

Quantum-Chemical Calculation of 1-Bis(dimethylamino)-4-bis(trimethylsilyl)-2,3-diphospha-1,3-butadiene

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Received December 11, 2002

Abstract—According to the results of *ab initio* quantum-chemical calculation 1-bis(dimethylamino)-4-bis(trimethylsilyl)-2,3-diphospha-1,3-butadiene exists as an *E*-isomer where electronic delocalization occurs involving donor dimethylamino and acceptor trimethylsilyl groups and also the multiple P=C bonds.

The spatial and electronic structure of compounds containing mono- and bicoordinate phosphorus attracted great interest of chemists since their first syntheses [1]. As heteroanalogs of classical π -systems (acetylenes, nitriles, alkenes, and imines) they possess high reactivity with respect to various classes of organic and inorganic compounds and have versatile chemical properties. The results of experimental studies concerning a wide series of these compounds both in crystals and in solution are summarized in [2, 3], and the electronic interactions involving multiple P=E bond and their role in stabilization of these systems also are treated. In particular, in phosphalkenes containing a substituent at the carbon atom with pronounced *n*-donor characteristics the np_{π} -conjugation may be relatively strong and can significantly contribute to stabilization of such substances [3]. As to the theoretical substantiation of the structures and electronic interactions existing in compounds of bicoordinate phosphorus up till recently only isolated semiempirical quantum-chemical calculations were published [4-11] which not always fit to experimental data and sometimes disagreed with each other. The nonempirical calculations are scanty and correspond to relatively simple molecules. For instance, for dimethylaminophosphalkenes H-P=C(H)NMe₂ [12] and Ph-P=C(H)NMe₂ [13], and also for halophosphalkenes R₂C=P-Hlg [14] the preference was established of conjugated structures; therewith σ, σ^* -hyperconjugation interactions significantly contribute to the electronic structure of the halophosphalkenes.

With a view to substantiate the spatial and electronic structure of 1-bis(dimethylamino)-4-bis(trimethylsilyl)-2,3-diphospha-1,3-butadiene (Me₂N)₂C¹=P²-P³=C⁴(SiMe₃)₂ (**I**) we carried out *ab initio*

quantum-chemical calculation of the substance and of five model compounds with isolated multiple C=P bonds or with an ordinary P-P bond (compounds **II-IV**). The suggestion that in compound **I** exist an intramolecular electronic interaction of a direct polar conjugation type was first made in [15-17] relying on ¹H, ¹³C, ²⁹Si, ³¹P NMR spectra and dipole moments. The calculation of dipole moment of the diphospha-butadiene **I** by the vector-additive procedure revealed [16, 17] a large exaltation of the experimental and the calculated dipole moments ($\Delta\mu$ equaled to 2.16 D corresponding to electron transmission from the donor C¹N₂ to the acceptor C⁴Si₂ center, Δq 0.17 atomic charge unit). This result could not be understood without invoking a concept of a π -electron delocalization in the molecule **I**. Note that the exaltation value was calculated with accounting for the slight noncoplanarity of the diene system C=P-P=C in the molecule found in the crystalline state [9]. Besides molecules of phosphalkenes (Me₂N)₂C=P-H and *t*-Bu-P=C-(SiMe₃)₂ were considered as models where all the possible electronic interactions of donor dimethylamino and acceptor trimethylsilyl groups with the double bonds C=P were already allowed for. Thus the revealed in [16, 17] additional transition of charge from the P² to the fragment C⁴Si₂ in the P²-P³=C⁴(SiMe₃)₂ moiety amounted to 0.11 atomic charge unit. This is fairly significant value, although half as that in the molecule of compound **II**, H-P=C(NMe₂)₂ (Δq 0.2 a.c.u.). This fact is manifested in the experimental structural parameters of diphospha-butadiene **I** [9]: the electronic interactions sufficiently strongly affect the geometry of just a half of the molecule (elongation of P²=C¹ bond up to 1.78, shortening of C_{sp²}-N bonds up to 1.36, and shortening of P²-P³ bond up to 2.15 Å) and do not almost show up in the P³=C⁴Si₂ fragment. It

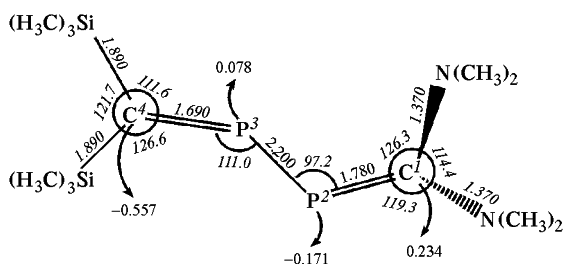


Fig. 1. Geometrical parameters and charge distribution in the molecule of diphosphabutadiene **I**.

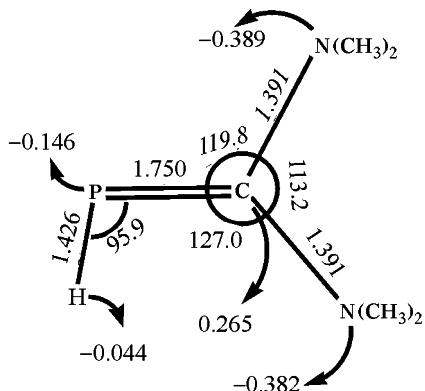


Fig. 2. Geometrical parameters and charge distribution in the molecule of phosphalkene **II**.

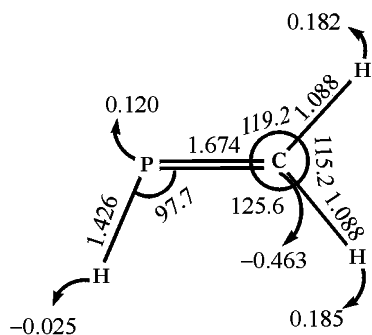


Fig. 3. Geometrical parameters and charge distribution in the molecule of phosphalkene **III**.

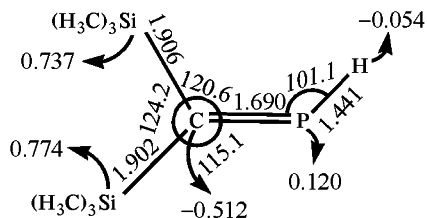


Fig. 4. Geometrical parameters and charge distribution in the molecule of phosphalkene **IV**.

is well known that the Me_3Si group unlike the isostructural Me_3C group is an acceptor by its overall electronic effect with respect to a π -system [18, 19]. It is also presumed in [19] that the resonance structure

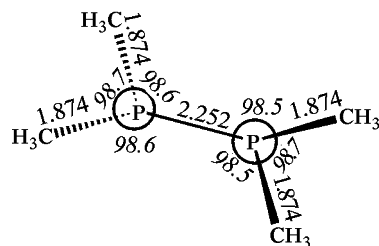


Fig. 5. Geometrical parameters in the molecule of diphosphine **V**.

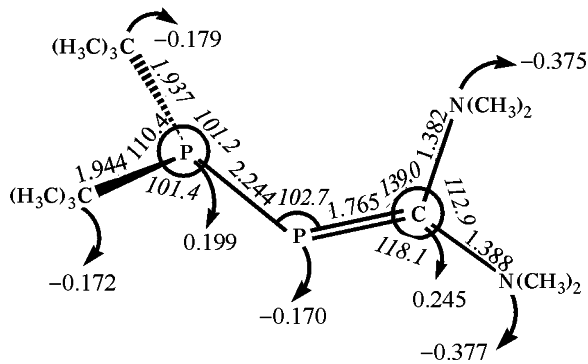
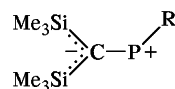


Fig. 6. Geometrical parameters and charge distribution in the molecule of phosphorus-substituted phosphalkene **VI**.

shown below makes a significant contribution into the ground state of the molecules of the following type:



Chernega *et al.* [9] relying on semiempirical calculations (MNDO) of diphosphabutadiene **I** molecule and on deviation from the planar structure of the main molecular skeleton (deviation from a plane was 0.12 Å) questioned the conclusion made in [16] and inferred that in this system the P-P bond was a barrier to the direct polar conjugation. Therewith in contrast to the X-ray analysis in [9] the quantum-chemical calculations of the authors described the $\text{SiC}=\text{P}-\text{P}=\text{C}$ moiety as a planar structure. Recently [20] a nonempirical quantum-chemical (RHF/6-31G^{*}) investigation was carried out on a series of model 2,3-diphospha- and 2-aza-3-phosphabuta-1,3-dienes, and the ^{13}C , ^{15}N , and ^{31}P NMR spectra were measured for compounds of similar structures. Unlike the conclusion made in [9] Rozhenko *et al.* [20] believe that in the systems $(\text{H}_3\text{Si})_2\text{C}=\text{P}-\text{X}=\text{C}(\text{NH}_2)_2$ where $\text{X} = \text{P}, \text{N}$ exists a π -electron delocalization. The same conclusion was actually made by Chernega *et al.* [21] for 4,4-bis(dimethylamino)-1-(2,4,6-tri-*tert*-butylphenyl)-1-aza-2,3-diphosphabuta-1,3-diene.

Our *ab initio* calculations of compound **I** showed that the global energy minimum corresponded to *E*-configuration of the molecule which is the most favorable for electronic interactions. Therewith the energy difference (ΔE) between the *trans*- and *gauche*-isomers (torsional angle 65.2 deg) was sufficiently large (9.17 kcal mol⁻¹). According to the data of calculation compound **I** cannot exist as *Z*-isomer because of steric hindrances from methyls belonging to dimethylamino and trimethylsilyl groups. The bond system C¹=P²-P³=C⁴ is virtually planar: the torsional angle equals to 3.6 deg.

The geometrical parameters obtained by calculation are presented in Fig. 1. The calculated parameters for compounds **II-VI** are compiled on Figs. 2-6. Although the lengths of double bonds in molecule **I** obtained by calculation are somewhat longer than the data from X-ray diffraction study [9], they fit into the range (1.674-1.790 Å) calculated for model compounds **II-VI**. The bond C¹=P² (1.780 Å) is even longer than that in compound **VI**, and the bond P²-P³ is shorter (2.200 Å) than the corresponding bond in diphosphine **V** (2.252 Å) and phosphorus-containing phosphalkene **VI** (2.244 Å).

The trend to elongation of the C=P bond at the donor end of the molecule and the shortening of the central P-P bond as compared with the model compounds containing an ordinary P-P bond are clear enough and testify to the transmission of the electron density throughout the whole molecule of compound **I**, although the data of the X-ray analysis indicate that it virtually does not affect the geometrical parameters of the acceptor end of the molecule. The same trend was found in [20] at calculation by Hartree-Fock method of a simplified analog of compound **I** (all methyl groups were replaced by hydrogen atoms). The greater bond lengths calculated in compound **I** as compared to the X-ray analysis data and the non-empirical calculations [20] may be due to the following reasons: firstly, the calculations concern an isolated molecule in the gas phase; secondly, it may be inherent to B3LYP method. The Hartree-Fock procedure [20, 21] is known to systematically underestimate the bond lengths. But the hybrid procedure B3LYP (among the methods of density functional theory) reproduces the most characteristics of molecules with the greatest accuracy (geometrical parameters included) [22]. This was the reason why we adhered just to this procedure. We made an assessment of the B3LYP method for calculation of geometrical parameters of compounds with presumable electron delocalization, and the test showed that we made a correct choice. Below are compiled the

bond lengths in the molecules of ethylene and 1,3-butadiene (the data for ethane are also given for the sake of comparison). In ethylene $r(\text{C}=\text{C})$ 1.331 Å; in ethane $r(\text{C}-\text{C})$ 1.531 Å; in *cis*-1,3-butadiene $r(\text{C}=\text{C})$ 1.330 Å and 1.339 Å, $r(\text{C}-\text{C})$ 1.470 Å; in *trans*-1,3-butadiene $r(\text{C}=\text{C})$ 1.341 Å and 1.341 Å, $r(\text{C}-\text{C})$ 1.450 Å.

As to the charge distribution in the molecule of compound **I**, on the carbon atom linked to the donor dimethylamino groups is located a positive charge, whereas on the carbon bonded to acceptor trisilylmethyl groups resides a negative charge (Fig 1). The similar pattern is observed in compounds **II-IV, VI** (Figs. 2-4, 6). Thus together with the data on the change in calculated bond lengths in compounds under study the charge distribution also evidences the electron delocalization in the bond system of diphosphabutadiene **I**, and the calculation data are well consistent with existing experimental data [16, 17].

All calculations were carried out with the use of Gaussian 98 software [23] by nonempirical method of density functional B3LYP employing basis set 6-31G(d) [each internal orbital was described by six Gauss type functions (GTO), valence 2s-AO by 3 GTO, and valence p-AO by one GTO; to each p-function a polarization d-GTO was added]. The correspondence to minima of the stationary points found was in every case proved by calculation of the second derivative. The calculations were carried out on a computation cluster of 11 Athlon 1200 processors (in Kazan State Technological University) and on a cluster of 9 Compac Alpha DS 10L and DS 20E processors (Institute of General and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences).

The study was carried out under financial support of the Russian Foundation for Basic Research (grant no. 00-5-97424) and Russian Ministry of Education (grant no. UR 05.02.016).

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