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Conjugation in Phosphabutadienes: *Ab initio* Investigation and NMR Spectral Manifestation: II.[1] Magnetic Shielding in Iminophosphines and Heterobutadienes Derived from Them

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Abstract — The conjugation effects in iminophosphines $H_3C–N=P–R$ (R = H, Hlg, OH, NH_2, PH_2, SiH_3, SH) and heterobutadienes $H_3C–N=P–X=CY_2$ (X = N, P; Y = NH_2, H) and their manifestations in NMR spectra are analyzed by RHF and MP2 calculations using the 6-31+G and 6-311+G basis sets with different numbers of polarization functions. The contribution of π-mesomeric interactions to the electronic structure of these compounds is estimated from the theoretical and experimental structural parameters, calculated natural atomic charges and bond indices, surfaces of rotational coordinates of the potential energy, and energy balances of isodesmic reactions, and also from the experimental and theoretically calculated (GIAO) ^{15}N and ^{31}P NMR chemical shifts. The configuration of model heterobutadienes relative to the P=N double bond and the *trans* conformation of the N=P–X=C fragment, suggested by the calculation results, are consistent with the structural data for the compounds Mes*–N=P–X=$C(NR_2)_2$ (X = N, P; R = Alk). The character of π-mesomeric interactions in the examined series of iminophosphines and butadienes derived from them is discussed. The conjugation effects influence the stability of phosphabutadienes insignificantly.

INTRODUCTION

Despite the fact that the chemical properties [2] and spectral characteristics [3–10] of iminophosphines R–N=P–X, as well as various aspects of their electronic structure [11–13], have been studied fairly comprehensively, these compounds are still of interest for theoretical chemists. Because of the tendency of iminophosphines to form dimers and polymers, they are difficultly accessible and can be stabilized only upon introduction of bulky substituents. It has been shown also that iminophosphines can be additionally stabilized by electronic interactions, e.g., p,π conjugation in the X–P=N bond system. These interactions are specifically responsible for the fact that some compounds of the series Mes*–N=P–X [X is an electonegative substituent, e.g., F, Cl, Br, OR, NR_2; Mes* is 2,4,6-tri(*tert*-butyl)phenyl, or supermesityl] exist in the crystalline state in the form of sterically unfavorable *Z* isomers [2]. The inductive and mesomeric effects of substituents X in model iminophosphines X–P=NH were repeatedly studied by theoretical methods using various approximation levels [11–13]. We have shown previously [1] for isostructural phosphaalkenes $R_2C=P–X$ that the sp^2-hybridized carbon atom of the C=P bond is very sensitive to the mesomeric effects of substituent X. However, as common π-donor substituents (e.g., NR_2, OR) are simultaneously σ acceptors, it was difficult to estimate the contribution of each effect. In this connection, more complex substitents such as N=$C(NR_2)_2$ and P=$C(NR_2)_2$, characterized by very high π-donor power, deserve particular attention [1, 14]. By analogy with "superacceptors" studied in detail in [15], such groups could be termed "superdonors." Their high donor power is apparently due to the increased stability of the amidinium residue $[C(NR_2)_2]^+$ [16] and predominant concentration of the π charge on the N (or P) atom. Another important feature of the P=$C(NR_2)_2$ substituent is weakness of its σ-acceptor properties due to low electronegativity of the P and C atoms. Despite the fact that butadiene structures **I**–**IV** with such "superdonor" groups are known for a relatively long time [17, 18], the role of π-electron delocalization in these formal analogs of push-pull 1,3-butadiene derivatives is still unclear. Previously [1] we revealed noticeable stabilization of butadienes **III** and **IV** due to conjugation. Similar conclusion for **I** and **II** follows from the NMR data and comparison of these compounds with other iminophosphines X–P=NMes*. Compounds of this series

[1] For communication I, see [1].

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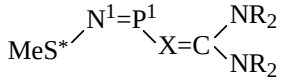
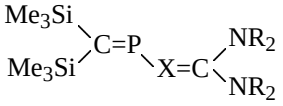
are characterized by a wide range of ^{31}P and ^{15}N chemical shifts. Abnormally low-field values of δ_N and δ_P in this series are due to high paramagnetic contribution to the shielding constant, made by electronic transitions from highest occupied to low-lying unoccupied molecular orbitals of different symmetry, initiated by rotating magnetic field [6]. Attempts to describe quantitatively the NMR chemical shifts for model compounds of this series on the Hartree–Fock level [6, 10] led to significant disagreement with the experiment. Recently [10] we performed quantum-chemical studies of model iminophosphines (*Z*/*E*)-R_2N–P=N–Ph (R = Me, Et, *i*-Pr, *t*-Bu), structurally related to the experimentally studied series X–P=N–Mes*. Despite the fact that the calculations qualitatively reproduced the trend of variation of the shielding of the phosphorus nuclei in going from *Z* to *E* isomers, the calculated δ_P values significantly differed from the experimental data. It is also known that the DFT approximation [19] in such critical situations does not improve the agreement with the experiment, whereas consideration of the electron correlation (MP2 approximation) gives better results [19, 20].



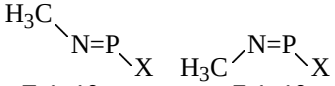
I, II



III, IV

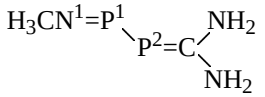
X = P (**I, III**), N (**II, IV**).

In this work we made a quantum-chemical study of model iminophosphines **1**–**10** and butadienes **11**–**14** containing a P=N double bond. It was the most interesting to determine the degree of delocalization of π electrons in iminophosphines and related phosphabutadienes and to elucidate how the delocalization affects the stability of specific conformations and the NMR parameters. The choice of *N*-methyl-substituted derivatives as model structures was due to their closer analogy with the experimentally studied series Mes*–N=P–X, as compared to unsubstituted iminophosphines H–N=P–X studied previously [6, 11, 13]. By using the higher level of approximation, MP2-GIAO [19, 20], in calculations of the NMR shielding, we tried to attain satisfactory quantitative agreement of the calculated chemical shifts (δ) with the experiment.

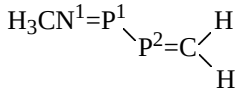


E-**1**–**10** *Z*-**1**–**10**

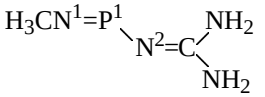
X = H (**1**), CH_3 (**2**), F (**3**), Cl (**4**), Br (**5**), OH (**6**), NH_2 (**7**), PH_2 (**8**), SiH_3 (**9**), SH (**10**).



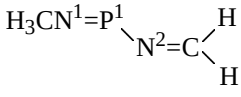
E,*Z*-**11**



E,*Z*-**12**



E,*Z*-**13**



E,*Z*-**14**

THEORETICAL AND EXPERIMENTAL METHODS

All quantum-chemcial calculations were performed with the GAUSSIAN 94 [21] and GAUSSIAN 98 [22] program packages. The molecular geometries were optimized on the RHF/6-31+G(d,p) and MP2(fc)/6-31+G(d,p) [23] levels (six *d* functions for heavy atoms). The geometric parameters of heterobutadienes **11**–**14** corresponding to the *trans* and *cis* conformations were optimized without symmetry restrictions; they correspond to the local energy minima, which is confirmed by the frequency analysis in the analytical approximation. The structures of the C_s symmetry corresponded to the local energy minima for all the iminophosphines except **7**, **9**, and *Z*-**10** (for which the C_1 structures corresponded to the local minimum), and also except *EN*-**7** and *ZN*-**7** (transition states; each structure has one imaginary vibration frequency). The optimized geometric parameters were subsequently used to calculated magnetic shielding using the GIAO procedure [24, 25] and GAUSSIAN program packages in the RHF/6-311+G(2d,p) and (for **1**–**10**) MP2/6-311+(2d,p) approximations {standard Pople basis set 6-311G [26] for hydrogen elements of the first period; McLean–Chandler (12*s*, 9*p*) basis set [27] for elements of the second period}. To compare with the experimental data, the calculated σ_{iso} values were converted to the δ scale. For this purpose, using the RHF/6-311+G(2d,p)//6-31G+(d,p) approximation, we optimized the geometry and calculated the magnetic shielding for PH_3 [σ_{iso}(P) 579.4 ppm] and $Si(CH_3)_4$ [σ_{iso}(C) 194.3 ppm]. The δ_P scale was transformed relative to the reference, 85% H_3PO_4 (δ_P 0 ppm), using the value of $\delta_P(PH_3)$ –240 ppm [28]. The ^{15}N shielding constants were converted to the δ scale using the conversion parameters for CH_3NO_2 [δ_N 0, σ_{iso}(N) –130 ppm] [29]. To refine the numerical values of the NMR chemical shifts, the diene structures [(*Z*)-*trans*-**11**, (*E*)-*trans*-**12**, (*Z*)-*trans*-**13**, (*Z*)-*trans*-**14**] were refined in the MP2(fc)/6-31+G(d) approximation. The vibration frequencies for the refined structures were not calculated. For the above conformations, we calculated the magnetic shielding using the GIAO

Table 1. Total and relative energies of *E* and *Z* isomers of **1**–**10**

No.	*E*[MP2(fc)/ 6-31+G(d,p)], au	*ZPE* [MP2(fc)/6-31+G(d,p)], au	*E*[MP2(full)/ 6-311+G(2d,p)], au	*E* + *ZPE*, au	Δ*E*, kcal mol^{-1}
E-**1**	–435.755506	0.052175	–436.023431	–435.971256	
Z-**1**	–435.755586	0.051766	–436.024432	–435.972666	–0.88
E-**2**	–474.953506	0.081655	–475.260948	–475.179293	
Z-**2**	–474.948816	0.081408	–475.257534	–475.176126	+1.99
E-**3**	–534.836593	0.046108	–535.205486	–535.159378	
Z-**3**	–534.846339	0.046310	–535.214008	–535.167698	–5.22
E-**4**	–894.817277	0.045144	–895.205092	–895.159948	
Z-**4**	–894.828495	0.045348	–895.218142	–895.172794	–8.06
E-**5**	–3005.226935	0.044717	–3008.380283	–3008.335566	
Z-**5**	–3005.241294	0.045127	–3008.395289	–3008.350162	–9.16
E-**6**	–510.851629	0.058300	–511.196231	–511.137931	
Z-**6**	–510.851290	0.058049	–511.195708	–511.137659	+0.17
E-**7**	–491.002493	0.070000	–491.324551	–491.254551	
Z-**7**	–491.001384	0.070056	–491.323710	–491.253654	+0.56
EN-**7**	–490.982032	0.069721	–491.304342	–491.234621	
ZN-**7**	–490.986175	0.069771	–491.308234	–491.238463	–2.41
E-**8**	–777.175733	0.062164	–777.622409	–777.560245	
Z-**8**	–777.174857	0.061968	–777.623711	–777.561743	–0.94
E-**9**	–725.935185	0.069850	–726.371795	–726.301945	
Z-**9**	–725.930067	0.069717	–726.368514	–726.298797	+1.98
E-**10**	–833.420622	0.053941	–833.872427	–833.818486	
Z-**10**	–833.424653	0.053913	–833.877163	–833.823250	–2.99

procedure from the GAUSSIAN 98 package in the MP2/6-311+G(d,p) approximation [because of limited computation facilities, the magnetic shielding for structure (*Z*)-*trans*-**11** was calculated on the MP2/6-311G(d,p) level]. The absolute shielding was converted to the δ scale using the experimental σ_{iso} values for $Si(CH_3)_4$ {σ_{iso}(C) 188.1 ppm [30]}, CH_3NO_2 {σ_{iso}(N) –130 ppm [29]} and 85% H_3PO_4 {σ_{iso}(P) 328.4 ppm [28, 31]; δ 0 ppm in all the cases}. Following Chesnut's recommendations [20], we corrected the chemical shifts obtained in the MP2 approximation using the formula $\delta_X(corr) = \delta_X(MP2) + 1/3[\delta_X(HF) - \delta_X(MP2)]$. The atomic charges and bond indices were calculated using the NBO procedure [32–35]. The energy balances of isodesmic reactions were obtained from MP2(fc)/6-31+G(d,p) energy calculations based on geometries optimized on the RHF/6-31+G(d,p) level. For corrections, we used zero-point vibration energies taken from the frequency analysis on the RHF/6-31+G(d,p) level with a coefficient of 0.9. To construct the surfaces of the rotational coordinates of the potential energy, we used the energies obtained in the MP2(fc)/6-31+G(d,p)//RHF/6-31+G(d,p) approximation without correction.

The experimental NMR data were taken from the literature [2, 4, 7, 8, 17, 18, 36–38]. The larger δ values (both calculated and experimental) correspond to lower fields (deshielding).

IMINOPHOSPHINES Me–N=P–X

The total and relative energies of the *E* and *Z* isomers are listed in Table 1 [all the structural parameters and other calculated data for the series under consideration are available (Tables 2, 3) as supplementary material and are not given here]. In full agreement with the experiment [2], the *Z* configuration is essentially preferable for *P*-halo-substituted iminophosphines **3**–**5** and thiol derivative **10**, and the *E* configuration, for compounds **2** and **8**. Silyl derivative **9** has not yet been prepared, and its structure is unknown. Aminoiminophosphines (*Z*)-**7** and (*E*)-**7** have approximately equal total energies. This is consistent with the fact that the compounds Mes*–N=P–NR_2 exist in both configurations depending on the bulkiness of R [27, 36]. In turn, planar iminophosphines (*E*)-**7** and (*Z*)-**7** are characterized by the lower total energy than their nonconjugated conformers (*EN*)-**7** and (*ZN*)-**7** (with the pyramidal NH_2 groups). According to published

Table 2. Geometries of **1**–**10** calculated on the RHF/6-31+G(d,p) level

No.	Bond length, Å			Bond angle, deg		CNPX torsion angle, deg
	P=N	P–X	C–N	PNX	CNP	
E-**1**	1.554	1.413	1.445	99.8	121.4	180.0
E-**2**	1.549	1.844	1.445	103.3	122.1	180.0
E-**3**	1.514	1.591	1.444	104.9	129.3	180.0
E-**4**	1.524	2.067	1.448	104.9	125.8	180.0
E-**5**	1.524	2.238	1.448	104.8	125.9	180.0
E-**6**	1.530	1.609	1.446	105.5	125.6	180.0
E-**7**	1.536	1.655	1.445	105.2	123.1	180.0
EN-**7**	1.542	1.709	1.446	105.1	121.8	180.0
E-**8**	1.549	2.217	1.447	101.7	122.3	–177.6
E-**9**	1.563	2.295	1.445	98.3	121.7	180.0
E-**10**	1.538	2.109	1.449	105.0	123.0	180.0
Z-**1**	1.542	1.437	1.438	103.5	129.0	0.0
Z-**2**	1.539	1.867	1.438	109.5	132.4	0.0
Z-**3**	1.500	1.617	1.438	109.7	140.0	0.0
Z-**4**	1.501	2.129	1.436	109.5	141.3	0.0
Z-**5**	1.500	2.302	1.435	109.2	141.3	0.0
Z-**6**	1.511	1.638	1.441	109.0	135.4	0.0
Z-**7**	1.523	1.677	1.436	111.8	135.4	0.0
ZN-**7**	1.530	1.736	1.440	114.8	132.6	0.0
Z-**8**	1.533	2.261	1.436	109.1	134.1	1.9
Z-**9**	1.547	2.338	1.435	108.8	132.2	0.0
Z-**10**	1.516	2.154	1.437	108.9	137.0	0.0

Table 3. Geometries of **1**–**10** calculated on the MP2/6-31+G(d,p) level

No.	Bond length, Å			Bond angle, deg		CNPX torsion angle, deg
	P=N	P–X	C–N	PNX	CNP	
E-**1**	1.610	1.416	1.463	97.7	116.5	180.0
E-**2**	1.607	1.840	1.465	101.1	117.5	180.0
E-**3**	1.562	1.633	1.461	103.7	124.2	180.0
E-**4**	1.580	2.059	1.467	103.6	119.1	180.0
E-**5**	1.581	2.238	1.468	103.4	118.9	180.0
E-**6**	1.581	1.647	1.463	103.8	121.6	180.0
E-**7**	1.590	1.676	1.464	102.9	118.4	178.7
EN-**7**	1.595	1.729	1.466	102.7	117.1	180.0
E-**8**	1.608	2.210	1.465	99.2	117.5	176.7
E-**9**	1.623	2.281	1.463	94.4	117.5	180.0
E-**10**	1.598	2.101	1.467	102.8	117.8	180.0
Z-**1**	1.592	1.444	1.453	102.5	124.1	0.0
Z-**2**	1.592	1.869	1.454	108.9	127.4	0.0
Z-**3**	1.540	1.672	1.449	111.0	138.7	0.0
Z-**4**	1.548	2.133	1.448	110.5	136.5	0.0
Z-**5**	1.547	2.318	1.447	109.6	136.2	0.0
Z-**6**	1.555	1.687	1.441	108.5	131.5	0.0
Z-**7**	1.575	1.702	1.455	109.9	126.7	0.0
ZN-**7**	1.578	1.761	1.455	108.0	128.2	0.0
Z-**8**	1.587	2.257	1.453	108.3	127.5	1.9
Z-**9**	1.601	2.332	1.451	108.3	127.5	0.0
Z-**10**	1.570	2.159	1.450	112.2	131.6	0.0

data, compounds Mes*–N=P–OR exist exclusively in the *Z* configuration. However, when estimating ΔE for (*E*)-**6**, we used a more favorable structure corresponding to the *cis* orientation of the OR group, untypical of real molecules; this, apparently, resulted in approximately equal energies of both isomers. The *Z*,*E* isomerism in the series Mes*–N=P–X' strongly affects δ_P and δ_N: Both P and N nuclei are more shielded in the *Z* isomers than in the *E* isomers [7, 8, 10, 38]. We have shown recently for a series of aminoiminophosphines that the δ_P values measured in solution can significantly differ from those measured in a solid. This is due to fast, on the NMR time scale, inversion of the imine nitrogen atom, so that actually we can only speak of prevailing configuration of iminophosphines. The same fact may also be responsible, to some extent, for deviations of the theoretical δ_P and δ_N values (Table 4) from the experiment. Nevertheless, even the values obtained on the Hartree–Fock level show a good correlation with the experimental ^{31}P and ^{15}N NMR chemical shifts (Fig. 1). The values for the structures with the alternative configuration lie essentially apart from the correlation straight line. However, both δ_P and δ_N values are still strongly overestimated because of the neglect of electron correlation effects in calculations of the magnetic shielding. This aspect, as well as orientation of the principal axes of the magnetization tensors and the absolute values of the tensor components around these axes, were considered in detail previously [6, 10] and will not be discussed here.

Let us discuss the correlation between the π-donor power of the substituent at the P atom and the magnetic shielding of the N nuclei in the series **1**–**10**. In going from aminoiminophosphines (*E*)-**7** and (*Z*)-**7** to the corresponding nonconjugated conformations, (*EN*)-**7** and (*ZN*)-**7**, the resonance of the N=P nitrogen nuclei is shifted downfield (Table 4). However, the quantitative correlation is considerably more complex. The δ_N values for the two conformations well correlate with the total natural charges on the corresponding nitrogen atoms, q_N (Fig. 2), but form two separate correlations for molecules in which the P atoms are bonded to substituents X with atoms of the lower (H, C, N, O, F) and higher (Si, P, S, Cl, Br) periods.

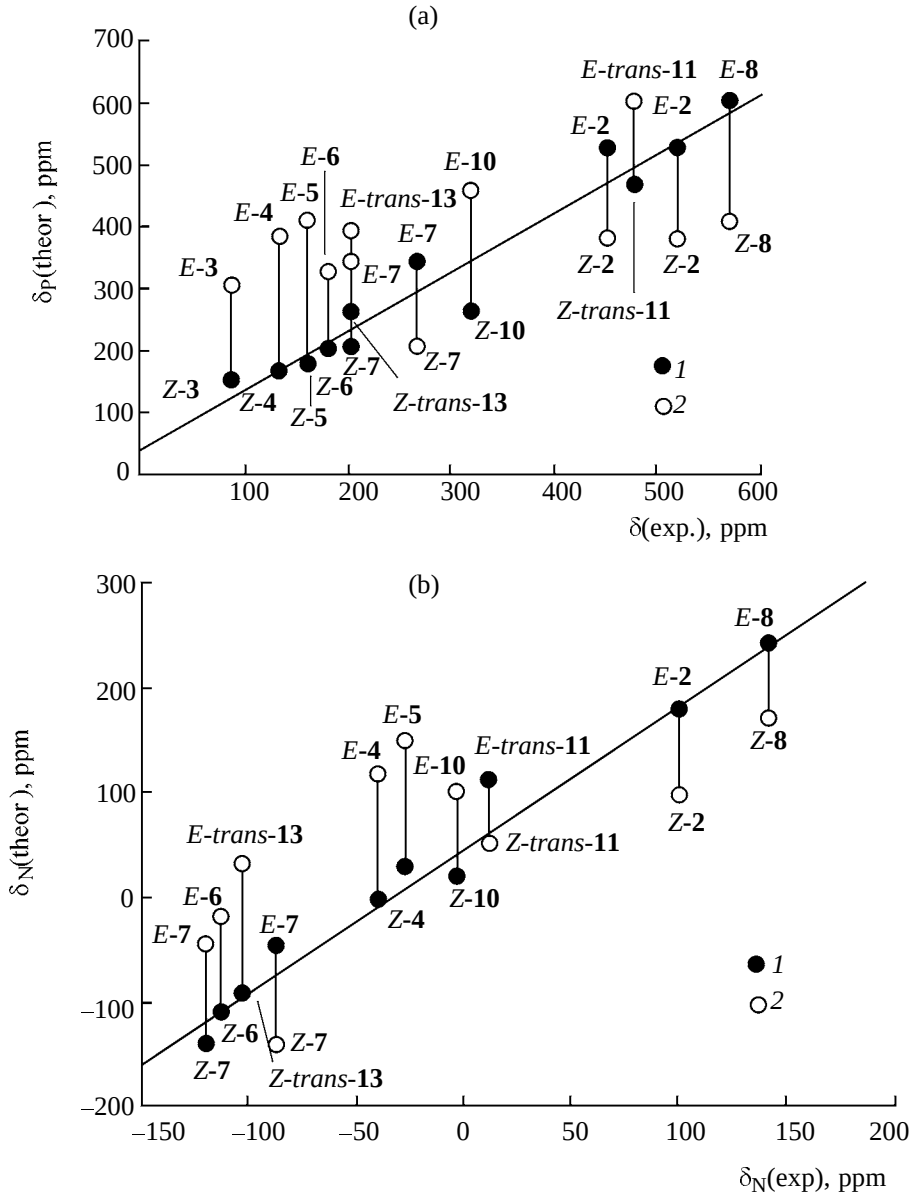


Fig. 1. Correlation of the (a) δ_P(theor) and (b) δ_N(theor) values calculated in the Hartree–Fock approximation with the corresponding experimental values obtained for the compounds Mes*–N=P–X [7, 8]. Compound, substituent X in real molecule, δ_P(exp), δ_N(exp): **2**, *t*-Bu, 452, 100; **2**, Mes*, 520, –; **3**, F, 87, –; **4**, Cl, 134, –40; **5**, Br, 162, –27; **6**, OMe, 180, –113; **7**, NMe_2, 203, –119; **7**, $N(Pr\text{-}i)_2$, 268, –87; **8**, $P(t\text{-}Bu)_2$, 541, 141; **10**, SBu-*t*, 320, 3. (*1*) Configuration coinciding with the structure of the real molecule and (*2*) alternative configuration.

This fact is apparently due to different polarizability of the electronic shells of the corresponding atoms. Furthermore, the correlation dependences δ_P–q_P for the *E* and *Z* isomers (Fig. 3) are inverse, i.e., lower values of δ_P correspond to lower electron densities (or higher positive charges) on the P atoms. On the whole, when correlating the calculated total charges with the corresponding chemical shifts, we should take into account the strong scepticism expressed today in connection with such attempts to interpret qualitatively the magnetic shielding values. Of course, a certain correlation between the total charges and magnetic shielding does exist in the series under consideration, but this correlation is very complex and

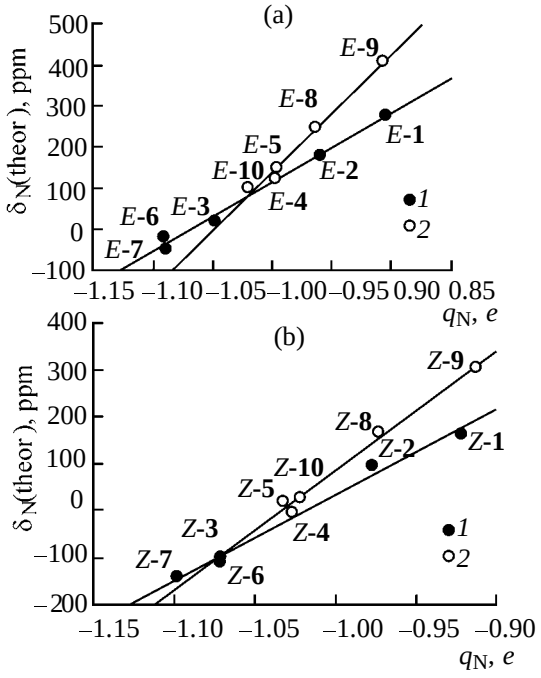


Fig. 2. Correlations of the theoretically calculated δ_N(theor) values for (a) *trans* and (b) *cis* isomers of iminophosphines **1**–**10** with the total charge on the N atom, q_N: (*1*) atoms of the first period and H; (*2*) atoms of the second period and Br.

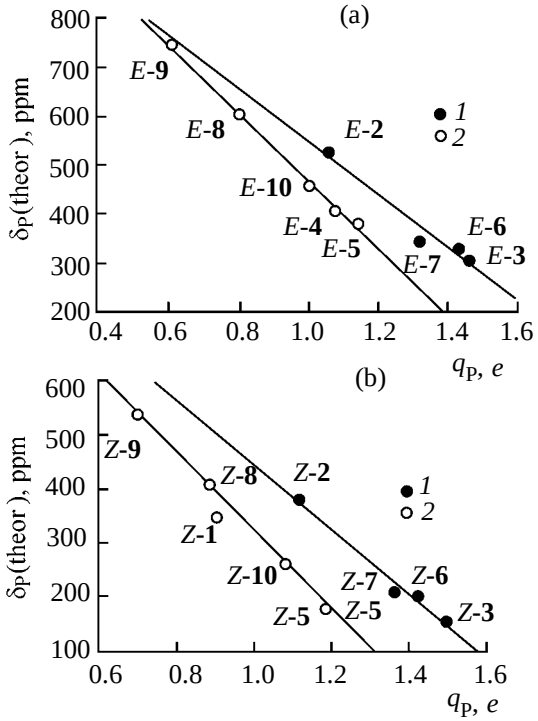


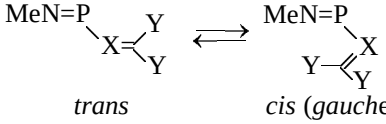
Fig. 3. Correlations of the theoretically calculated δ_P(theor) values for (a) *trans* and (b) *cis* isomers of iminophosphines **1**–**10** with the total charge on the P atom, q_P: (*1*) atoms of the first period and H; (*2*) atoms of the second period and Br.

indirect. For example, our studies of substituted phosphaalkenes $R_2C{=}P{-}X$ [39] showed that electronegative substituents X, decreasing the total charge on the P atom, simultaneously increase the energy gap between the highest occupied and lowest unoccupied molecular orbitals. As a result, the mean excitation energy increases, the paramagnetic contribution decreases, and ultimately the phosphorus nuclei become shielded rather than deshielded.

It seemed interesting to find to what extent consideration of the electron correlation (MP2 approximation) in calculations of the NMR shielding [19, 20] will improve the agreement with the experiment. To our knowledge, no such systematic studies have been performed for low-coordinate P(III) compounds. The structural parameters of **1**–**10** were refined in the MP2/6-31+G* approximation and were used subsequently for calculating the magnetic shielding. The calculation results are listed in Table 5. As noted previously [20], the MP2 method underestimates δ. The simplest way to take into account this error is empirical correction of the magnetic shielding (see Theoretical and Experimental Methods section). In Table 5, these values are presented in the δ_P(corr) and δ_N(corr) columns. Comparison with the available experimental data (Fig. 4) shows that the correlation points satisfactorily fall on a straight line $y = x$, i.e., the calculation adequately reproduces the experimental δ values for the iminophosphines. This approach allows not only determination of the *Z* or *E* configuration of real compounds from the experimental δ values, but also fairly accurate prediction of the magnetic shielding of nuclei in low-coordinate P(III) compounds that have not yet been studied experimentally.

PHOSPHABUTADIENES

Compounds **I** and **II** can be characterized, along with the *Z* or *E* configuration relative to the P=N bond, also by different mutual orientation of the formally double bonds: *trans* or *cis* (*gauche*).



trans *cis* (*gauche*)

Various possible π-mesomeric interactions in these

Table 4. Magnetic shielding (σ_{iso}) of nuclei, shielding anisotropy ($\Delta\sigma$), and NMR chemical shifts (δ) for **1**–**10** (ppm), calculated on the RHF/6-311+G(d,p)//RHF/6-31+G(d,p) level

No.	Shielding of ^{31}P nuclei			Shielding of ^{15}N nuclei		
	σ_{iso}	$\Delta\sigma$	δ_P	σ_{iso}	$\Delta\sigma$	δ_N
E-**1**	–180.0	664.3	519.4	–405.0	1102.5	275.0
E-**2**	–187.3	670.6	526.7	–309.9	889.9	179.9
E-**3**	35.8	739.3	303.6	–146.9	555.7	16.9
E-**4**	–42.5	718.3	381.9	–249.6	753.3	119.6
E-**5**	–67.0	705.1	406.5	–278.9	806.2	148.9
E-**6**	12.9	558.3	326.5	–109.2	507.6	–20.8
E-**7**	–2.7	410.9	342.1	–81.6	524.3	–48.4
EN-**7**	–96.5	573.0	435.9	–305.0	822.7	175.0
E-**8**	–262.2	747.3	601.6	–372.7	1033.8	242.7
E-**9**	–408.1	1015.1	747.5	–538.4	1316.6	408.4
E-**10**	–116.7	472.0	456.1	–228.9	753.8	98.9
Z-**1**	–6.6	410.8	346.0	–293.8	905.9	163.8
Z-**2**	–39.8	499.8	379.2	–227.3	802.7	97.3
Z-**3**	188.2	614.5	151.2	–27.9	342.9	–102.1
Z-**4**	176.3	613.1	163.1	–126.9	525.4	–3.1
Z-**5**	164.3	605.2	175.1	–159.8	576.7	29.8
Z-**6**	140.6	418.1	198.8	–19.2	381.6	–110.8
Z-**7**	133.4	238.3	206.0	11.5	404.5	–141.3
ZN-**7**	66.3	325.7	273.1	–180.9	651.7	50.9
Z-**8**	–68.0	510.2	407.5	–296.1	913.6	166.1
Z-**9**	–196.6	721.2	536.0	–434.0	1148.1	304.0
Z-**10**	78.2	249.4	261.2	–149.7	650.3	19.7

Table 5. Calculated [MP2/6-311+G(2d,p)//MP2/6-31+G(d,p)] NMR chemical shifts (δ, ppm) for **1**–**10**

No.	Shielding of ^{31}P nuclei			Shielding of ^{15}N nuclei		
	δ_P (MP2)	δ_P (RHF)	δ_P (corr)[a]	δ_N (MP2)	δ_N (RHF)	δ_N (corr)
E-**1**	412.7	585.4	470.3	66.7	358.2	163.9
E-**2**	437.6	595.4	490.2	40.9	257.6	113.1
E-**3**	271.9	371.5	305.1	–81.0	95.2	–22.3
E-**4**	337.4	462.2	379.0	–14.4	201.3	57.5
E-**5**	369.5	492.5	410.5	1.3	232.8	78.5
E-**6**	282.9	390.7	318.8	–90.7	46.4	–45.0
E-**7**	284.0	397.2	321.7	–102.5	10.1	–65.0
EN-**7**	290.3	508.4	363.0	27.0	259.6	104.5
E-**8**	496.8	680.1	557.9	60.0	321.2	147.1
E-**9**	582.8	821.0	662.2	138.1	494.6	256.9
E-**10**	381.8	532.8	432.1	–18.7	168.2	43.6
Z-**1**	337.0	410.9	361.6	–295.5	229.2	–120.6
Z-**2**	363.4	439.8	388.9	12.1	156.9	60.4
Z-**3**	138.0	174.6	150.2	–155.2	–58.7	–123.0
Z-**4**	176.4	215.1	189.3	–94.6	50.0	–46.4
Z-**5**	200.0	229.3	209.8	–78.8	87.1	–23.5
Z-**6**	194.7	240.6	210.0	–150.0	–55.4	–118.5
Z-**7**	183.2	247.3	204.6	–166.7	–97.3	–143.6
ZN-**7**	272.0	324.9	289.6	–31.8	114.1	16.8
Z-**8**	408.8	461.8	426.5	52.8	270.6	125.4
Z-**9**	498.1	604.9	533.7	111.5	368.0	197.0
Z-**10**	267.0	323.9	286.0	–69.0	77.0	–20.3

[a] $\delta_X(\text{corr}) = \delta_X(\text{MP2}) + 1/3[\delta_X(\text{HF}) - \delta_X(\text{MP2})]$.

phosphabutadienes can be represented in the form of a resonance model:

$$\underset{\mathbf{A}}{R\text{–}N{=}P\text{–}X{=}CY_2} \rightleftharpoons \underset{\mathbf{B}}{R\text{–}N^{(-)}\text{–}P{=}X\text{–}CY_2^{(+)}} \rightleftharpoons \underset{\mathbf{C}}{R\text{–}N{=}P\text{–}X^{(-)}\text{–}CY_2^{(+)}} \rightleftharpoons \underset{\mathbf{D}}{R\text{–}N^{(-)}\text{–}P{=}X^{(+)}{=}CY_2}.$$

The contributions of specific mesomeric structures should significantly affect the shielding of nuclei. Strong shielding of the ^{15}N nuclei in the P=N moiety of compounds **I** and **II** (Table 6) was explained previously [36] by significant contributiuon of polar structure **B**. This matter is discussed in the remaining part of our paper.

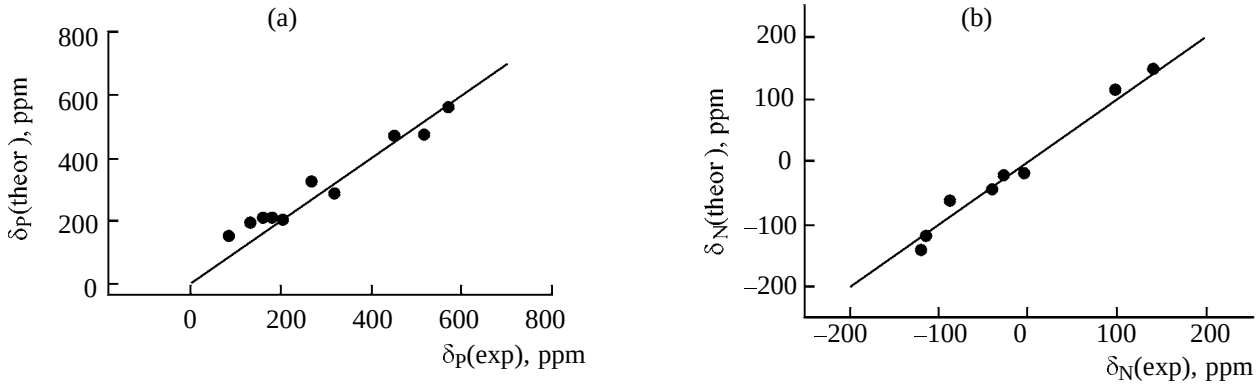


Fig. 4. Correlation of the theoretically calculated [MP2/6-311+G(2d,p), with empirical correction] values of (a) δ_P(corr) and (b) δ_N(corr) with the corresponding experimental values obtained for iminophosphines Mes*–N=P–X.

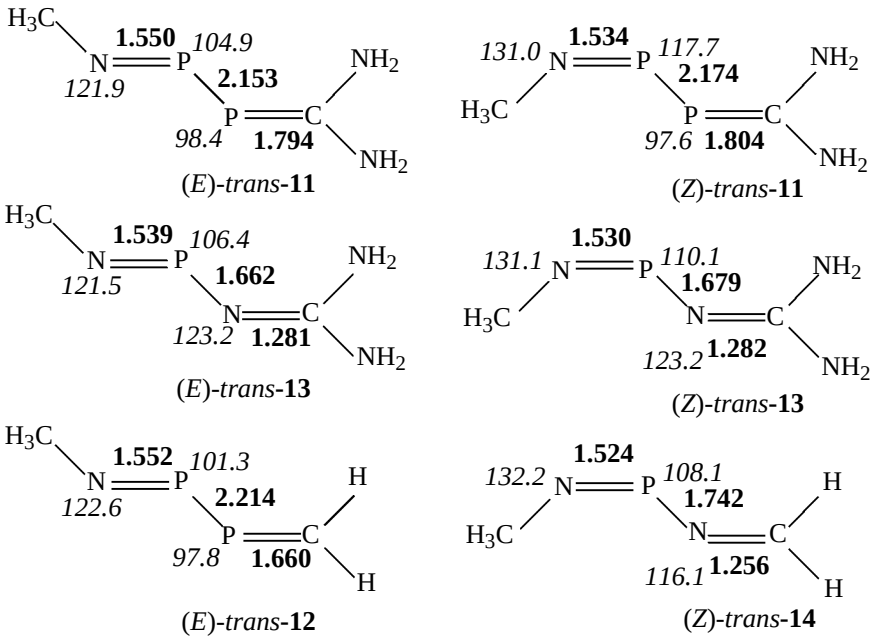


Fig. 5. Main geometric parameters of (*E*)-*trans*-**11**, (*Z*)-*trans*-**11**, (*E*)-*trans*-**13**, (*Z*)-*trans*-**13**, (*E*)-*trans*-**12**, and (*Z*)-*trans*-**14** (the bond lengths and bond angles are printed bold and italic, respectively).

The total energies and vibration corrections for model compounds **11** and **13** and for unsubstituted dienes **12** and **14**, with the structures optimized on the Hartree–Fock level, are listed in Table 7. For the *E* isomers of **11** and **13**, the *cis* (*gauche*) conformers appeared to be the global energy minima. It should be noted, however, that the (*E*)-*cis*-**11** and (*E*)-*cis*-**13** structures are additionally stabilized by the $N^1\cdots H$–NH hydrogen bond (the $N^1\cdots H$ interatomic distances are 1.828 and 1.984 Å, respectively). Such an interaction is untypical of *N*-alkyl derivatives **I** and **II**. The (*Z*)-*trans*-**11** conformation is by 7.22 kcal mol^{-1} less favorable than the (*E*)-*cis* form and, in turn, by only 0.92 kcal mol^{-1} more favorable than the (*E*)-*trans* structure. Thus, consideration of the calculated energies of the model structures is insufficient for determining the conformations of real compounds **I** and **II**.

The (*Z*)-*gauche* conformation ($\angle N^1P^1P^2C$ 36.3°) appeared to be a local minimum in the case of (*Z*)-**11** only. However, it has a higher energy than the corresponding *trans* structure (ΔE +3.87 kcal mol^{-1}). Both energy minima are separated by a transition state whose energy is by only 0.19 kcal mol^{-1} higher than that of the *gauche* structure. Hence, for **11**–**14**, the (*Z*)-*gauche* conformation can be eliminated from further consideration.

The geometries of (*E*)-*trans*-**11**, (*E*)-*trans*-**13**, (*Z*)-*trans*-**11**, (*E*)-*trans*-**12**, (*Z*)-*trans*-**13**, and (*Z*)-*trans*-**14** are given in Fig. 5. The main structural parameters for the four latter compounds, determined by optimization on the MP2(fc)/6-31+G* level, are also listed in Table 8. The P^1–P^2 (P–N^2) bonds in compounds **11** and **13** are clearly shorter than those in compounds **12** and **14**, respectively. On the other hand, the P^2=C^2 bond in **11** is appreciably elongated, suggesting delocalization of the lone electron pairs of the N atoms.

According to a single crystal X-ray diffraction study, compound **Ia** has the (*Z*)-*trans* structure [38, 41]. The P–P bond is appreciably shortened (2.133 Å), as well as the Me_2N–C bonds (1.340 and 1.347 Å), whereas the formally double P=CN_2 bond (1.809 Å) appeares to be even longer than that in the previously studied butadiene $(Me_3Si)_2C$=P–P=$C(NEt_2)_2$ (1.777 Å) [42]. The structure of model butadiene (*Z*)-*trans*-**11**, obtained in the MP2(fc) approximation (Table 8), differs somewhat from that determined by X-ray diffraction. In particular, the calculated P–P bond length is overestimated, and the P=CN_2 bond length, on the contrary, underestimated. The structure of hypothetical molecule (*Z*)-*trans*-**11** is essentially planar (torsion angles $\angle P^1P^2CN$ 3.9° and 180.0°, $\angle C^{Me}NP^1P^2$ 0°), whereas the sterically hindered real molecule of **Ia** is strongly twisted ($\angle P^1P^2CN$ 44.3° and –137.3°). In this case, the P=CN_2 virtually loses its double character with predominant localization of two lone electron pairs on the P atom (resonance form **C**). The contribution of polar structure **B** is determined by further transfer of the electron density from the P^2 atom to the N^1 atom due to p,π interaction. For quantitative description of the electron density distribution in the

Table 6. Experimental values of the NMR chemical shifts (δ, ppm) and coupling constants (*J*, Hz) in compounds **I** and **II**

Comp. no.	R	δ_{P^1}	δ_{N^1}	$^1J_{NP}$	$^1J_{P^1P^2}$ ($^1J_{P^1N^2}$)	δ_{P^2}	δ_{N^2}	δ_{C^2}	$^1J_{C^2P^2}$	References
Ia	Me	479.4	12.1	108	472	171.5	–	202.9	90	[17, 18]
Ib	Et	476.3	12.4	106	466	176.0	–	203.9	90	[17, 18]
IIa	Me	204.1	–102.4	106	108	–	–144.7	157.2	–	[17, 18]
IIb	*t*-Bu	178	–	–	–	–	–	185.2	–	[40]
IIc	Fluorenyl	124	–	–	–	–	–	169.3	–	[40]

Table 7. Total energies *E* at 0 K (au), vibration corrections at 0 K (*ZPE*, au), and relative energies (Δ*E*, kcal mol^{-1}) of **11**–**14**

No.	Conformation	*E*[RHF/6-31+G(d,p)]	*ZPE*(RHF)	*E*(MP2)	*E*(MP2) + 0.9*ZPE*(RHF)	Δ*E*
E-**11**	*trans*	–924.574270	0.112795	–925.587470	–925.485955	8.14
	cis	–924.587181	0.113714	–925.601273	–925.498930	0.00
	TS[a]	–924.562794	0.112583	–925.580977	–925.479632	12.11
Z-**11**	*trans*	–924.576022	0.112691	–925.580977	–925.487425	7.22
	gauche	–924.564774	0.113102	–925.583054	–925.481262	11.09
	TS	–924.563193	0.112875	–925.582534	–925.480947	11.28
E-**12**	*trans*	–814.475726	0.075217	–815.151452	–815.083757	0.00
	cis	–814.470292	0.075135	–815.146745	–815.079124	2.91
	TS	–814.468519	0.074919	–815.146147	–815.078720	3.16
Z-**12**	*trans*	–814.473569	0.075282	–815.150109	–815.082355	0.88
E-**13**	*trans*	–638.335466	0.117366	–639.401415	–639.295786	9.15
	gauche	–638.350790	0.117791	–639.416382	–639.310370	0.00
	TS	–638.333806	0.117087	–639.401281	–639.295903	9.08
Z-**13**	*trans*	–638.341221	0.117481	–639.407051	–639.301318	5.68
E-**14**	*trans*	–528.218122	0.079152	–528.942919	–528.871682	2.98
	gauche	–528.220929	0.079371	–528.946490	–528.875056	0.86
	TS	–528.217448	0.078921	–528.943369	–528.872340	2.56
Z-**14**	*trans*	–528.223346	0.079280	528.947775	528.876423	0.00

[a] Here and hereinafter, TS denotes transition state.

molecule, we analyzed the atomic charges and Wiberg bond indices in **11**–**14** (Fig. 6). The total charge on the N^1 atoms in **11** and **13** is appreciably larger as compared to **12** and **14**, respectively (in the same conformations). The increase in the charge on N^1 is accompanied by its decrease on $C(NH_2)_2$. The previously found charge transfer and decrease in the $P^1{=}N^1$ bond indices in the *trans* conformations of (*E*)-**11** and (*E*)-**13**, relative to (*E*)-**12** and (*E*)-**14**, at first glance, is consistent with the conjugated form **B**.

The optimized structures with the *trans* conformations are characterized by only slight deviations from planarity. Therefore, consideration of the π constituents of the total charges (Table 9) obtained for the planar molecules (C_s symmetry) is a good approximation. For example, comparison of the *trans* isomers of **12** and **11** shows that the π charge on P^1 changes insignificantly (by less than 0.04 *e*), and that on P^2 and N^1 noticeably increases (by ~0.60 and 0.09–0.10 *e*, respectively). Thus, the contribution of polar mesomeric structure **C** for *trans* isomers of model compounds (*E*,*Z*)-**11** is 5–6 times higher than the contribution of structure **B**. Similar but still less pronounced trends in variation of the π charges are also observed with planar forms of **13** and **14**. An increase in the π charge on the imine nitrogen atoms in going from iminophosphines (*E*)-**7** and (*Z*)-**7** to nonconjugated structures (*EN*)-**7** and (*ZN*)-**7** (Table 9) is 0.169 and 0.164 *e*, respectively. This increase is ~2 times more pronounced as compared to that determined for (*E*)-*trans*-**13** and (*E*)-*trans*-**14** relative to (*E*)-**14** and (*Z*)-**14** (0.076 and 0.073 *e*, respectively). The total decrease in the π charge on the amino groups in **13** is ~0.10 *e*

Table 8. Total energies and vibration corrections at 0 K (au), bond lengths (*l*, Å), bond angles (deg), and magnetic shielding (σ_{iso}) and chemical shifts (δ, ppm) of nuclei in (*Z*)-*trans*-**11**, (*E*)-*trans*-**12**, (*Z*)-*trans*-**13**, and (*Z*)-*trans*-**14**

Calculated parameters	Compound			
	(*Z*)-*trans*-**11**	(*E*)-*trans*-**12**	(*Z*)-*trans*-**13**	(*Z*)-*trans*-**14**
E(MP2)	–925.597091	–815.155046	–639.412551	–528.951892
ZPE(MP2)	0.107728	0.071466	0.107388	0.075011
E + *ZPE*	–925.489364	–815.083581	–639.305163	–528.876881
$l(P^1–X)$	2.187	2.201	1.714	1.778
$l(P^1=N^1)$	1.597	1.612	1.582	1.574
l(X–C)	1.756	1.687	1.300	1.288
$\angle N^1P^1X$	110.2	99.5	109.1	107.5
$\angle P^1XC$	95.2	95.3	121.3	113.3
σ_{iso}(RHF)[a]:				
N^1	–314.3	–526.5	–149.7	–209.8
P^1	–195.1	–389.4	16.9	12.2
X	238.4	–31.9	15.1	–192.1
C	–32.5	–21.8	22.6	15.6
σ_{iso}(MP2):				
N^1	–119.9	–180.3	–40.8	–79.0
P^1	–65.1	–173.9	99.0	72.3
X	251.1	12.0	30.0	–118.6
C	1.9	25.3	37.8	36.4
δ(corr)				
N^1	54.7	165.7	–52.9	–7.4
P^1	436.8	574.1	256.8	276.1
X	81.5	331.0	–155.0	13.1
C	197.7	178.5	155.4	158.4

[a] Calculated with the 6-311+G(d,p) basis set [6-311G(d,p) in the case of (*Z*)-*trans*-**11**].

Table 9. Calculated π charges on atoms in planar conformations of **11**–**14**

No.	Conformation	$q^\pi(P^1)$	$q^\pi(N^1)$	$q^\pi(P^2)$ [$q^\pi(N^2)$]	$q^\pi(C^2)$	$q^\pi(N^{cis})$	$q^\pi(N^{trans})$
E-**11**	*trans*	0.234	–0.379	–0.541	0.265	0.216	0.210
	cis	0.291	–0.485	–0.594	0.302	0.285	0.212
Z-**11**	*trans*	0.249	–0.405	–0.560	0.278	0.223	0.215
E-**12**	*trans*	0.245	–0.276	0.070	–0.046	–	–
	cis	0.265	–0.290	0.001	0.017	–	–
Z-**12**	*trans*	0.269	–0.311	0.055	–0.024	–	–
E-**13**	*trans*	0.306	–0.397	–0.530	0.284	0.168	0.177
	cis	0.370	–0.485	–0.579	0.306	0.220	0.180
Z-**13**	*trans*	0.321	–0.417	–0.534	0.286	0.169	0.176
E-**14**	*trans*	0.286	–0.321	–0.211	0.243	–	–
	cis	0.325	–0.357	–0.273	0.304	–	–
Z-**14**	*trans*	0.304	–0.344	–0.216	0.248	–	–
E-**7**	–	0.346	–0.462	0.124	–	–	–
Z-**7**	–	0.361	–0.482	0.123	–	–	–
EN-**7**	–	0.283	–0.293	–	–	–	–
ZN-**7**	–	0.302	–0.318	–	–	–	–

Table 10. Calculated [RHF/6-311+G(2d,p)] values of the magnetic shielding of nuclei in **11**–**14** (‘ppm)

No.	Conformation	Shielding of $^{31}P^1$ nuclei			Shielding of $^{15}N^1$ nuclei			Shielding of $^{31}P^2$ nuclei			Shielding of ^{13}C nuclei		
		σ_{iso}	$\Delta\delta$	δ_{P^1}	σ_{iso}	$\Delta\delta$	δ_{N^1}	σ_{iso}	$\Delta\delta$	$\delta_{P^2}(\delta_{N^2})$	σ_{iso}	$\Delta\delta$	δ_C
E-**11**	*trans*	–262.8	738.6	602.2	–237.3	848.5	107.3	251.6	317.0	87.8	–26.6	260.8	220.9
	cis	–279.1	788.4	618.5	–129.5	672.9	–0.5	294.0	316.0	45.4	–16.0	235.6	210.3
Z-**11**	*trans*	–129.1	607.7	468.5	–180.1	754.7	50.1	216.1	393.8	123.3	–22.2	255.8	216.5
E-**12**	*trans*	–286.8	685.1	626.2	–401.1	1059.6	271.1	–17.1	696.5	356.5	–8.3	297.8	202.6
E-**13**	*trans*	–49.6	392.8	389.0	–163.6	651.7	33.6	40.9	255.8	–170.9	25.7	144.6	168.6
	cis	–41.0	408.1	380.4	–106.0	554.9	–24.0	93.5	207.1	–223.5	30.4	135.0	163.9
Z-**13**	*trans*	78.7	267.7	260.7	37.6	293.5	–167.6	–60.3	506.4	–69.7	28.0	140.3	166.3
Z-**14**	*trans*	78.3	333.8	261.1	–127.2	581.8	–2.8	–161.5	651.0	31.5	23.3	190.7	171.0

smaller compared to the corresponding conformations of **11**. This determines weaker, as compared to **11**, growth of the π charge on the N^2 atom (0.31– 0.32 *e*), which, however, still exceeds by a factor of more than 4 the increase in the π-electron density on the N^1 atom corresponding to direct polar conjugation by scheme **B**. The charge distribution obtained in the MP2 approximation differs from that considered above insignificantly and therefore will not be analyzed here. Our results could be interpreted as follows: $P{=}C(NH_2)_2$ is a stronger π donor than its nitrogen analog, $N{=}C(NH_2)_2$. However, both substituents are weaker π donors with respect to the β position than the amino group, which is unexpected.

Apparently, localization of the negative charge on the P^2 (second period) atom is preferable compared to the electronegative N^1 atom. The P=N π bond is strongly polarized toward the N atom even in **12** and **14**, and additional transfer of the electron density to this atom is hindered, because the N atom has no vacant *d* orbitals, and significant delocalization of the excess charge to adjacent atoms and groups is impossible.

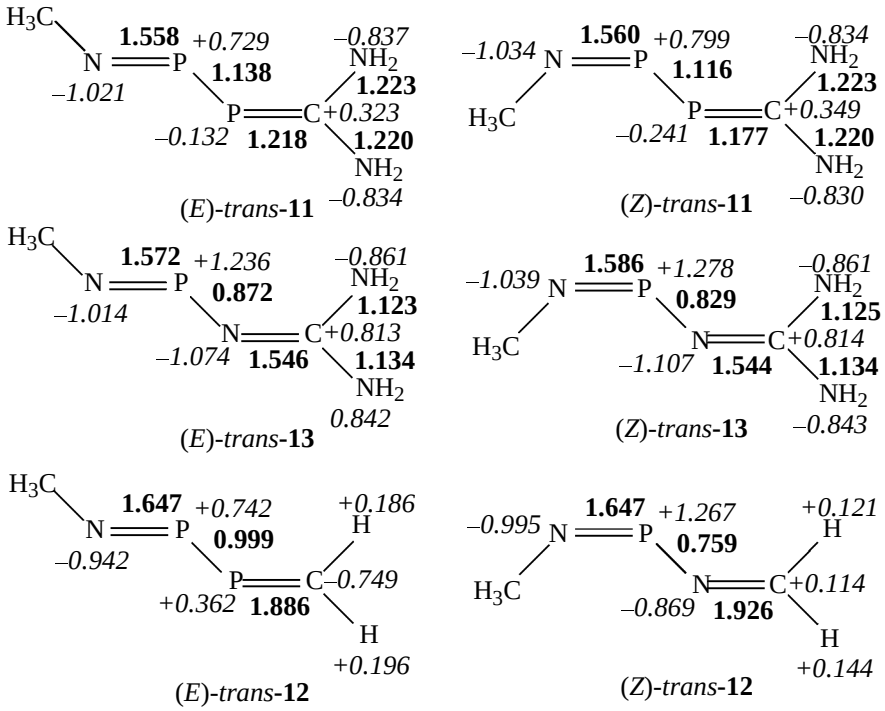


Fig. 6. Total charges (printed italic) and Wiberg indices (printed bold) for structures (*E*)-*trans*-**11**, (*Z*)-*trans*-**11**, (*E*)-*trans*-**13**, (*Z*)-*trans*-**13**, (*E*)-*trans*-**12**, and (*Z*)-*trans*-**14**.

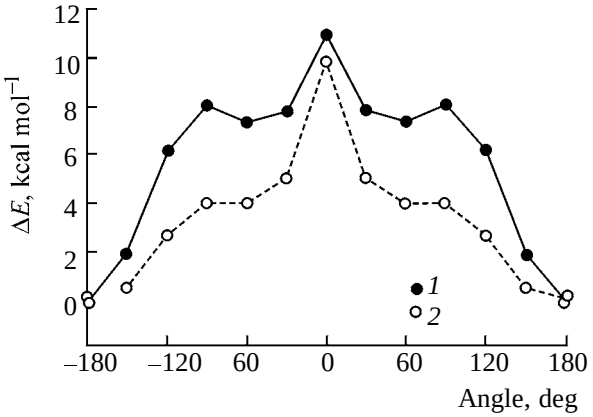


Fig. 7. Variation of the total energy of (**Z**)-**11** at rotation around the P^1–P^2 bond ($N^1P^1P^2C$ dihedral angle). Approximation: (*1*) RHF/6-31+G(d,p) and (*2*) MP2/6-31+G(d,p)//RHF/6-31+G(d,p).

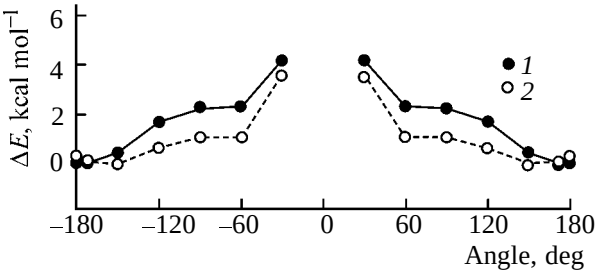


Fig. 8. Variation of the total energy of (*Z*)-**13** at rotation around the P^1–N^2 bond ($N^1P^1N^2C$ dihedral angle). Approximation: (*1*) RHF/6-31+G(d,p) and (*2*) MP2/6-31+G(d,p)//RHF/6-31+G(d,p).

The correlation between the calculated (Table 10) and experimental (Table 6) ^{31}P and ^{15}N NMR chemical shifts can be used to determine the configuration of **Ia**, **Ib**, and **IIa** in solution. The values calculated for the (*Z*)-*trans* structures of **11** and **13** are better consistent with the general correlation (Figs. 1, 2) than those calculated for the alternative (*E*)-*trans* forms. Consideration of the electron correlation effects in the MP2 approximation and subsequent empirical correction of the NMR chemical shifts obtained [20] substantially improve the quantitative agreement with the experiment for the imine nitrogen atom in (*Z*)-*trans*-**11** and (*Z*)-*trans*-**13**, which additionally confirms the suggested conformations.

POTENTIAL ENERGY SURFACES FOR ROTATION AROUND THE P–X BOND

Variation of the potential energy of a conjugated structure at distortion of its planarity reflects the extent of stabilization of the molecules by conjugation. The potential energy curves for some unsubstituted phospha- and azabutadienes are given in [43].

The potential energy curve for (*Z*)-**11** is shown in Fig. 7. The energy maximum correspond to the *cis* conformation (θ 0°), which is due to the strongest steric repulsion betwen the Me and NH_2 fragments. For the same reason, optimization of the *cis* conformation of (*Z*)-**13** (Fig. 8) with fixation of θ 0° leads to inversion of the imine nitrogen atom. The differences in the MP2(fc) energies of the *trans* and orthogonal (θ 90°) conformers of (*Z*)-**11** (4.0 kcal mol^{-1}) and (*Z*)-**13** (1.1 kcal mol^{-1}) are somewhat smaller than those found previously for $(H_3Si)_2C{=}P{-}P{=}C(NH_2)_2$ and $(H_3Si)_2C{=}P{-}N{=}C(NH_2)_2$ (5.5 and 1.5 kcal mol^{-1}, respectively) [1]. Insignificant destabilization of the orthogonal conformation of **13** is due to competing conjugation of the lone electron pair of the N^2 atom with the π system of the $P{=}N^1$ double bond. This type of conjugation is untypical of **11** and **12** because of the high *s* character of the lone electron pair of the P atom [1, 11]. Hence, the insignificant destabilization of the orthogonal conformation of (*Z*)-**11**, compared to (*Z*)-**12**, reflects very small (~1 kcal mol^{-1}) energy gain due to the donor effect of amino groups.

Since the NMR data were used to determine the conformation of the phosphabutadienes in solution, it should be noted that the δ_{N^1} values for **11** (Fig. 9) appreciably vary at rotation around the P^1–P^2 bond. The dependences obtained predict significant shielding in the planar conformations (θ 180° and 0°), whereas the calculated chemical shift for the orthogonal structure does not noticeably differ from that obtained for model **12** (Table 10). The corresponding curves for molecule **13** (Fig. 10) do not show noticeable variation of δ_{N^1} with variation of the torsion angle θ, and hence δ_{N^1} cannot serve as criterion of the presence or absence of conjugation of type **B**.

ENERGIES OF ISODESMIC REACTIONS

The calculated balance of reaction (1) suggests the higher stability of the diene structure (ΔE^1 +8.23 kcal mol^{-1}). However, as already noted, this energy gain is largely due to hydrogen bonding and favorable electrostatic interactions. For the (*Z*)-*trans*-**11** conformation corresponding to the experimental structure, the energy gain is minor (ΔE^1 +1.01 kcal mol^{-1}). This value is well consistent with the low height of the barrier to rotation around the P–P bond (~1 kcal mol^{-1}); it shows that the contribution of the conjugation effects to stabilization of heterobutadiene structures of this type is insignificant.

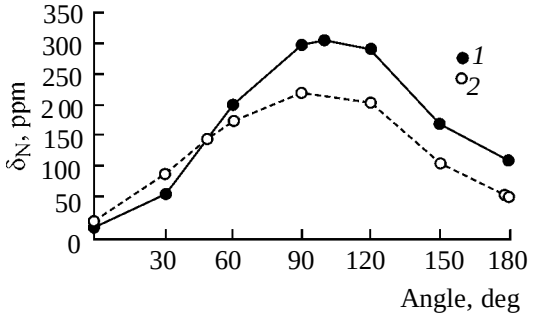


Fig. 9. Variation of δ_{N^1} in (*Z*)-**11** at rotation around the P^1–P^2 bond ($N^1P^1P^2C$ dihedral angle). Approximation: (*1*) RHF/6-31+G(d,p) and (*2*) MP2/6-31+G(d,p)// RHF/6-31+G(d,p).

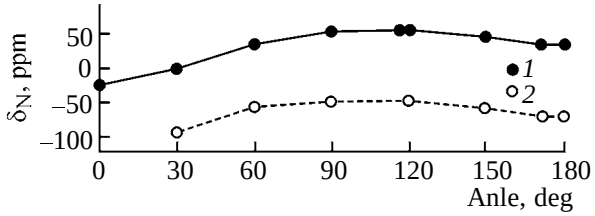


Fig. 10. Variation of δ_{N^1} in (*Z*)-**13** at rotation around the P^1–N^2 bond ($N^1P^1N^2C$ dihedral angle). Approximation: (*1*) RHF/6-31+G(d,p) and (*2*) MP2/6-31+G(d,p)// RHF/6-31+G(d,p).

$$\mathbf{11} + H_2P\text{–}PH_2 \longrightarrow H_3C\text{–}N{=}P\text{–}PH_2 + H_2P\text{–}P{=}C(NH_2)_2 + \Delta E^1, \quad (1)$$

$$\mathbf{13} + H_2P\text{–}NH_2 \longrightarrow H_3C\text{–}N{=}P\text{–}NH_2 + H_2P\text{–}P{=}C(NH_2)_2 + \Delta E^2. \quad (2)$$

In contrast to **11**, both conformations of **13** [(*E*)-*cis*-**13** and (*Z*)-*trans*-**13**] are substantially stabilized relative to the molecules with the localized double bonds (ΔE^2 +16.58 and 10.90 kcal mol^{-1}, respectively). However, the other calculation results given in this paper suggest that so high thermal effect of reaction (2) can hardly be due solely to the conjugation effects.

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