The Mills—Nixon and anomeric effects in 2,3-dihydro-1*H*-1,3,2-benzodiazaphospholes: a gas-phase electron diffraction study of $C_6H_4(NMe)_2PCl$ using quantum-chemical data and "*a priori*" force field

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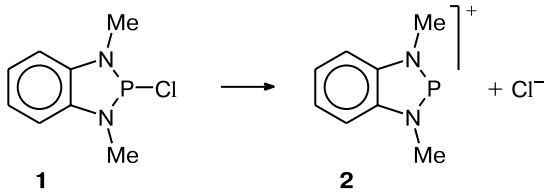
Geometric parameters and the force fields of the molecule of 2-chloro-1,3-dimethyl-2,3-dihydro-1*H*-1,3,2-benzodiazaphosphole, $C_6H_4(NMe)_2PCl$ (**1**), and the 1,3-dimethyl-2,3-dihydro-1*H*-1,3,2-benzodiazaphospholium cation, $C_6H_4(NMe)_2P^+$ (**2**), containing a dicoordinated P atom were calculated by the restricted Hartree—Fock (RHF) method using the 6-31G* and 6-311G** basis sets. Vibrational characteristics of the internuclear distances in molecule **1** were calculated using the "*a priori*" scaled force field. Structural analysis of the gas-phase electron diffraction data for this molecule was performed with inclusion of nonlinear kinematic effects at the first-order level of perturbation theory. Substantial lengthening of the P—Cl bond and conformational peculiarities of the phosphole fragment of molecule **1** are consistent with the expected manifestations of the anomeric effect. The type of partial localization of the π-bonds in the benzene fragment (relative weights of two resonance Kekule structures, or the Mills—Nixon effect) changes on going from covalent to ionized state of the P atom in the annelated five-membered ring.

Key words: 2-chloro-1,3-dimethyl-2,3-dihydro-1*H*-1,3,2-benzodiazaphosphole, 1,3-dimethyl-2,3-dihydro-1*H*-1,3,2-benzodiazaphospholium cation, gas-phase electron diffraction; *ab initio* quantum-chemical calculations, molecular structure, force field, scaling, the Mills—Nixon effect, the anomeric effect.

Gas-phase electron diffraction study of the molecular structure of 2-chloro-1,3-dimethyl-2,3-dihydro-1*H*-1,3,2-benzodiazaphosphole (**1**, Fig. 1) concerns a number of stereochemical problems. Previously,[1—3] we showed that the P—Cl bond lengths in tricoordinated phosphorus compounds, the corresponding stretching force constants, and the frequencies of the stretching modes in the vibrational spectra are strongly dependent on the presence of O or N atoms near the P atom. Lengthening of the P—Cl bond in amino/aza- and oxy/oxachlorophosphines is consistent with the concept of the anomeric effect[4—9] and indicative of a low strength and increased polarity of this bond. It also points to a rather high probability for processes involving cleavage of the P—Cl bond and formation of a stable cation **2** (Scheme 1) to occur.

Scheme 1



A commonly accepted model[5] of the anomeric effect in tetraatomic fragments, in which the atom adjacent to the terminal polar bond has the lone electron pairs (LEP), is based on the assumption of $n\rightarrow\sigma^*$-overlap of the LEP orbital and the nonbonding orbital of the polar bond. This model holds preferableness of the *gauche*-conformation of such fragments and implies lengthening of the polar bond, shortening of the adjacent bond, and an increase in the angle between them. Sometimes, the conformational behavior of five-membered heterocycles cannot be rationalized without invoking the concept of the generalized anomeric effect.[10] The influence of this effect on the equi-

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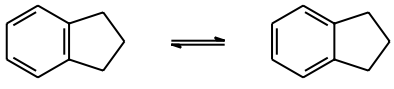
Fig. 1. Equilibrium conformations of molecule **1** (C_s symmetry) and cation **2** (C_{2v} symmetry). A projection at the center illustrates the deviations of the atoms in molecule **1** from the N—C_α—C′$_\alpha$—N′ plane. Shown are the notations of the atoms, bonds, and bond angles, as well as the Mulliken atomic charges calculated in the RHF/6-311G** approximation.

librium conformation of the diazaphosphole ring and on the orientation of substituents in this ring has not been studied so far.

In our case, the presence of a fused aromatic π-system must favor stabilization of cation **2** due to conjugation with the diazaphosphole fragment[11,12] and, hence, greater lengthening of the P—Cl bond. Conjugated systems similar to cation **2** containing the P atom with a low coordination number are of interest from the viewpoint of chromaticity theory and synthesis of dyes.[13]

The aim of this work was, in particular, to study the manifestations of the Mills—Nixon effect[14] in the benzene fragment of the 2,3-dihydro-1*H*-1,3,2-benzodiazaphosphole derivatives. The idea of partial localization of π-bonds in the benzene ring due to annelation by strained small ring was first proposed[14] to rationalize anomalous electrophilic substitution in benzocyclopentene (indan). According to this concept, small-ring fusion to benzene affects resonance of the Kekule structures (Scheme 2), thus changing their relative weights. Shortening of a particular carbon—carbon bond in the benzene ring is associated with an increase in the contribution of that Kekule structure in which the bond in question is the double bond. More recently,[15] it was shown that changes in the carbon—carbon bond lengths in the benzene fragment of benzocycloalkene derivatives are accompanied by pronounced deformation of intra-ring bond angles.

Scheme 2



A **B**

Despite the fact that the influence of various substituents on the geometry of the benzene ring has been studied in detail,[16] the effects of hetero-substitution of the atoms of the small ring in annelated benzenes have been little studied so far. In particular, single-crystal X-ray diffraction data for a series of 2,3-dihydro-1*H*-1,3,2-benzodiazaphosphole derivatives have been reported.[17—21] However, the accuracy of these data is insufficient for detailed study of the structure of the benzene fragment and only point to a decrease in the intra-ring angle at the C atom in *ortho*-position relative to small ring, which is analogous to that found for benzocycloalkenes.[15]

Scheme of joint use of gas-phase electron diffraction, quantum-chemical, and "*a priori*" spectroscopic data

Previously,[22] we failed to unambiguously establish the molecular structure of compound **1** based on the results of gas-phase electron diffraction study because of correlations between the geometric and vibrational parameters. The root-mean-square (RMS) amplitudes and shrinkage corrections for this molecule can be reliably estimated by using the reliable force field. Unfortunately, no vibrational spectra of molecule **1** have been reported so far and the inverse spectral problem is still to be solved.

In this work we obtained initial approximations of the force field and vibrational frequencies of molecule **1** using quantum-chemical calculations by the restricted Hartree—Fock (RHF) method in the 6-31G* and 6-311G** basis sets. The RHF method is known[23,24] to systematically overestimate the force constants. The most widely used way of correcting their values is to use the scaling procedure according to Pulay.[23—25] This procedure has been to some extent theoretically substantiated.[26—29] By the variational method it was found[26] that if the ground electronic state of a molecule meets some requirements (usually, they are met by most of compounds), the force constants determined by the *ab initio* self-consistent field method near the Hartree—Fock limit

are nearly linearly related to the force constants obtained from calculations in the *ab initio* configurational interaction approximation.[26] These values differ by a factor equal to the square of the C_0 coefficient of the Hartree—Fock determinant in a complete configurational interaction expansion of the exact electronic wave function. Taking into account the normalization condition for the wave function, one gets $C_0^2 \leq 1$. Thus, it was shown that scaling provides a way of effective inclusion of dynamic electron correlation. Though in the Hartree—Fock limit one would expect the same values of the scale factors (SFs) for all internal coordinates, the SF values obtained using force field calculations with the above-mentioned basis sets are scattered in the interval from 0.7 to 0.9. This can be due to both the incompleteness of the basis set and the anharmonicity of the experimental vibrational frequencies involved in the scaling procedure.

The SF transferability problem is of particular importance when studying series of related molecules. Mention may be made that, in principle, experience suggests transferability of the scale factors.[24,30—36] Additional arguments in favor of transferability are provided by localizability of the MOs and by minor changes in the localized MOs for related compounds, which serves as the basis for relating the C_0 coefficients to particular internal coordinates.[24] Each SF compensates the systematic error of calculations of the force constant for a certain internal coordinate, which is typical of a given level of computations. Therefore, in the case of related compounds the SFs must be transferable much better than the force constants.[23,25] Since the results of scaling procedure (force constants and vibrational frequencies) were obtained before carrying out the spectral experiment on the compound under study, we call them "*a priori*", thus following the authors of a known study.[30] According to our calculations,[31—36] the differences between the calculated and experimental vibrational frequencies in the long-wavelength region (the most important spectral region when calculating the vibrational parameters of the molecular structure) were at most 10 to 15 cm^{-1}. The *a priori* scaling procedure can be treated as the use of additional experimental information known for the model fragments of a given compound.

In the absence of experimental vibrational spectra of molecule **1** the scaling using transferable SFs for the model structural fragments provided a real possibility of transforming the quantum-chemical force field obtained from our calculations into a more faithful form. These SFs were found by fitting the theoretical vibrational frequencies to the frequencies observed in the experimental spectra of dimethylaminodichlorophosphine,[1] 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholene,[37] and nitrobenzene.[38a] We believe that spectroscopic calculations based on the scaled force field allowed us to obtain reliable estimates of the RMS vibrational amplitudes ($u_{ij,h1}$), harmonic and anharmonic vibrational corrections ($\delta_{ij,h1}^{vib}$ and $\delta_{ij,anh1}^{vib}$), and centrifugal distortion corrections (δ_{ij}^{rot}) for the internuclear distances in molecule **1**.

A good confirmation of transferability of the SFs employed in this work is provided by the results of a recent experimental and theoretical study of the IR and Raman spectra of five bicyclic compounds, namely, benzofuran, benzothiophene, indole, benzothiazole, and benzoxazole.[38b] In that study the vibrational spectra were interpreted using the quantum-chemical force fields calculated by the RHF and DFT (B3LYP) methods with the 3-21G* and 6-31G* basis sets and scaled according to Pulay[23,25] with fitting the theoretical characteristics to the experimental vibrational frequencies, band intensities, and degrees of depolarization. The SF values obtained (common to the five related structures) were very close to those used in this work.

Experimental and Calculation Procedure

The sample of compound **1** synthesized following a known procedure[12,39] was a wax-like white solid with a sublimating temperature of 130 °C (1 Torr). Compound **1** undergoes fast hydrolysis in air, which precludes the use of conventional identification techniques. Purity of the sample was confirmed by mass spectrometry[12] and by comparing the ^{1}H NMR spectra and published data.[39] The thermal stability of the compound was assessed by *in vacuo* maintaining at 200 °C for 0.5 h. Comparison of the ^{1}H NMR spectra recorded before and after heating showed that no chemical transformations occurred on heating.

Electron diffraction patterns were obtained on a modified EG-100A electron diffraction apparatus[40] with an accelerating voltage of 60 keV and two nozzle—plate distances, 406.37 (LD) and 186.95 mm (SD), at ~473 K. The electron beam wavelength was determined using the diffraction patterns from the crystalline standard (ZnO) and the published data on the lattice parameters.[41] Six photoplates exposed to the diffraction patterns from 2-chloro-1,3-dimethyl-2,3-dihydro-1*H*-1,3,2-benzodiazaphosphole vapors were found to be suitable for structural analysis. The optical densities for these photoplates were measured on a modified MF-4 microphotometer.[40] Initially, the background lines, $I^B(s)$, were plotted using the results of quantum-chemical calculations of the molecular structure of **1**. Then, they were corrected in the course of the analysis.

Structural parameters of molecule **1** were refined by the least squares processing of the experimental molecular scattering intensity curves $sM^{exp}(s)$ (Fig. 2) with diagonal weight matrices. The theoretical molecular scattering intensities, $sM^{theor}(s)$, were calculated using complex scattering factors.[42] The anharmonicity parameters, $a_3(ij)$, for bonds were set equal to their values for diatomic molecules. For the distances between the nonbonded atoms, these parameters were set to zero.[43] The experimental total errors were estimated with inclusion of the standard deviations of the least squares method and scale uncertainties.[44]

The vibrational parameters $u_{ij,h1}$ and $\delta_{ij,h1}^{vib}$ of molecule **1** were calculated at the first-order level of perturbation theory[45,46] taking into account local centrifugal distortions due to intramolecular motions.[47,48] Centrifugal distortions due to the overal

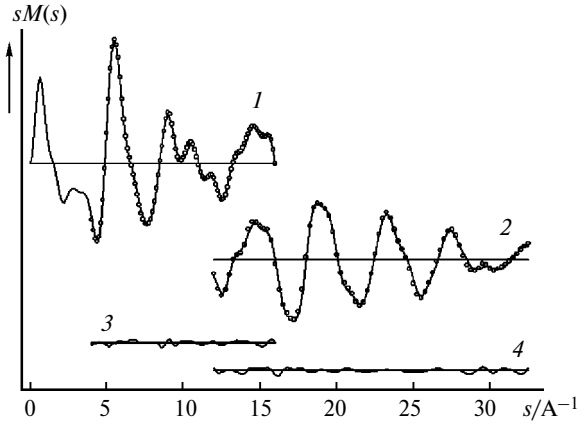


Fig. 2. Experimental (points) curves of the molecular scattering intensty, $sM(s)$, obtained at nozzle—plate distances of 406.37 (*1*) and 186.95 mm (*2*), the corresponding theoretical curves (solid lines), and the difference curves, $\Delta sM(s)$ (*3* and *4*, respectively) for molecule **1**.

rotation of the molecule (δ_{ij}^{rot}) were calculated following the known procedure.[49] The contributions of anharmonic terms of the Taylor expansion of the potential function $V(q)$ ($\delta_{ij,anh1}^{vib}$) were estimated using the solution of the equations of motion for the molecular system at the first-order level of perturbation theory.[50] The diagonal cubic expansion terms corresponding to stretching vibrations were calculated as $h_{kkk} = -3f_{kk}a_3^{(k)}$, where $a_3^{(k)}$ is the cubic anharmonicity parameter in the diatomic approximation.[43] All other cubic terms of the expansion were set to zero.

Scaling[23,25] of the quantum-chemical force constant matrix F_{mn}^{theor} was carried out according to the formula $F_{mn} = (C_m C_n)^{0.5} F_{mn}^{theor}$ using a previously found[1,37,38a] small set of transferable factors C_m for the standard system of local-symmetry internal coordinates.[25]

Structural analysis of the gas-phase electron diffraction data was performed using the KCED-25 program[51] adapted for IBM-compatible PC at the Electron Diffraction Team of the L. Eotvos Budapest University (Hungary) and modified at the M. V. Lomonosov Moscow State University (Russian Federation). Quantum-chemical calculations were carried out on an HP735 Work Station computer using the GAUSSIAN-92 program package[52] at the Littoral University (Dunkirk, France). Spectroscopic calculations were carried out using the ANCO/SCAL/PERT[53,54] and SHRINK[45,46] (updated 2000 version) program packages.

Quantum-chemical calculations of equilibrium geometry of molecule 1 and cation 2

According to our RHF/6-31G* and RHF/6-311G** calculations, the equilibrium structure of molecule **1** has a C_s symmetry (Table 1, see Fig. 1). The benzene fragment is nearly planar, while the diazaphosphole ring adopts a P-envelope conformation (the P atom deviates from the plane passing through the other atoms of the ring). The appreciably lengthened P—Cl bond has axial orientation, and the Me groups at "flattened" N atoms occupy equatorial positions.

The variations of the carbon—carbon bond lengths in the annelated benzene ring of molecule **1** lie in the range from −0.02 Å to 0.02 Å (see Table 1), which is nearly twice as large as those obtained from X-ray diffraction studies of benzocyclopentenes.[15] The *a* and *c* bonds are longer than the *b* and *d* bonds (for notations, see Fig. 1). The carbon—carbon bond length distribution in the benzene ring (these are the most reliable results of our calculations) corresponds to larger contribution of the Kekule structure **B** (see Scheme 2) as an explanation of partial localization of the π-bonds of the annelated benzene.[14] This distribution is similar to that found earlier[15] for a number of benzocyclopentenes in the crystalline phase. The bond angles in the benzene ring annelated with the five-membered ring are somewhat different from those in the benzene molecule, namely, the β angle decreases down to 118.5°, while the α and γ angles increase to 120.7—120.8° (see Table 1). The calculated values of the α, β, and γ angles and of the carbon—carbon bond lengths in molecule **1** are virtually independent of the basis set employed.

The carbon—carbon bond length distribution in the annelated benzene ring of cation **2** is quite different from that found for **1** (see Table 1), though the bond angles in both structures differ insignificantly. The calculated values of the geometric parameters of cation **2** coincide with the single-crystal X-ray diffraction data[17] to an accuracy of ±0.01 Å for the bond lengths and ±0.4° for the bond angles. Comparison with the results obtained for molecule **1** indicates that fusion of the benzene ring and the five-membered diazaphosphole ring not necessarily increases the weight of the same Kekule structure in the former.

Based on the results of calculations of molecule **1** and cation **2**, the dissociation energy of molecule **1** into **2** and the Cl^- ion ($E_{tot}(Cl^-) = -459.564047$ a.u.) can be estimated at ~107.5 kcal mol^{-1} with inclusion of zero-point vibrational energy correction, which is nearly half the appearance potential (8.68 eV or ~200 kcal mol^{-1}) corresponding to the fragmentation reaction $PCl_3 + e \rightarrow PCl_2^+ + Cl^- + e$, which was obtained in a mass spectrometric study.[55]

"*A priori*" force field and vibrational spectrum of molecule 1

The local-symmetry internal coordinates and corresponding quantum-chemical estimates of harmonic force constants are listed in Tables 2 and 3, respectively. The potential energy matrices of molecule **1** and cation **2** are structurally similar and include a great number of large (in absolute values) interaction constants between internal coordinates. This virtually excludes the possibility of reliable empirical determination of the force fields using a conventional method of solving the inverse spectral problem. For most of skeletal deformation vibrations the dif-

Table 1. Geometric parameters, dipole moments, and energy characteristics of the molecule of 2-chloro-1,3-dimethyl-2,3-dihydro-1*H*-1,3,2-benzodiazaphosphole, $C_6H_4(NMe)_2PCl$ (**1**, C_s symmetry) and the 1,3-dimethyl-2,3-dihydro-1*H*-1,3,2-benzodiazaphospholium cation, $C_6H_4(NMe)_2P^+$ (**2**, C_{2v} symmetry) calculated in the RHF/6-311G** approximation

Parameter[a]	**1**	**2**
Bond length/Å		
P—Cl	2.209	—
P—N	1.672	1.630
N—C_{Me}	1.450	1.471
e (N—C_α)	1.400	1.387
a (C_α—C'_α)	1.396	1.389
b (C_α—C_β)	1.375	1.396
c (C_β—C_γ)	1.394	1.371
d (C_γ—C'_γ)	1.378	1.405
C_β—H_β	1.074	1.073
C_γ—H_γ	1.075	1.074
C_{Me}—H	1.083	1.081
C_{Me}—H′	1.086	1.081
C_{Me}—H″	1.084	
Bond angle/deg		
N—P—Cl	102.1	—
N—P—N′	90.8	92.8
P—N—C_{Me}	123.2	124.4
C_α—N—C_{Me}	121.7	122.5
P—N—C_α	112.6	113.1
ε (N—C_α—C'_α)	110.6	110.5
ρ (N—C_α—C_β)	128.7	128.4
α (C'_α—C_α—C_β)	120.8	121.1
β (C_α—C_β—C_γ)	118.5	117.6
γ (C_β—C_γ—C'_γ)	120.7	121.3
C_α—C_β—H_β	121.2	121.5
C_γ—C_β—H_β	120.3	121.0
C_β—C_γ—H_γ	119.3	119.5
C'_γ—C_γ—H_γ	120.0	119.2
N—C_{Me}—H	109.3	109.2
N—C_{Me}—H′	111.4	109.5
N—C_{Me}—H″	110.0	

Parameter[a]	**1**	**2**
Dihedral angle/deg		
N—P—N′/N—C_α—C'_α—N′ (φ)	15.3	0.0
N—C_α—C'_α—N′/C_β—C_α—C'_α—C'_β	–0.7	0.0
C_α—C_β—C'_β—C'_α/C_γ—C_β—C'_β—C'_γ	–0.4	0.0
C_β—C_γ—C'_γ—C'_β/H_γ—C_γ—C'_γ—H'_γ	–0.4	0.0
P—Cl/N—P—N′[b]	72.7	—
N′—P—N—C_{Me}	±177.8	180.0
C'_α—C_α—N—C_{Me}	±174.1	180.0
C_β—C_α—N—C_{Me}	±6.6	0.0
Cl—P—N—C_{Me}	±75.2	—
N—C_α—C_β—H_β	±1.3	0.0
C'_α—C_α—C_β—H_β	±179.4	180.0
C'_γ—C_γ—C_β—H_β	±180.6	180.0
H_γ—C_γ—C_β—H_β	±0.1	0.0
P—N—C_{Me}—H	±22.5	0.0
P—N—C_{Me}—H′	±97.5	±119.5
P—N—C_{Me}—H″	±141.0	
C_α—N—C_{Me}—H	±176.8	180.0
C_α—N—C_{Me}—H′	±63.2	±60.5
C_α—N—C_{Me}—H″	±58.3	
Dipole moment/D	3.5	2.4
Energy/a.u.		
$-(E_{tot} + 1218.0)$[c]	0.050020	—
$-(E_{tot} + 758.0)$[c]	—	0.314457
ZPE[d]	0.182869	0.182679

[a] For notations of the atoms and geometric parameters, see Fig. 1.
[b] The angle of deviation of the P—Cl bond from the NPN′ plane.
[c] E_{tot} is the total energy.
[d] Zero-point vibrational energy.

ferences between the force constants of both compounds are minimum, while the force constants of deformation vibrations of the Me groups and of the C—H bonds of the benzene ring can be considered transferable. The scaled force constant of the P—Cl stretch in molecule **1** (1.10 mdyn $Å^{-1}$) is by a factor of 2 or 2.5 smaller than those in Me_2NPCl_2 **1** and $Me_2C_2O_2PCl$.[37]

Most of the skeletal normal modes of molecule **1** can be strongly mixed. The low-frequency vibrations including the P—Cl stretching vibration with a frequency of ~320 cm^{-1}, which is much lower than the frequencies observed in the spectra of Me_2NPCl_2 **1** and $Me_2C_2O_2PCl$,[37] belong to vibrations with the lowest degree of mixing. According to our calculations, the lowest lying vibrations of molecule **1** are the wagging motions of the amino groups (~106 and ~90 cm^{-1}) and the puckering vibration of the unsaturated five-membered ring (~67 cm^{-1}). In these cases, large-amplitude intramolecular motions can occur.

Structural analysis

The number of peaks in the experimental radial distribution curve $f(r)$ (Fig. 3) is much less than that of the internuclear distances determining the molecular structure of **1** since half the nonbonded distances between the

Table 2. Nonredundant sets of local-symmetry internal coordinates for molecule **1** and cation **2** and the transferable scale factors for quantum-chemical force field calculated in the RHF/6-31G* approximation

Coordinate number	Coordinate notation[a]	Typical local-symmetry internal coordinate definition	Scale factor[1,37,38a]
1, 2	PN str	—	0.904
3, 4	*e* (NC_α) str	—	0.811
5	*a* ($C_\alpha C'_\alpha$) str	—	0.780
6, 7	*b* ($C_\alpha C_\beta$) str	—	
8, 9	*c* ($C_\beta C_\gamma$) str	—	
10	*d* ($C_\gamma C'_\gamma$) str	—	
11, 12	$C_\beta H_\beta$ str	—	0.825
13, 14	$C_\gamma H_\gamma$ str	—	
15, 16	NC_{Me} str	—	0.811
17[b]	PCl str	—	0.814
18, 19	Me s.str	$(C_{Me}H\ str + C_{Me}H'\ str + C_{Me}H''\ str)/\sqrt{3}$	0.800
20, 21	Me str	$(2\ C_{Me}H\ str - C_{Me}H'\ str - C_{Me}H''\ str)/\sqrt{6}$	
22, 23	Me str′	$(C_{Me}H'\ str - C_{Me}H''\ str)/\sqrt{2}$	
24, 25	Me s.def	$(H'C_{Me}H''\ bend + HC_{Me}H''\ bend + HC_{Me}H'\ bend - NC_{Me}H\ bend - NC_{Me}H'\ bend - NC_{Me}H''\ bend)/\sqrt{6}$	0.780
26, 27	Me def	$(2\ H'C_{Me}H''\ bend - HC_{Me}H''\ bend - HC_{Me}H'\ bend)/\sqrt{6}$	0.794
28, 29	Me def′	$(HC_{Me}H''\ bend - HC_{Me}H'\ bend)/\sqrt{2}$	
30, 31	Me rock∥	$(2\ NC_{Me}H\ bend - NC_{Me}H'\ bend - NC_{Me}H''\ bend)/\sqrt{6}$	0.767
32, 33	Me rock⊥	$(NC_{Me}H'\ bend - NC_{Me}H''\ bend)/\sqrt{2}$	
34, 35	$C_\beta H_\beta$ rock	$(C_\alpha C_\beta H_\beta\ bend - C_\gamma C_\beta H_\beta\ bend)/\sqrt{2}$	0.825
36, 37	$C_\gamma H_\gamma$ rock	$(C_\beta C_\gamma H_\gamma\ bend - C'_\gamma C_\gamma H_\gamma\ bend)/\sqrt{2}$	
38, 39	NC_{Me} rock	$(C'_\alpha N'C_{Me}\ bend - PN'C_{Me}\ bend)/\sqrt{2}$	0.803
40, 41[b]	NPCl bend		0.795
42	def (5)	$(N'PN\ bend + \cos144°\ (C'_\alpha N'P\ bend + (PNC_\alpha\ bend) + \cos72°\ (C_\alpha C'_\alpha N'\ bend + (NC_\alpha C'_\alpha\ bend))/\sqrt{2.5}$	0.877
43	def′ (5)	$((\cos144° - \cos72°)(C'_\alpha N'P\ bend - (PNC_\alpha\ bend) + (1 - \cos144°)(C_\alpha C'_\alpha N'\ bend - NC_\alpha C'_\alpha\ bend))/3$	0.800
44	def (6)	$(C'_\alpha C_\alpha C_\beta\ bend + C_\beta C_\gamma C'_\gamma\ bend + C'_\gamma C'_\beta C'_\alpha\ bend - C_\alpha C_\beta C_\gamma\ bend - C_\gamma C'_\gamma C'_\beta\ bend - C'_\beta C'_\alpha C_\alpha\ bend)/\sqrt{6}$	0.860
45	def′ (6)	$(2\ C_\alpha C_\beta C_\gamma\ bend - C'_\alpha C_\alpha C_\beta\ bend - C_\beta C_\gamma C'_\gamma\ bend + 2\ C'_\gamma C'_\beta C'_\alpha\ bend - C_\gamma C'_\gamma C'_\beta\ bend - C'_\beta C'_\alpha C_\alpha\ bend)/\sqrt{12}$	
46	def″ (6)	$(C'_\beta C'_\alpha C_\alpha\ bend - C_\gamma C'_\gamma C'_\beta\ bend + C_\beta C_\gamma C'_\gamma\ bend - C'_\alpha C_\alpha C_\beta\ bend)/2$	
7, 48	NC_{Me} wag	NC_{Me}/PNC_α out-of-plane	0.900
49, 50	$C_\beta H_\beta$ wag	$C_\beta H_\beta / C_\alpha C_\beta C_\gamma$ out-of-plane	0.820
51, 52	$C_\gamma H_\gamma$ wag	$C_\gamma H_\gamma / C_\beta C_\gamma C'_\gamma$ out-of-plane	
53, 54	NC_{Me} tors	$(H,H',H'')C_{Me} - N(P,C_\alpha)$ tors	0.840
55	tors (5)	$(C'_\alpha C_\alpha\ tors + \cos144°\ (C_\alpha N\ tors + N'C'_\alpha\ tors) + \cos72°\ (NP\ tors + PN'\ tors))/\sqrt{2.5}$	0.850
56	tors′ (5)	$((\cos144° - \cos72°)(C_\alpha N\ tors - N'C'_\alpha\ tors) + (1 - \cos144°)(NP\ tors - PN'\ tors))/3$	
57	tors (6)	$(C'_\alpha C_\alpha\ tors + C_\beta C_\gamma\ tors + C'_\gamma C'_\beta\ tors - C_\alpha C_\beta\ tors - C_\gamma C'_\gamma\ tors - C'_\beta C'_\alpha\ tors)/\sqrt{6}$	0.795
58	tors′ (6)	$(C_\alpha C_\beta\ tors + C'_\gamma C'_\beta\ tors - C_\beta C_\gamma\ tors - C'_\beta C'_\alpha\ tors)/2$	
59	tors″ (6)	$(2\ C_\gamma C'_\gamma\ tors - C_\beta C_\gamma\ tors - C'_\gamma C'_\beta\ tors + 2\ C'_\alpha C_\alpha\ tors - C'_\beta C'_\alpha\ tors - C_\alpha C_\beta\ tors)/\sqrt{12}$	
60	$tors_b$	$(C_\beta C_\alpha C'_\alpha N'\ tors - NC_\alpha C'_\alpha C'_\beta\ tors)/\sqrt{2}$	0.800

[a] Notations of vibrations: str is stretching, bend is bending for the bond angle; def is local-symmetry deformation vibration for the five- (5) and six-membered (6) rings or for the methyl group; rock is rocking (∥ and ⊥ denote parallel and normal to the local plane chosen for a given methyl group); wag is wagging, out-of-plane is the out-of-plane vibration; tors is torsional (defined as the sum of the motions in the tetraatomic fragments), $tors_b$ is the torsional vibration in the bicyclic system; and s is symmetric vibration. For notations of the atoms and geometric parameters, see Fig. 1.

[b] Only for molecule **1**.

Table 3. Force constants of molecule **1** and cation **2** calculated in the RHF/6-311G** approximation (I) and the scaled force constants for molecule **1** obtained using the results of RHF/6-31G* calculations (II) (in internal vibrational coordinates)[a]

Force constant[b]	I		II,
	1	**2**	**1**
PN str	**5.22**	**6.28**	**4.63**
/PN´ str	0.24	0.21	0.19
/*e* (NC_α) str	0.49	0.82	0.42
/*e* ($N´C´_\alpha$) str	−0.31	0.02	−0.26
/*a* ($C_\alpha C´_\alpha$) str	−0.14	−0.24	−0.12
/*b* ($C´_\alpha C´_\beta$) str	−0.11	−0.26	−0.10
/NC_{Me} str	0.23	0.27	0.20
/PCl str	0.38	—	0.33
/def (5)	0.15	0.26	0.13
/def´ (5)	±0.39	±0.43	±0.33
***e* (NC_α) str**	**6.78**	**6.91**	**5.57**
/*e* ($N´C´_\alpha$) str	−0.06	−0.56	−0.05
/*a* ($C_\alpha C´_\alpha$) str	0.61	0.72	0.49
/*b* ($C_\alpha C_\beta$) str	0.67	0.77	0.54
/*c* ($C´_\beta C´_\gamma$) str	−0.10	−0.31	−0.09
/NC_{Me} rock	±0.29	±0.30	±0.24
/def (5)	−0.31	−0.46	−0.26
/def (6)	±0.35	±0.40	±0.29
/def´ (6)	0.24	0.22	0.20
/def″ (6)	±0.51	±0.48	±0.43
***a* ($C_\alpha C´_\alpha$) str**	**7.57**	**7.96**	**6.00**
/*b* ($C_\alpha C_\beta$) str	1.02	0.87	0.80
/*c* ($C_\beta C_\gamma$) str	−0.78	−0.58	−0.60
/*d* ($C_\gamma C´_\gamma$) str	0.50	0.30	0.38
/def (5)	0.21	0.27	0.17
***b* ($C_\alpha C_\beta$) str**	**8.16**	**7.35**	**6.46**
/*b* ($C´_\alpha C´_\beta$) str	−0.61	−0.63	−0.48
/*c* ($C_\beta C_\gamma$) str	0.92	0.92	0.73
/*c* ($C´_\beta C´_\gamma$) str	0.56	0.53	0.42
/*d* ($C_\gamma C´_\gamma$) str	−0.74	−0.75	−0.58
/def´ (5)	±0.31	±0.29	±0.25
/def´ (6)	0.24	0.26	0.20
***c* ($C_\beta C_\gamma$) str**	**7.43**	**8.33**	**5.92**
/*c* ($C´_\beta C´_\gamma$) str	−0.67	−0.62	−0.53
/*d* ($C_\gamma C´_\gamma$) str	1.01	1.00	0.80
/def″ (6)	±0.29	±0.26	±0.24
***d* ($C_\gamma C´_\gamma$) str**	**8.00**	**7.05**	**6.35**
/def´ (6)	−0.36	−0.32	−0.30
$C_\beta H_\beta$ str	**6.16**	**6.22**	**5.19**
$C_\gamma H_\gamma$ str	**6.11**	**6.19**	**5.16**
NC_{Me} str	**5.93**	**5.28**	**4.90**
/Me s.str	0.30	0.21	0.25
/Me s.def	−0.56	−0.59	−0.45
/def (5)	0.18	0.14	0.16
PCl str	**1.27**	—	**1.10**
Me s.str	**5.85**	**5.97**	**4.80**
Me str	**5.72**	**5.85**	**4.70**
Me str´	**5.63**	**5.83**	**4.63**
Me s.def	**0.76**	**0.78**	**0.61**
Me def	**0.68**	**0.66**	**0.56**
Me def´	**0.66**	**0.64**	**0.54**
Me rock∥	**0.98**	**0.98**	**0.76**
Me rock⊥	**0.95**	**0.94**	**0.74**
$C_\beta H_\beta$ rock	**0.60**	**0.60**	**0.51**
$C_\gamma H_\gamma$ rock	**0.61**	**0.62**	**0.51**
NC_{Me} rock	**0.87**	**0.84**	**0.70**
NPCl bend	**1.13**	—	**0.92**
/N´PCl bend	0.21	—	0.17
def (5)	**2.04**	**2.11**	**1.78**
/def´ (6)	−0.26	−0.27	−0.23
def´ (5)	**2.20**	**2.19**	**1.76**
/def (6)	−0.49	−0.50	−0.41
/def″ (6)	0.52	0.49	0.44
def (6)	**1.62**	**1.63**	**1.40**
/def″ (6)	−0.19	−0.21	−0.16
def´ (6)	**1.61**	**1.60**	**1.40**
def″ (6)	**1.71**	**1.66**	**1.48**
NC_{Me} wag	**0.23**	**0.40**	**0.20**
$C_\beta H_\beta$ wag	**0.52**	**0.53**	**0.43**
$C_\gamma H_\gamma$ wag	**0.54**	**0.58**	**0.45**
NC_{Me} tors	**0.09**	**0.08**	**0.07**
tors (5)	**0.26**	**0.30**	**0.23**
tors´ (5)	**0.27**	**0.42**	**0.23**
tors (6)	**0.35**	**0.35**	**0.28**
tors´ (6)	**0.41**	**0.40**	**0.33**
tors″ (6)	**0.33**	**0.29**	**0.27**
$tors_b$	**0.49**	**0.43**	**0.39**

[a] For notations of vibrations, see Note[a] to Table 2. For notations of the atoms and bonds, see Fig. 1.
[b] For each internal coordinate, the diagonal force constant indicated in boldface print is followed by the force constants of interactions between this and other coordinates (slashed). The force constants of the stretching vibrations and interactions between them are given in mdyn $Å^{-1}$, the force constants of the interactions between the stretching and deformation (including torsional) vibrations are given in mdyn, and those of all types of deformation vibrations and interactions between them are given in mdyn Å. The off-diagonal force constants, whose moduli do not exceed 0.15 after scaling, are not listed.

skeleton atoms along with the P—Cl bond (Table 4) contributes to only one of the complex peaks in the $f(r)$ curve (at $r \approx 2$—3 Å, see Fig. 3). Practically, it is impossible to resolve the overlap of the contributions of particular geometric parameters without invoking the data obtained by other methods.

Based on the results of quantum-chemical calculations, we performed structural analysis of the gas-phase

Table 4. Results of analysis of gas-phase electron diffraction data (T = 473 K) for 2-chloro-1,3-dimethyl-2,3-dihydro-1*H*-1,3,2-benzodiazaphosphole using the small-amplitude harmonic vibration approximation with inclusion of nonlinear kinematic effects at the fisrt-order level of perturbation theory ($h1$)

Parameter[a]	r_a	$r_{h1} - r_a$	r_{h1}	u_{h1}^{calc}	u_{h1}' [b]
Distance					
P—Cl	2.1833	–0.0006	2.183(5)	0.0844	0.085(2)[c]
P—N	1.6979	0.0001	1.698(4)	0.0483	0.050(2)
N—C_{Me}	1.4541	0.0002	1.454(6)	0.0506	0.048(3)[d]
e (N—C_α)	1.4108	0.0003	1.411(4)	0.0489	0.046[d]
a (C_α—C'_α)	1.4017	0.0031	1.405(3)	0.0487	0.046[d]
b (C_α—C_β)	1.3819	0.0014	1.383(3)	0.0475	0.045[d]
c (C_β—C_γ)	1.4032	–0.0005	1.403(3)	0.0489	0.046[d]
d (C_γ—C'_γ)	1.3886	–0.0016	1.387(3)	0.0479	0.045[d]
C_β—H_β	1.0662	0.0015	1.068(4)	0.0768	0.073(4)[e]
C_γ—H_γ	1.0672	0.0014	1.069(4)	0.0769	0.073[e]
C_{Me}—H	1.0753	0.0011	1.076(4)	0.0785	0.075[e]
C_{Me}—H′	1.0784	0.0011	1.080(4)	0.0791	0.076[e]
C_{Me}—H″	1.0765	0.0011	1.078(4)	0.0788	0.075[e]
N...C'_α	2.3079	0.0029	2.311(5)	0.0570	0.057[c]
N...N′	2.3853	–0.0018	2.383(8)	0.0596	0.060[c]
C_α...C_γ	2.3956	0.0052	2.401(8)	0.0581	0.059[c]
C_α...C'_β	2.4155	0.0052	2.421(6)	0.0587	0.059[c]
C_β...C'_γ	2.4204	0.0011	2.422(6)	0.0584	0.059[c]
C_α...C_{Me}	2.4757	0.0096	2.485(9)	0.0765	0.077[c]
N...C_β	2.5169	0.0074	2.524(6)	0.0652	0.066[c]
P...C_α	2.5774	0.0094	2.587(5)	0.0566	0.057[c]
C_α...C'_γ	2.7703	0.0068	2.777(8)	0.0659	0.068(3)[f]
P...C_{Me}	2.7851	0.0107	2.796(7)	0.0814	0.084[f]
C_β...C'_β	2.8062	0.0031	2.809(10)	0.0661	0.068[f]
C_β...C_{Me}	3.0116	0.0132	3.025(11)	0.1170	0.119[f]
N...Cl	3.0459	0.0051	3.051(9)	0.1217	0.124[f]
C_α...Cl	3.5593	0.0206	3.580(17)	0.1803	0.1803[h]
N...C'_β	3.6062	0.0087	3.615(8)	0.0635	0.0635[h]
C_α...C'_{Me}	3.6606	0.0203	3.681(10)	0.0731	0.0731[h]
C_{Me}...Cl	3.7358	0.0292	3.77(3)	0.2570	0.2570[h]
N...C_γ	3.7462	0.0113	3.757(9)	0.0684	0.0684[h]
N...C'_{Me}	3.8075	0.0163	3.824(12)	0.0729	0.0729[h]
P...C_β	3.9122	0.0176	3.930(8)	0.0685	0.0685[h]
N...C'_γ	4.1622	0.0121	4.174(10)	0.0699	0.0699[h]
C_γ...C_{Me}	4.3987	0.0223	4.421(12)	0.1185	0.1185[h]
C_β...Cl	4.5860	0.0354	4.62(2)	0.2426	0.2426[h]
C_β...C'_{Me}	4.8598	0.0280	4.888(12)	0.0851	0.0851[h]
P...C_γ	4.9006	0.0227	4.923(11)	0.0716	0.0716[h]
C_γ...C'_{Me}	5.1503	0.0288	5.179(13)	0.1057	0.1057[h]
C_{Me}...C'_{Me}	5.2091	0.0382	5.247(17)	0.0861	0.0861[h]
C_γ...Cl	5.4307	0.0441	5.48(3)	0.2786	0.2786[h]

Parameter[a]	r_{h1}
Bond angle	
N—P—Cl	103.0(4)
N—P—N′	89.1(3)
P—N—C_{Me}	124.8(4)
C_α—N—C_{Me}	120.3(5)
P—N—C_α	112.3(2)
ε (N—C_α—C'_α)	110.3(1)
ρ (N—C_α—C_β)	129.2(3)
α (C'_α—C_α—C_β)	120.5(2)
β (C_α—C_β—C_γ)	119.0(4)
γ (C_β—C_γ—C'_γ)	120.5(2)
C_α—C_β—H_β	124(2)
C_γ—C_β—H_β	117(2)
C_β—C_γ—H_γ	117(2)
C'_γ—C_γ—H_γ	123(2)
Dihedral angle	
N—P—N′/	
N—C_α—C'_α—N′ (φ)	21.3(10)
P—Cl/N—P—N′ [g]	71.7(5)
N′—P—N—C_{Me}	±177(2)
C'_α—C_α—N—C_{Me}	±179(2)
C_β—C_α—N—C_{Me}	±2(2)
Cl—P—N—C_{Me}	±80(2)
Cl—P—N—C_α	±82(1)
P—N—C_{Me}—H	±23(2)
P—N—C_{Me}—H′	±97(2)
P—N—C_{Me}—H″	±142(2)
Relative scale factor	
K'_{LD}	1.000(9)
K'_{SD}	0.991(28)
Convergence factor[i] (%)	
R_{LD}	4.36
R_{SD}	5.89
R_{tot}	4.84

[a] For notations of the atoms and geometric parameters, see Fig. 1. The internuclear distances (r_a and r_{h1}), vibrational corrections ($r_{h1} - r_a$), and RMS vibrational amplitudes (u_{h1}) are given in Å and the angles (r_{h1}) are given in degrees. The estimates of experimental total errors given in parentheses include the least-squares standard deviations and the scale uncertainties.[44]

[b] Refined value.

[c,d,e,f] The RMS vibrational amplitudes labeled by the same letter were refined in group; in each group, the differences between the amplitudes obtained from spectroscopic calculations were retained.

[g] The angle of deviation of the P—Cl bond from the N—P—N′ plane.

[h] Fixed value.

[i] $R = 100\{\Sigma_j \omega_{jj} \Delta_j^2 / \Sigma_j \omega_{jj} [s_j M^{exp}(s_j)]^2\}^{0.5}$, where $\Delta_j = s_j M^{exp}(s_j) - K s_j M^{theor}(s_j)$ with the unity weight matrix.

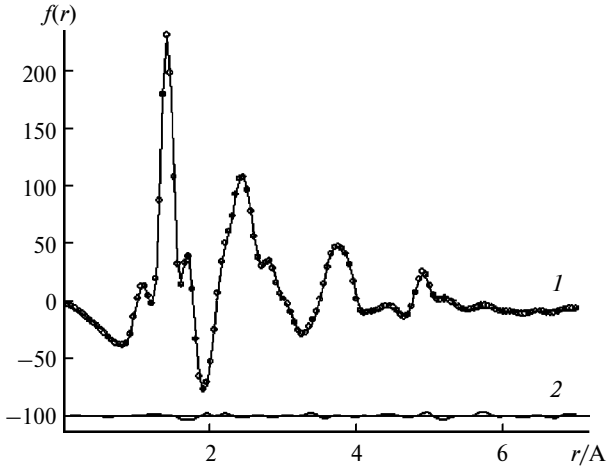


Fig. 3. Experimental (points) and theoretical (solid lines) radial distribution curves $f(r)$ (*1*) and the difference curve $\Delta f(r)$ (*2*) for molecule **1**. The damping constant was set to 0.0022 Å^2.

electron diffraction data assuming a C_s molecular symmetry. Nonlinear kinematic effects were found to have little effect on the RMS vibrational amplitudes, namely, the maximum increase in the $u_{ij,h1}$ parameters compared to those calculated in the conventional approximation ($u_{ij,h0}$) just exceeds 0.001 Å for $T = 298$ K and is less than 0.003 Å at 473 K. Taken altogether, this fact as well as the small values and weak temperature dependence of the RMS vibrational amplitudes provide an indirect evidence[1] that the small-amplitude harmonic vibration approximation is sufficient for structural analysis.

The RHF estimates of the differences between the carbon—carbon bond lengths in the benzene ring and between the C—H bonds, and of the bond angles and dihedral angles in the Me groups of molecule **1** are virtually independent of the basis set employed. As a rule, theoretical estimates of this kind are in good agreement with experimental data.[31—36,38] When performing structural analysis, the values of these parameters were set equal to those obtained from RHF/6-311G** calculations.

Table 4 presents the results of refinement of the structural parameters of molecule **1** in the harmonic r_{h1}-approximation.[45—47] Table 5 lists the estimates of the $r_{ij,h1}{}^0$ parameters for the chemical bonds in the ground vibrational state of the molecule under study, obtained using partial anharmonic corrections in the diatomic approximation,[56] $r_{ij,g} - r_{ij,g}{}^0 \simeq 1.5a_3(u_{ij,h1}{}^2(T) - u_{ij,h1}{}^2(0))$, and the $\delta_{ij,h1}{}^{vib}$ corrections for $T = 0$ K. In Table 5 we also give the estimates of the parameters of the equilibrium r_e-structure, obtained after correcting the $r_{ij,h1}$ parameters for anharmonicity and centrifugal distortion using the $\delta_{ij,anh1}{}^{vib}$ and $\delta_{ij}{}^{rot}$ values, respectively (the validity of this procedure is based on the additivity of contributions in calculations at the first-order level of perturbation theory).

The convergence factors (see Table 4) indicate good agreement between the theory and experiment and very small deviations of the varied RMS vibrational amplitudes from the calculated values. For all chemical bonds, except for the P—Cl bond, the estimates of the $r_{ij,h1}{}^0$ parameters (see Table 5) virtually coincide with the $r_{ij,h1}$ parameters. For the P—Cl bond in molecule **1**, the anharmonic correction $\delta_{ij,anh1}{}^{vib}$ (0.013 Å for $T = 298$ K) is twice as large as the corresponding value for the Me_2NPCl_2 molecule.[1] In this case, such a large difference between the $r_{ij,h1}$ and $r_{ij,e}$ parameters of the P—Cl bond can be the reason for some increase in the estimated errors of determination of the dependent distances between the Cl atom and the carbon atoms of the benzene fragment compared to the errors of determination of other distances in molecule **1** (see Table 4). Taking into account this fact, the $r_{ij,h1}{}^0$ (see Table 5) rather than $r_{ij,h1}$ value seems to be a more correct estimate of the equilibrium P—Cl bond length in molecule **1**.

Table 5. Vibrational corrections used for passage from the experimental bond lengths (r_a) in molecule **1** ($T = 473$ K) to the $r_{h1}{}^0$ parameters for the ground vibrational state and to the estimates of the parameters of the equilibrium r_e-structure, and the values of the $r_{h1}{}^0$ and r_e parameters (in Å)

Distance*	$r_{h1}{}^0 - r_a$	$r_{h1}{}^0$	$r_e - r_a$	r_e
P—Cl	−0.0056	2.178(5)	−0.0203	2.163
P—N	−0.0006	1.697(4)	−0.0038	1.694
N—C_{Me}	0.0004	1.455(6)	−0.0058	1.448
a (C_α—C'_α)	0.0020	1.404(3)	0.0059	1.408
b (C_α—C_β)	0.0013	1.383(3)	0.0021	1.384
c (C_β—C_γ)	−0.0006	1.403(3)	−0.0029	1.400
d (C_γ—C'_γ)	−0.0013	1.387(3)	−0.0025	1.386
e (N—C_α)	−0.0002	1.411(4)	−0.0030	1.408
C_β—H_β	0.0019	1.068(4)	−0.0128	1.053
C_γ—H_γ	0.0018	1.069(4)	−0.0131	1.054
C_{Me}—H	0.0016	1.077(4)	−0.0141	1.061
C_{Me}—H′	0.0016	1.080(4)	−0.0144	1.064
C_{Me}—H″	0.0017	1.078(4)	−0.0180	1.059

* For notations of the atoms and bonds, see Fig. 1.

Results and Discussion

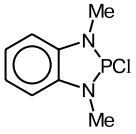
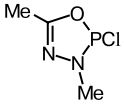
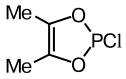
The Mills—Nixon effect due to annelation of the benzene ring and diazaphosphole ring. According to our calculations of **1** and **2**, structural manifestations of the fusion of the small rings can correspond to different relative weights of the two resonance Kekule structures in their aromatic fragments. Namely, the contribution of structure **B** dominates for molecule **1**, whereas in the case of cation **2** the major contribution comes from structure **A** (see Scheme 2). According to the gas-phase electron diffraction data for molecule **1**, annelation with the diazaphosphole ring induces a decrease in the β angle in the benzene fragment down to 119°, whereas the α and γ angles increase to 120.5° (see Table 1, *cf.* Ref. 15). The changes

in the bond angles in the benzene ring compared to the benzene molecule should be considered as the most characteristic manifestation of the Mills—Nixon effect.

Anomeric effect and equilibrium conformation of the diazaphosphole ring. The anomeric effect in the C—N—P—N chain due to the n→σ*-overlap of the LEP orbital of the N atom with the nonbonding orbital of the adjacent P—N polar bond makes the *gauche*-conformation energetically most favorable. Therefore, the diazaphosphole ring in molecule **1** must be nonplanar, since in the planar conformation these orbitals are orthogonal and the interaction between them is impossible. Puckering vibrations of the phosphorus "flap" in the five-membered heterocycle of molecule **1** determine the nonplanar deformation of this cycle and must favor the n→σ*-interaction. The results obtained indicate that the diazaphosphole ring adopts a nonplanar P-envelope equilibrium conformation, which is consistent with the concept described above. This conformation likely corresponds to a balance of the contributions of the anomeric and ring-angle strain effects, the latter increasing with the puckering deformation. We believe that the planar five-membered ring in cation **2** is stabilized by its diaminophosphenium fragment $(>N—P=N<)^+$.

In Table 6 we compare the gas-phase electron diffraction data for compounds with unsaturated five-membered heterocycles that adopt a P-envelope conformation and contain a different number of the N and O atoms bound to the P atom. The observed change in the angle of deviation of the P atom from the plane passing through the other four atoms of the ring (φ) illustrates successive weakening of the anomeric effect on going from the diaza to dioxa derivatives, which can be explained by higher electron-donating ability of the LEP of the N atom compared to that of the LEP of the O atom.

Table 6. Geometric parameters of unsaturated five-membered phosphorus-containing heterocyclic compounds (according to gas-phase electron diffraction data)

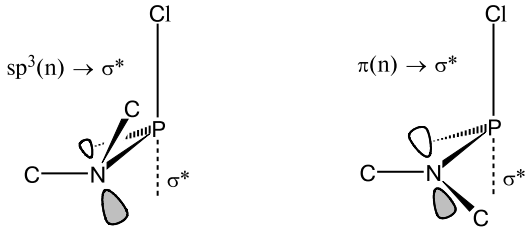
Parameter			
	(C_s), r_{h1}[a]	(C_1), r_g[3]	(C_s), r_{h1}[2]
Bond length/Å			
P—Cl	(r_{h1}^0) 2.178(5)	2.170(4)	2.101(6)
P—N	1.698(4)	1.701(6)	—
P—O	—	1.630(5)	1.633(3)
Angle/deg			
N—P—N	89.1(3)	—	—
N—P—O	—	91.1(6)	—
O—P—O	—	—	93.3(5)
P—N—C	112.3(2)	—	—
P—N—N	—	108.7(10)	—
P—O—C	—	109.3(10)	109.6(4)
N—P—Cl	103.0(4)	100.4(6)	—
O—P—Cl	—	100.9(7)	100.2(4)
φ[b]	21.3(10)	20.0(25)	18.7(8)

[a] This work.

[b] The angle of deviation of the P atom from the plane passing through the other atoms of the five-membered ring.

Anomeric effect, axial orientation of P—Cl bond, and lengthening of this bond in aminochlorophosphines. Axial orientation of P—Cl bonds is charactetistic of cyclic phosphite and aminophosphite molecules and can be considered as an analog of the *gauche*-orientation of such bonds adjacent to the P—N or P—O bonds in acyclic derivatives.[57] Higher stability of the axial orientation compared to the equatorial orientation of the P—Cl bond can be explained by the anomeric effect in the C—N—P—Cl chains. This effect favors *trans*-arrangement of the P—Cl bond relative to the LEP of each N atom of molecule **1** due to the n→σ*-overlap of the LEP orbitals of these atoms with the nonbonding orbital of the P—Cl bond. Depending on the bond configuration at the N atom, two patterns of n→σ*-conjugation can be suggested (Scheme 3); however, this does not affect the possibility of interaction.

Scheme 3



Analysis of the data listed in Table 6 shows that the P—Cl bond adjacent to the P—N bond is more lengthened than the P—Cl bond adjacent to the P—O bond. These differences between manifestations of the anomeric effect can be rationalized by higher electron-donating ability of the LEP of the N atom compared to the LEP of the O atom.

As mentioned above, lengthening of the P—Cl bond in molecule **1** can be due to not only the anomeric effect[5] but also the presence of the unsaturated ring system.[11,12] To check this possibility, we performed the RHF/6-311G** calculations* of equilibrium structures for the derivatives of phosphole ($C_2H_2(NMe)_2PCl$ (**3**)) and phospholidine ($C_2H_4(NMe)_2PCl$ (**4**)) and acyclic molecule $(Me_2N)_2PCl$ (**5**). It was found that the P—Cl bonds in the cyclic molecules **3** (2.260 Å) and **4** (2.223 Å) are ~0.01—0.05 Å longer, while that in molecule **5**

* L. S. Khaikin and O. E. Grikina, unpublished data.

(2.182 Å) is ~0.03 Å shorter than in molecule **1**. Thus, incorporation of P atom into the five-membered ring is no less important than the presence of the multiple carbon—carbon bond in this ring when analyzing changes in the P—Cl bond length.

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