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#### STABILIZATION OF POLYHETEROATOMIC AZA AND PHOSPHA ANALOGS OF CYCLOBUTADIENE AND BENZENE

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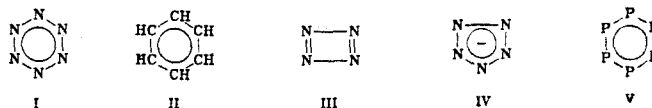
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A method is proposed for the stabilization of polyheteroatomic rings consisting only of nitrogen or phosphorus atoms by introduction of acceptors of the unshared electron pair of the heteroatom, particularly oxygen atoms, with the formation of oxide forms. The positions of introduction of the acceptor groups into four- and six-membered rings were determined. The conclusions drawn were confirmed by calculations by the MNDO method of tetrazete 1,3-dioxide and 1,3-ylid and hexaphosphorine 1,3,5-trioxide and 1,3,5-ylid.

An aromatic cyclic conjugated system in which the ring is formed by different heteroatoms may be stable. Borazine is a characteristic example [1, 2]. However, conjugated rings formed by heteroatoms of the same element are unstable [3, 4], and the possibility of their experimental detection frequently raises doubts.

The polyheteroatomic aza and phospho analogs of cyclobutadiene and benzene have  $\pi$ -electron systems that are similar to the  $\pi$  systems of cyclobutadiene  $(CH)_4$  and benzene  $(CH)_6$ . Nevertheless, despite the closeness of the  $\pi$ -electron energies of the resonance of hexazine  $N_6$  (I) and benzene  $(CH)_6$  (II) [5], hexazine is exceptionally unstable, and doubts regarding its synthesis [6] were raised on the basis of the results of nonempirical calculations, which indicate the considerably higher (as compared with hexazine) stability of the acyclic  $N_6$  structure [7, 8] (also see [5] and the literature cited therein). It is assumed that the experimental detection of tetrazete  $N_4$  (III) [9] and the pentazole anion  $N_5^-$  (IV) [10, 11] is realizable only in the form of organometallic complexes. Nonempirical calculations [12], according to which the activation barrier of its cyclodecomposition to three  $P_2$  molecules is 54 kJ/mole, provide evidence for the possibility of the experimental detection of hexaphosphorine  $P_6$  (V) in an inert matrix at low temperatures.

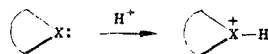
Scientific-Research Institute of Physical and Organic Chemistry, M. A. Suslov Rostov State University, Rostov-on-Don 344071. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 2, pp. 250-255, February, 1988. Original article submitted August 19, 1986.



### Ways of Stabilizing $X_4$ and $X_6$ Molecules ( $X = N, P$ )

The destabilizing effect of the unshared electron pairs is the chief reason for the instability of the systems under discussion. The orbitals in which these electrons are located are high-lying orbitals, whereas in the hydrocarbon analogs these MO are stabilized as a consequence of the formation of C-H bonds [4, 13, 14]. A way of stabilizing such compounds follows from this.

The protonation of even some of the heteroatoms in the ring is electrostatically unfavorable in view of the charge accumulation and does not lead to stabilization of the molecule.

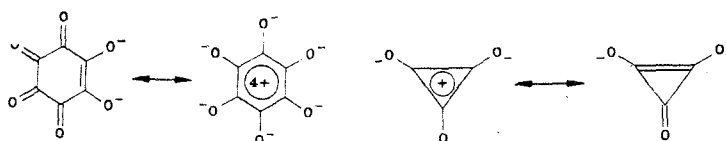


In this connection, the formation of bonds of the semipolar type - ylids, N- or P-oxides, and N-imines - seems more acceptable. It is apparent that the introduction of a  $\sigma$  acceptor of the unshared electron pair such as, for example, the oxygen atom will lead to stabilization of the conjugated heteroring.



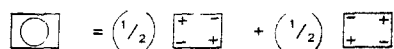
In fact, it is known that, with respect to its structure, pyridine N-oxide is more similar to benzene than pyridine itself: the ring angles deviate only slightly from  $120^\circ$ , and the C-N bond is longer than in pyridine [15]. The length of the N-O bond in pyridine N-oxide is shorter than the length of the same bond in, for example, trimethylamine oxide. This constitutes evidence for feeding of electrons into the  $\pi$  system of the ring by oxygen.

The formation of N(P)-oxides for all of the ring heteroatoms would not lead to substantial stabilization as a consequence of the significant separation of charges on the ring atoms and the endocyclic oxygen atoms with localization of the large positive charge in the ring. The decrease in the contribution of the ionic resonance form in dianions of oxocarbons with an increase in the ring charge serves as an example of the disadvantageousness of an increase in the formal charge of the ring [16]:



Consequently, only some of the ring atoms should be converted to the ylid, oxide, or imine form. In other words, taking into account the above-noted significantly higher stability of heterorings formed by different heteroatoms as compared with rings consisting of heteroatoms of the same element, in forming this form we will actually make the ring atoms different with respect to their electron properties without changing the type of hybridization of the AO.

The choice of the ring heteroatoms to be converted to, for example, the oxide form can be made on the basis of the "ionic" [17]  $\pi$ -electron models of cyclobutadiene and benzene:



It is apparent that the formation of the 1,3-dioxide forms of the aza and phospho analogs of cyclobutadiene and the 1,3,5-trioxide forms of hexazine and hexaphosphorine should lead to stabilization. In accordance with the rule of Dewar and Longuet-Higgins (for example, see [18]), the corresponding hydrocarbons - 1,3-dimethylenecyclobutadiene and 1,3,5-trimethylenebenzene - should have, within the framework of Hückel MO theory, two and three nonbonding  $\pi$  MO, respectively. In particular, this is responsible for the instability of 1,3-dimethy-

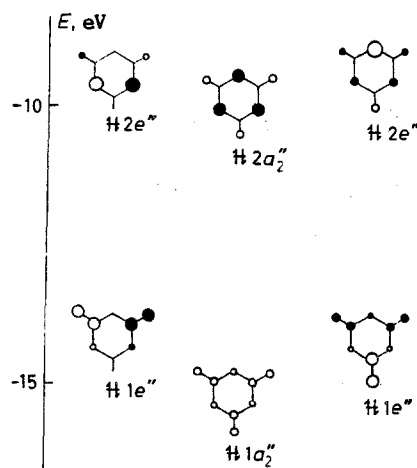
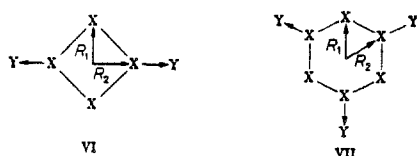
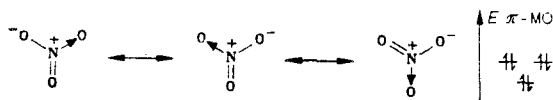


Fig. 1.  $\pi$  MO of hexaphosphorine 1,3,5-trioxide (IX) calculated by the MNDO method.

lenecyclobutadiene, the ground state of which is a triplet ( ${}^3B_{2u}$ ) [19]. However, in the N(P)-ylids or N(P)-oxides of heterorings VI and VII the nonbonding  $\pi$  MO will be completely filled with electrons provided by methylene groups or oxygen atoms and will be stabilized as a consequence of the significant electronegativity of the ring heteroatoms. The result of the decrease in the repulsion of the unshared electron pairs in the formation of ylid, oxide, or N-imine forms should be that the heteroatoms bonded to oxygen will be found closer to the center of the ring than the heteroatoms that have retained the unshared pair (i.e.,  $R_1 > R_2$ ).



System VII can be regarded as an analog of the carbonate ion, which is stabilized as a consequence of Y-aromatic character, or the isoelectronic nitrate ion [20], in which the central carbon (nitrogen) atom is replaced by a heteroatomic conjugated ring.

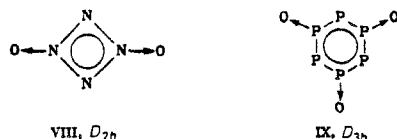


### Tetrazete 1,3-Dioxide and Hexaphosphorine 1,3,5-Trioxide

As examples of the stabilization of azaheterocycles and phosphaheterocycles, respectively, we examined tetrazete III and hexaphosphorine V.

Only the corresponding monoheterosubstituted azete [21] and phosphorine [22] have been experimentally studied.

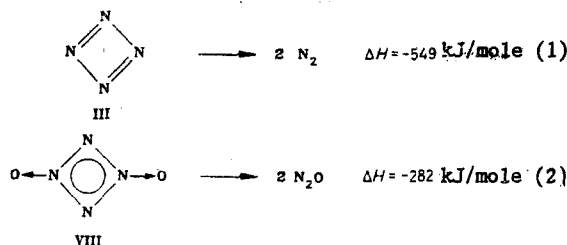
For the calculations we used the MNDO method [23], which in quantum-chemical investigations of aza-substituted cyclobutadiene and benzene leads to results that are in agreement with the results of nonempirical calculations (see [5] and the literature cited therein). The results of calculations by the MNDO method of  $P_n$  molecules and phosphorus oxides are also satisfactory [24].



Calculations of tetrazete 1,3-dioxide (VIII) showed that the minimum on the potential energy surface (PES) corresponds to the  $D_{2h}$  structure ( $\Delta H_f = 540.9$  kJ/mole,  $q_{N_1} = 0.367$ ,  $q_{N_2} = -0.263$ , and  $q_o = -0.104$ ) without the alternation of the lengths of the bonds in the ring that

is peculiar to tetrazete [5] as an antiaromatic compound [25]. As we assumed,  $R_1$  (102.4 pm)  $>$   $R_2$  (93.1 pm); this confirms the decrease in the destabilizing effect of the unshared pairs in the formation of the N-oxide.

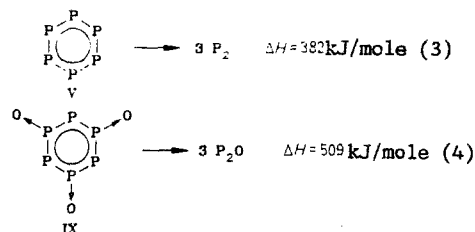
The instability of tetrazete (III) and hexazine (I) is associated chiefly [14, 26, 27] with the ease of ring destruction to give nitrogen molecules, and the heats of ring-destruction reactions (1) and (2) were therefore calculated by the MNDO method for comparison of the stabilities of tetrazete (III) and tetrazete 1,3-dioxide (VIII); the  $\Delta H_f(N_2O)$  and  $\Delta H_f(N_2)$  values calculated by the MNDO method were taken from [28]:



According to the calculations, hexaphosphorine 1,3,5-trioxide (IX) has the  $D_{3h}$  structure without alternation of the lengths of the bonds in the ring ( $\Delta H_f = -87.6$  kJ/mole,  $R_{pp} = 196.9$  pm,  $R_{pO} = 146.8$  pm,  $q_{p1} = 0.419$ ,  $q_{p2} = -0.097$ , and  $q_o = -0.322$ ), which corresponds to the minimum on the PES. As we assumed,  $R_1$  (206.7 pm)  $>$   $R_2$  (185.3 pm).

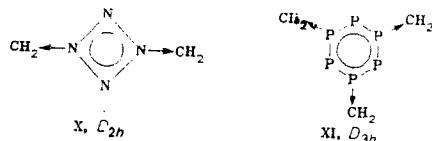
Of the three nonbonding (within the framework of the Hückel method)  $\pi$  MO in calculations by the self-consistent field (SCF) method only two turn out to be degenerate; all three of these MO are, as a consequence of the stabilizing effect of the oxygen atoms, bonding orbitals (Fig. 1). The system of bonding  $\pi$  levels in IX consists of two filled (by aromatic sextets of electrons) subsystems - three bonding  $\pi$  MO  $1a''_2$  and  $1e''$ , analogous to the  $a_{2u}$  and  $e_{1g}$  orbitals of benzene, and three  $\pi$  MO  $2a''_2$  and  $2e''$ , which form a subsystem of levels corresponding to the  $\pi$  levels of a  $\gamma$ -aromatic molecule [20] in which the central atom is replaced by the heteroring.

A comparison of the heats of ring-destruction reactions (3) and (4) actually attests to the greater stability of hexaphosphorine 1,3,5-trioxide; the  $\Delta H_f$  values of hexaphosphorine  $P_6$  (V),  $P_2$ , and  $P_2O$  calculated by the MNDO method were taken from [24]:



#### Tetrazete 1,3-Diylid (X) and Hexaphosphorine 1,3,5-Triylid (XI)

Calculations of X and XI led to results that were similar to those obtained for oxides VIII and IX.



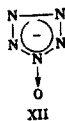
Structures X and XI correspond to the minima on the PES. The alternation of the lengths of the bonds in the ring that is peculiar to tetrazete is absent in diylid X. For this compound  $\Delta H_f = 648.5$  kJ/mole,  $R_{NN} = 137.8$  pm,  $R_{NC} = 131.3$  pm,  $R_{CH} = 109.1$  pm, and  $R_1$  (100.8 pm)  $>$   $R_2$  (93.9 pm). A comparison of the heats of ring destruction of tetrazete (III) and tetrazete 1,3-diylid (X) calculated by the MNDO method provides evidence for greater stability of the latter (the  $\Delta H_f$  value for diazomethane calculated by the MNDO method was taken from [29]):



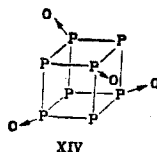
For triylid XI,  $\Delta H_f = 322.2$  kJ/mole,  $R_{pp} = 196.5$  pm,  $R_{pc} = 158.5$  pm,  $R_{ch} = 108.5$  pm, and  $R_1$  (208.1 pm)  $>$   $R_2$  (182.3 pm). A comparison of the heats of ring destruction of hexaphosphorine (3) and the corresponding ylid XI also indicates the higher stability of the ylid.



Thus the calculations confirm the proposed ways of stabilizing the  $X_n$  ring ( $n = 4, 6$ ). It might be assumed that one will be able to stabilize tetraphosphete  $P_4$ , hexazine  $N_6$  (I), and systems of the type of the pentazole anion  $N_5^-$  (IV) in, let us say, the form of oxide XII in the same way:



In addition, a similar way of stabilization may prove to be effective also for polyhedral systems such as, for example, cubic structure  $P_8(O)_8$  (XIII), which, according to the results of nonempirical calculations [30-33], corresponds to the minimum on the PES of  $P_8$  but is thermodynamically unstable relative to decomposition into two  $P_4$  molecules ( $T_d$  structure). However, the XIII molecule is more stable than  $4P_2$  [33]. This provides a basis for the assumption that the experimental detection of a compound with a  $P_8$  carcass in the form of tetroxide XIV is possible.



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NEW HETEROCYCLIC SYSTEM - BIS[1,2,3-BENZOTRIAZOLO[5,6-b;5',6'-k]]-

18-CROWN-6

É. I. Ivanov, A. A. Polishchuk,  
and P. B. Terent'ev

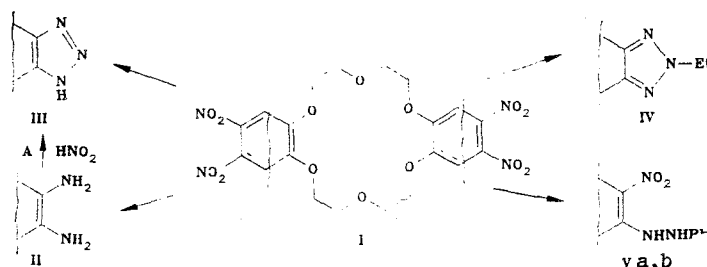
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It was shown that 1,2,3-triazole derivatives are formed in the reaction of tetranitrodibenzo-18-crown-6 with excess hydrazine or ethylhydrazine in DMSO, while the reaction with phenylhydrazine leads to isomeric products of nucleophilic substitution of the nitro group.

Substituted dibenzo-18-crown-6 compounds are fungicides and plant-growth regulators [1, 2]. Derivatives of crown ethers that fragmentarily include thiazole, imidazole, 2,1,5-oxadiazole, pyridine, pyrazine, pyrimidine, and 1,4-diazepine rings were described relatively recently [3-6]. Substances that have ergotropic and bactericidal activity have been found among the synthesized compounds [5, 6].

In attempts to obtain triazole derivatives of the III type we found that it was necessary to reject the traditional method of synthesis (scheme A), since the corresponding tetramine II could not be isolated. The formation of a vis-triazole ring, which is based on the reaction of hydrazine and 5,6-dinitrobenzimidazoles [7], has not been widely used in the arene series, since 1,2-dinitrobenzenes are less accessible than the corresponding o-phenylenediamines. On the other hand, tetranitrodibenzo-18-crown-6 (I) can be easily obtained [8], and this makes the scheme presented below suitable for the synthesis of bistriazole analogs of crown ethers.

The corresponding bis(1,2,3-benzotriazole) derivative III was obtained by the reaction of crown ether I with excess hydrazine hydrate in DMSO at room temperature. Under these conditions the reaction of I with ethylhydrazine leads to 2H-benzotriazole derivative IV, while nucleophilic substitution products Va, b are formed with phenylhydrazine.



The formation of isomeric V, which contains 2-phenylhydrazino groups in the 2.14 or 2.13 positions of the crown ether, constitutes evidence that the reaction does not proceed regioselectively and in a stepwise manner; the initial step is replacement of a nitro group by a hydrazine residue. The ease of formation of a cyclic compound in this case evidently depends on the basicity of the nitrogen atom of the hydrazine fragment.

Three absorption bands at 238-242, 300-324, and 335-445 nm appear in the UV spectra of the synthesized compounds. The first two bands correspond to excitation of the aromatic

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