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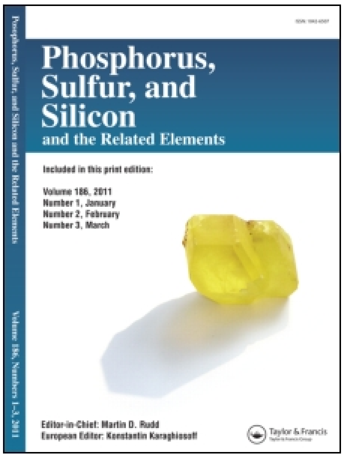

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FEATURES OF PHOSPHABUTADIENES STRUCTURE: NMR SPECTROSCOPY AND X-RAY INVESTIGATION

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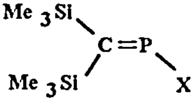
Abstract Conjugation effects in various phosphabutadienes are considered.

INTRODUCTION

There has been revealed an essential contribution of the n,π-conjugation effect to thermodynamical stabilization of phosphaalkenes **1** and **2**. It should be expected that having combined the moieties which characterized by π-donating (D^1 and D^2) and π-withdrawing (A^1) properties into the diene systems **3a-c** and **4a-c** one could reveal conjugation effects of the π-type bonds with low-coordinate phosphorus involved.



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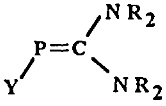

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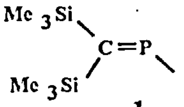
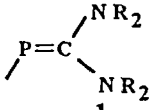
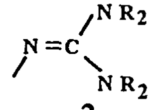


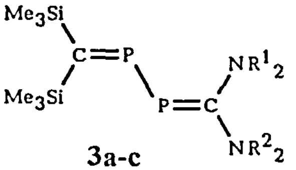
A^1



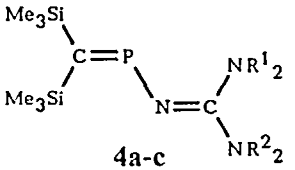
D^1



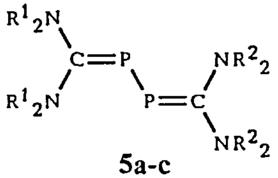
D^2



3a-c



4a-c



5a-c

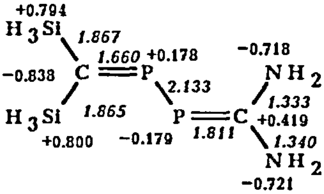
a R^1=R^2=Me; b R^1=R^2=Et; c R^1=Me, R^2=Et

RESULTS AND DISCUSSION

The X-ray investigation of structure of phosphadiene **3b** shows neither essential P-P bond shortening (2.155 Å) nor Si_2P=C and P=CN_2 bonds lengthening (1.683 and 1.777 Å). The comparison of the NMR chemical shifts in **3a** with those in compounds **6** and **7** indicates charge alternation in phosphabutadienes **3**.

$(Me_3Si)_2C{=}P{-}P(Bu^t)_2$	$(Me_3Si)_2C^1{=}P^1{-}P^2{=}C^2(NMe_2)_2$		$(But)_2P^2{-}P^1{=}C(NMe_2)_2$
6	3a		7
δP^1=450 ppm.	δP^1=454 ppm.	δP^2=99 ppm.	δP^1=-11 ppm.
δC=228 ppm.	δC^1=172 ppm.	δC^2=201 ppm.	δC=201 ppm.
$^1J_{PP}$=245 Hz	$^1J_{PP}$=396 Hz	$^1J_{PP}$=396 Hz	$^1J_{PP}$=256 Hz
$^1J_{CP1}$=98 Hz	$^1J_{C1P1}$=88 Hz	$^1J_{C2P2}$=87 Hz	$^1J_{CP1}$=83 Hz

The *ab initio* (6-31G**/3-21G*) calculations of the model compounds **8-10** lead to the planar structures and enable one to suggest the π,π-interaction between the $(H_3Si)_2C{=}P$- and the $-P{=}C(NH_2)_2$ moieties.



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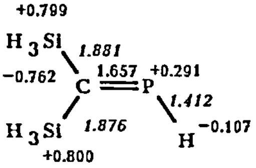

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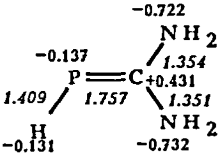


10

In symmetric phosphabutadienes **5** both moieties are characterized by π-donating properties, and, as judged from the NMR data for **5a** [δP= 34 ppm, δC= 197 ppm, $^1J_{CP}$= 32 Hz, $^1J_{PP}$= 289 Hz (for **5c**)] the conjugation between the moieties is absent.

In the context of the problem considered, of interest is the possibility of the P=C bond conjugation with a classical π-system, i.e. the -N=C bond (dienes **4a-c**).

Analysing the NMR data for **4a** and **6,11,12** one can note the significant π-donating influence of the $-N{=}C(NMe_2)_2$ moiety.

$(Me_3Si)_2C{=}P{-}NMe_2$	$(Me_3Si)_2C^1{=}P{-}N^1{=}C^2(NMe_2)_2$		$Ph{-}N^1{=}C(NMe_2)_2$
11	4a		12
δP=330 ppm.	δP=338 ppm.	δN^1= -151 ppm.	δN^1=-173 ppm.
δC=125.4 ppm.	δC^1=144.4 ppm.	δC^2= 161.4 ppm.	δC=159.1 ppm.
$^1J_{CP}$ = 77 Hz	$^1J_{C1P}$=71 Hz	$^1J_{PN}$=81 Hz	$^1J_{CP1}$=83 Hz

Successive replacement of the dimethylamino groups in **4a** with less donating phenyl substituents (transition to dienes **4d** and then to **4e**) is accompanied by appreciable deshielding of carbon C^1.

$(Me_3Si)_2C^1{=}P{-}N{=}C^2(NMe)Ph$		$(Me_3Si)_2C^1{=}P{-}N{=}C^2Ph_2$	
	4d	4e	
δP=357 ppm.	δC^2= 165.7 ppm.	δP=323 ppm.	δC^2= 170.5 ppm.
δC^1=161.5 ppm.	$^1J_{C1P}$= 72 Hz	δC^1=159.5 ppm.	$^1J_{C1P}$= 74 Hz

The X-ray structure analysis of the compound **4d** shows no shortening of the P-N bond (1.683 Å). This seems to result from both mutual repulsing of sterically bulky substituents in the compound **4d** and the P-N bond twist (the torsional angle

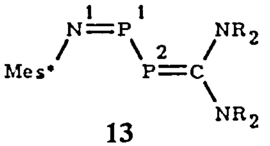
C^1PNC^2=155.3°). A value for the C =P bond length experimentally obtained (1.668 Å) is within the limits of the values typical of phosphaalkenes (1) (1.64-1.67 Å). But the analysis of *ab initio* calculation data for some model compounds makes it possible to conclude that along with the bond lengthening (weakening) by means of the conjugation effects, its shortening (strengthening) occurs due to inductive withdrawing properties and the group electronegativity of π-donating substituents, in particular.

This conclusion is also confirmed by the data on the barrier of hindered rotation around the multiple C=P and C=N bonds in dienes 3,4 and 5. One can observe free rotation of this moiety (Si_2C=P) around the P=C bond in the NMR time scale in diene 4b only; whereas for other compounds the barrier values exceed 113 KJ/mole. Our research shows the π-donating ability of the substituents D^1 and D^2 to be considerably lower than that of dialkylamino groups and, at the same time, they are also characterized by σ-withdrawing properties, which, on the contrary, favor the bond shortening.

Table.1. Barriers of Hindered Rotation Around P=C and N=C Bonds ($\Delta G^{\neq}_{303K}$) in Compounds of Interest, kJ/mol.

Compound	Chemical formula	$(Me3Si)_2C$=P- (A^1)	P=$C(NR_2)_2$ (D^1)	N=$C(NR_2)_2$ (D^2)
3a	$(Me_3Si)_2C=P-P=C(NMe_2)_2$	>113	<40	-
4a	$(Me_3Si)_2C=P-N=C(NMe_2)_2$	>113	-	<40
4b	$(Me_3Si)_2C=P-N=C(NEt_2)_2$	112	-	<40
5a	$(Me_2N)_2C=P-P=C(NMe_2)_2$	-	68	-

It was of interest to study the possibility of realization of the π,π-conjugation in the diene systems (13-15).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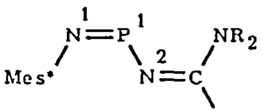
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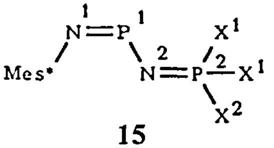
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13,14 a $R^1=R^2$=Me; b $R^1=R^2$=Et; c R^1=Me, R^2=Et; **15** a $X^1=X^2$=NMe2; b $X^1=X^2$=Ph; c X^1= Bu^t, X^2=Ph

A characteristic feature of phosphabutadienes **13** is a large P-P coupling value (Jpp=472 Hz for **13a**), which exceeds even the values of 396-403 Hz obtained for compounds 3a-c and is close to the values typical of diphosphenes (550-650 Hz). This can be explained by the higher polarity of the P-P bond, which is confirmed by the results of *ab initio* calculations performed for the model compounds. The X-ray analysis data showed that the P-P bond in compound **13a** (2.133 Å) is even shorter than in phosphabutadiene **3b** (2.155 Å) that is likely due to its larger polarity. The Mes* moiety is turned out relative to the plane of the P=N π-system by the angle 89.1°. Both Me_2N-C bonds are shortened (1.340 and 1.347 Å) and the P=C bond is lengthened (1.809 Å). Some P-P bond twisting (torsional angle NPPC=176.7°) does not exclude the conjugation between the N=P and P =C π-systems.

The replacement of the phosphorus atom with nitrogen going to dienes **14a**, is accompanied by the shielding of the ^{31}P (δP=204 ppm) and $^{15}N^1$ (δN= -102 ppm)] nuclei. These chemical shift values obtained can be attributed to those in compound Mes*-N=P-$N(Me)_2$ (**16**) wherein the n,π-conjugation between a lone electron pair of the nitrogen atom and the N=P-system is observed. Thus, the π-systems in dienes **13,14** are also capable of conjugation provided the molecule is coplanar enough.

16	**15a**		**17**
δP^1= 203 ppm.	δP^1= 141 ppm.	δP^2= 16 ppm.	δP= 40 ppm.
δN^1= -119 ppm.	δN^1= -90 ppm.	δN^2= -224 ppm.	δN^2= -348 ppm.
$^1J_{PN^1}$=91 Hz	$^1J_{P^1N^1}$= 108 Hz	$^1J_{P^2N^2}$= 8 Hz	$^1J_{PN^2}$= 30 Hz
δN^2= -257 ppm	$^1J_{P^1N^2}$= 98 Hz		
$^1J_{PN^2}$= 103 Hz			

As follows from the X-ray structure analysis of the compound **15b** containing both the three- and penta-valent phosphorus atoms, the central $CN^1P^1N^2P^2$ group is practically planar. The P-N bond (1.597 Å) is shortened, as compared to the interval (1.65-1.70 Å), typical of the single phosphorus-nitrogen bond. The double P =N bond is essentially lengthened. An unusual increase in the valence angle $P^1N^2P^2$ (159.7°) seems to be due to the fact that the molecule **15b** is sterically crowded. Analysis of the ^{15}N and ^{31}P NMR data obtained shows an essential π-donating effect of -N=$P(NMe_2)_3$ substituent. Taking into account a semipolar character of the N^2=P^2 bond, as well as the absence of the appreciable changes in the shielding of the P^2 nuclei, one could assume that such a drastical change in δN on going from HN=$P(NMe_2)_3$ (**17**) to phosphabutadiene **15a** is due to the conjugation of the electron pair, which forms the π-bond and is mainly localized along the p_z-orbital of the nitrogen atom, with the N=P bond. On its action the above conjugation is similar to the n,π-conjugation of a lone electron pair of the nitrogen atom of the dimethylamino group in the compound **16**.

Thus, the NMR spectroscopy and quantum chemistry investigation of phosphabutadienes (**3,4,5,13,14**, and **15**) containing the two-coordinate phosphorus atom, prove the significant role of the conjugation effects in their stabilization.