi high-angle refinement the Seiler-Dunitz weighting scheme with $w = (\sigma^2(F) + 0.00044\ F^2)^{-1}$ and B = 6.0 Å^2 was used; H-atoms during this refinement were included with fixed positions. Final results of this refinement

TABLE II

Hydrogen coordinates (×10³) and temperature factors (Å² × 10²)

Atom	x	y	z	U
H(1)	882(3)	-16(1)	350(2)	4(1)
H(2)	754(3)	-53(1)	415(2)	3(1)
H(3)	829(3)	39(1)	445(2)	4(1)
H(4)	459(3)	104(2)	402(2)	4(1)
H(5)	402(3)	7(1)	402(2)	4(1)
H(6)	313(3)	72(2)	293(2)	5(1)
H(7)	615(3)	-59(2)	114(2)	5(1)
H(8)	486(3)	-104(2)	194(2)	5(1)
H(9)	405(5)	-15(2)	108(3)	9(1)
H(10)	941(3)	20(2)	158(2)	5(1)
H(11)	1062(3)	78(2)	96(2)	6(1)
H(12)	876(4)	53(2)	47(3)	6(1)
H(13)	795(3)	297(2)	114(2)	5(1)
H(14)	949(4)	262(2)	67(3)	7(1)
H(15)	772(3)	231(2)	17(2)	5(1)
H(16)	1100(3)	211(1)	307(2)	3(1)
H(17)	1028(3)	139(2)	376(2)	5(1)
H(18)	941(4)	228(2)	361(2)	6(1)

TABLE III

Anisotropic temperature factors (A² × 10³)

Atom	U11	U22	U33	U23	U13	U12
Cl(1)	42(1)	37(1)	61(1)	-19(1)	16(1)	1(1)
Cl(2)	30(1)	31(1)	114(1)	20(1)	23(1)	14(1)
P	20(1)	28(1)	33(1)	6(1)	-1(1)	4(1)
Si(1)	21(1)	20(1)	22(1)	1(1)	1(1)	2(1)
Si(2)	17(1)	24(1)	22(1)	-0(1)	1(1)	1(1)
N	19(1)	20(1)	22(1)	1(1)	1(1)	3(1)
C(1)	24(1)	22(1)	54(1)	6(1)	13(1)	5(1)
C(2)	28(1)	30(1)	31(1)	7(1)	0(1)	5(1)
C(3)	27(1)	38(1)	36(1)	7(1)	11(1)	2(1)
C(4)	45(1)	26(1)	34(1)	-5(1)	2(1)	-6(1)
C(5)	30(1)	42(1)	36(1)	-10(1)	9(1)	5(1)
C(6)	28(1)	43(1)	47(1)	20(1)	6(1)	0(1)
C(7)	23(1)	36(1)	31(1)	-7(1)	-3(1)	0(1)

The anisotropic temperature factor exponent takes the form:

$-2\pi(H^2a^{*2}U11+K^2b^{*2}U22+\dots+2HKa^*b^*U12)$

are: $R = 0.0395$, $R_w = 0.0465$, GOF = 1.96. Correction for Lorentz and polarisation effects but not for absorption were applied. Atomic coordinates and thermal parameters are listed in Tables I–III. All crystal data have been deposited at the Cambridge Crystallographic Data Centre.[8]

DED distribution maps in the section discussed were calculated using as a model high-angle refinement results and low-angle reflections with $\sin \theta/\lambda \leq 0.80$ Å^{-1}. All calculations were performed with the PC/AT computer using SHELXTL PC programme package.

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