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Ab Initio Calculations on 1,3,2-Diazaphospholes: New Heteroaromatic Systems

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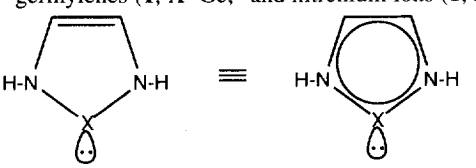
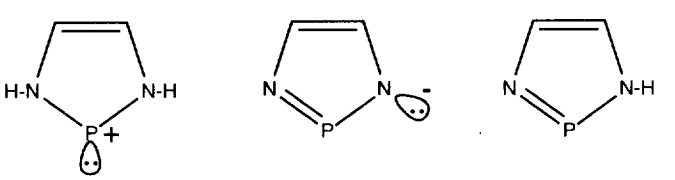
Abstract: *Ab initio* calculations on three 1,3,2-diazaphosphole derivatives [(MP2/6-31G(d,p)] gave rise to structural and energetic data that are interpreted in context of aromaticity. The 1,3,2-diazaphospholenium ion is shown to have a degree of aromatic stabilization energy (24.0 kcal/mol) comparable to that of pyrrole. Cyclic delocalization is supported by analysis of computed charge distribution data, natural bond orbital data, bond lengths, and magnetic susceptibility data. © 1997, Elsevier Science Ltd. All rights reserved.

The resurgence of interest in aromaticity[1] has led to numerous experimental and computational studies of heterocyclic 6 π systems containing combinations of one or more atoms of nitrogen, oxygen, silicon, and germanium.[2-7] Energetic and structural considerations have shown that geminal trivalent nitrogen atoms are particularly effective at propagation of cyclic π interactions through adjacent vacant p-orbitals as symbolized by **1a <-> 1b**. The resulting systems range from carbenes (**1**, X=C)[2,3,5,6] or carbene analogs to cations, and include silylenes (**1**, X=Si),[4,5,6] germylenes (**1**, X=Ge,[5] and nitrenium ions (**1**, X=N^+).[7]

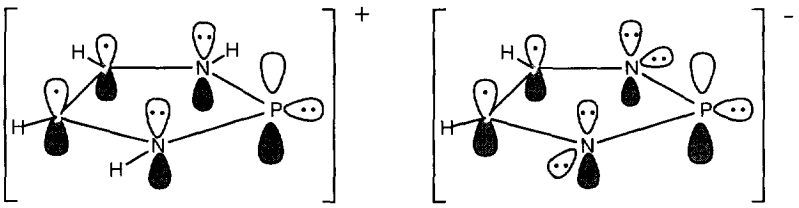


1a **1b**

In contrast, few related studies have been carried out involving cyclic phosphorous compounds. Although acyclic bis-aminophosphenium ions have been known for some time and some salts have been isolated or examined by NMR spectroscopy,[8] the potentially aromatic heterocyclic 6 π system **2** has not been reported. The work of Schmidpeter *et al.* has revealed a rich variety of experimental chemistry for some 1,3,2-diazaphospholes that involves derivatives of the structures **3** and **4**.[9] Since some of this chemistry can be interpreted to include analogs of **2**, we undertook a computational study of the energetics and structures of these systems. Our results speak to the properties and inter-relationships of **2**, **3**, and **4** their aromaticity as implied by the orbital representations **2a** and **3a**.

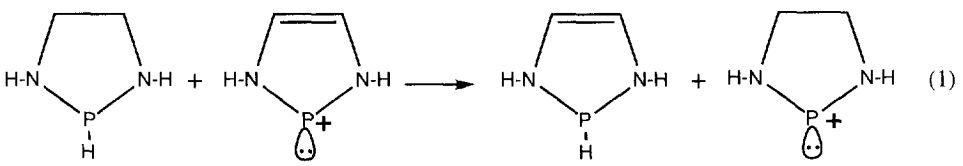


2 **3** **4**



2a **3a**

Discussion. Our first objective was to evaluate criteria relating to the "aromaticity" of **2**. Schleyer, *et al.*[1b] have previously established linear correlations between aromatic properties and computed energetic, structural, and magnetic properties of five-membered heterocycles. In this study we utilize the aromatic stabilization energy (ASE)[1b] of **2** as a gauge of its aromaticity since comparison with more conventional aromatic systems, *e.g.* furan, pyrrole is straightforward. To this end we used the isodesmic comparison shown in eq. 1, analogous to



5 **2** **6** **7**

our treatment of related carbenes.[2] The change in energy for this reaction corrected for zero point energy differences is defined as the ASE and was calculated at the MP2/6-31G(d,p) level from the data in **Table 1**. The result, +24.0 kcal/mol, compares favorably with the ASE calculated for furan (20.3 kcal/mol) and pyrrole[2] (25.7 kcal/mol) and is of the same order of magnitude as that calculated[2,5,7] for imidazol-2-ylidene (**1**, X=C): 21.2-27.8 kcal/mol.

Table 1. Total Energies

Molecule	Point Group	energy (hartrees)	zero point energy (hartrees)	Sum of Electronic-Thermal energy 298.15 Kelvin (hartrees)
2	C2v	-528.1885145	0.069970	-528.145164
3	C2v	-527.2400327	0.042654	-527.223761
4	Cs	-527.8126662	0.056174	-527.783672
5	C1	-530.1643894	0.103004	
6	C1	-528.9486880	0.076409	
7	C1	-529.3636120	0.094213	

Additional support for the concept of cyclic delocalization implied by the orbital picture **2a** is provided by examination of the natural molecular orbitals obtained from a natural bond orbital calculation (NPA).[10b] The calculated 3pπ electron density on phosphorous was 0.94 or about 79% of the π occupancy for a perfectly delocalized system.

N-P-N bond angles (**Table 2**) varied from 86.4° to 98.4° due to molecular constraints imposed by the ring size. For comparison with **2** and **7**, we examined the diaminophosphenium ion [NH_2–P^+–NH_2] at the

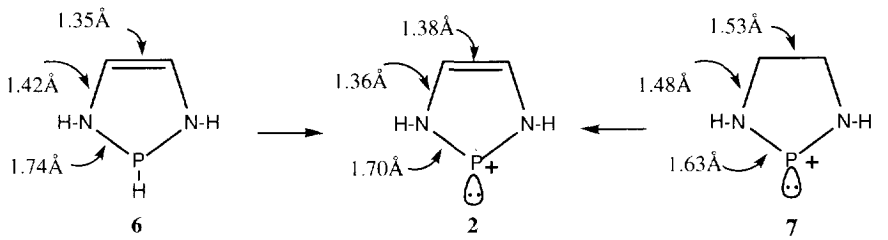
same computational level and found a value of 104.1°.[11] Experimental values for salts vary from 114.8° to 117.0°.[8a,b]

Table 2. Select Molecular Bond Angles

Angle (Degrees)	2	3	4[a]	5	6	7
Θ(N-P-N)	86.4	98.4	92.3	95.2	87.7	92.6
Θ(P-N-C)	116.5	105.6	111.4(111.0)	110.4	108.3	116.1
Θ(N-C-C)	110.3	115.2	109.7(115.5)	106.7	111.9	104.7

[a] Values in parentheses are for Θ(P=N-C) and Θ(=N-C-C), respectively.

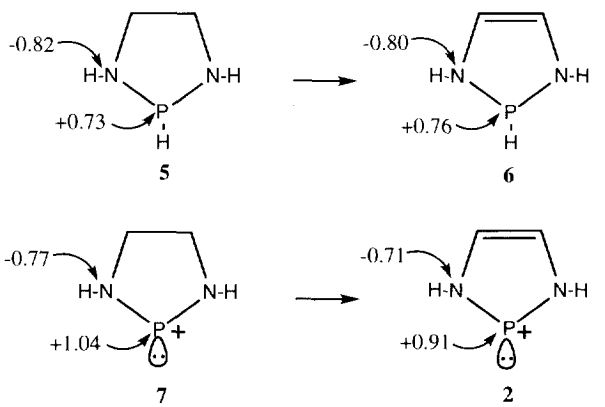
Bond length and atomic charge data is discussed in the sequel in the context of aromaticity. Our thesis is that the onset of aromaticity should result in longer double bonds and shorter single bonds on incorporation of the double bond into the diazaphospholines *vs* the diazaphospholes. This criterion is satisfied by the data shown in **Scheme 1**. Conversion of **6** to **2** results in longer a C=C bond and shorter P-N and N-C bonds. Similarly, the conversion from **7** to **2** results in a significantly longer P-N bond.[11]



6 **2** **7**

Scheme 1

An alternative analysis takes into consideration charge distribution changes caused by the onset of aromaticity. Here, we expect that dispersal of charge on phosphorous would characterize aromatic *vs* non-aromatic models. Comparisons of charges among the four systems as shown in **Scheme 2**.



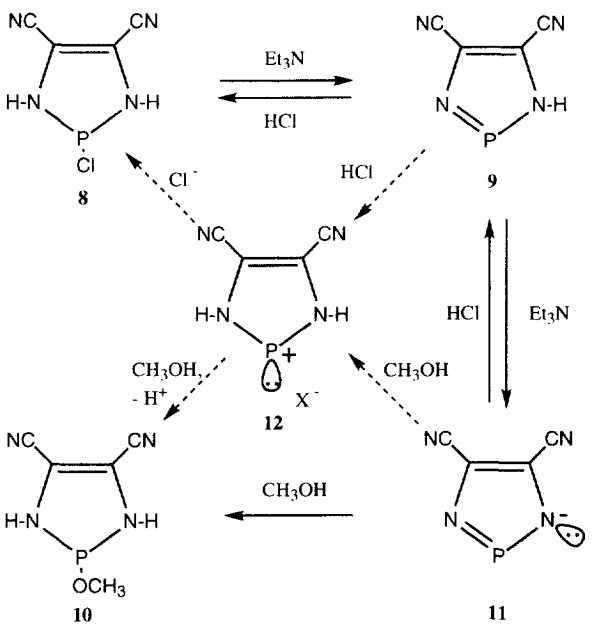
5 **6**

7 **2**

Scheme 2

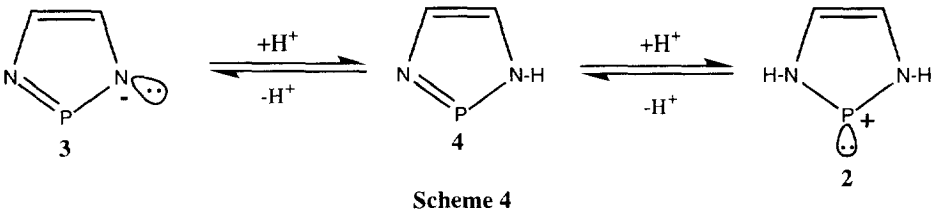
By way of reference, the calculated charge on phosphorous becomes slightly more positive (+0.73 *vs.* +0.76) in the diazaphosphine series on introduction of the double bond (**5**->**6**). In the phosphenium series, however, the same change (**7**->**2**) leads to a substantial *decrease* in charge at phosphorous (1.04 *vs.* 0.91), a consequence that we attribute to delocalization.

Some of the experimental results reported by Schmidpeter *et al.*[9] can now be conveniently rationalized by way of a diazaphosphenium ion intermediate. These workers observed the interconversions of the dicyano systems **8, 9, 10, 11** shown in **Scheme 3**, but did not invoke cationic intermediates. In view of the expected stability of **2**, it is likely that formation of **8** from **9** proceeds *via* N-protonation of **9** by HCl to form phosphenium ion **12** (X=Cl^-), followed by its capture by chloride ion. Similarly, addition of methanol to **11** probably involves proton transfer to form **12** (X=CH_3O^-) followed by attack of methanol at phosphorous although a highly concerted attack by methanol with proton transfer to produce **10** in one stage cannot be excluded.



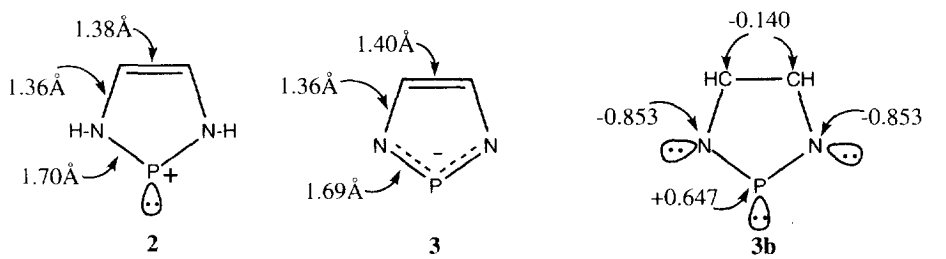
Scheme 3

In view of the importance of the related intermediates **9** and **11** in the above **Scheme**, we extended this study to include the properties of the unsubstituted analogs: 1,3,2-diazaphospole **4** and the negatively charged 1,3,2-diazaphospholide **3.** Each of these systems contains a cyclic 6-π system and it was of interest to examine their various aspects of their structures and the proton affinities of the conjugate bases for comparison with related heterocycles (**Scheme 4**).



Scheme 4

A comparison between the calculated structures of the diazaphospholenium ion **2** and the diazaphospholide **3** reveals a remarkable similarity in geometry suggesting that delocalization is an important property of both systems. Furthermore, the charge distribution of **3** calculated by a NPA routine revealed significant delocalization in the phospholide (**3b**).[10b] By the same method, the calculated 3pπ electron density on phosphorous was 1.15 or about 98% of the π density expected for a perfectly delocalized system. Phospene **4** has more conventional double and single bond character bond lengths (N-P = 1.72Å; N=P, 1.65Å; C=C, 1.38Å; N-C 1.36, 1.37Å).



We also examined the basicity of **3** and **4** by calculation of proton affinities (PA).[12] This parameter is a measure of the affinity toward protons and nucleophilicity in general and in this context is defined by the free energy changes for the following reactions:

4 + H^+ ⟶ **2** PA = 226.2 kcal/mol

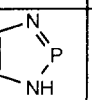
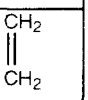
3 + H^+ ⟶ **4** PA = 350.8 kcal/mol

By this criterion, **4** is a rather weak base comparable in its PA to both dimethylamine (223 kcal/mol)[13] and imidazole (PA=228 kcal/mol).[3a] Not surprisingly, **3** is a rather strong base being anionic and is not expected to be significantly deprotonated by triethylamine. Although the base strength of **11** is would be diminished by combined effects of the two cyano groups in Schmidpeter's systems, the effects can be attributable solely to inductive electron withdrawal since the n-orbital containing the negative charge and the π systems are orthogonal. In view of this, the disparity in expected base strength between **11** and triethylamine is expected to be very large and the formation of **11** under these conditions appears to be problematic.

Another important criterion of aromaticity is the anisotropy of magnetic susceptibility ($\Delta\chi_{anis}$).[1a-c,14-16] Briefly, the tensor normal to a planar aromatic ring is expected to be much larger than the average of the in-plane tensors as a consequence of field-induced ring currents.[14b] This effect gives rise to the experimental observations that aromatic molecules display large negative $\Delta\chi_{anis}$ (deshielding) and anti-aromatic systems

display positive $\Delta\chi_{anis}$ (shielding). The unusually low field chemical shifts of aromatic protons represent the most common manifestation of this effect. In this context, we explored the use of density functional methods in combination with the individual gauges for atoms in molecules method for computation of magnetic susceptibilities.[15] We first established that reliable predictions can be made by comparisons $\Delta\chi_{anis}$ calculated using this IGAIM/Becke3LYP/6-311+G(d,p)//Becke3LYP/6-31G(d,p) protocol with data obtained by others using IGLO methods.[16] The results of these comparisons and data for **2**, **3**, **4** and **7** are shown in **Table 3**.

Table 3. Anisotropy of Magnetic Susceptibility ($\Delta\chi_{anis}$ in ppm, cgs)

					 **13**	 **14**
Calculated[a] $\Delta\chi_{anis}$	-39.8	-45.0	-67.5	-30.8	-40.7	-13.5
Calculated[b] $\Delta\chi_{anis}$	-36.2[1c]	-41.8[1c]	-63.4[16a] -62.9[1c]	-30.5[17]	-27.7[5] -38.8[6]	-9.0[5] -14.1[6]
	 **2**	 **7**	 **3**	 **4**	 **15**	 **16**
Calculated[a] $\Delta\chi_{anis}$	-45.0	-7.56	-50.6	-50.9	-2.64	-8.11

[a] IGAIM/Becke3LYP/6-311+G(d,p)//Becke3LYP/6-31G(d,p). All molecules are planar except **7** and **14**.
[b] IGLO/II/MP2/6-31G*.

The data in the first row agree well with published $\Delta\chi_{anis}$ data calculated by the IGLO protocol for a variety of compounds. The difference (27.2 ppm cgs) in calculated $\Delta\chi_{anis}$ between the unsaturated diazacarbene **13** and its saturated counterpart **14** is serves as a point of reference and has been used to support the concept of cyclic delocalization in **13**, *i.e.* aromaticity.[3a,5-7] An even greater enhancement between the phosphorous analogs **2** and **7** (37.4 ppm cgs) further supports the assignment of aromatic character to **2**. Alternatively, one can compare the sum of the $\Delta\chi_{anis}$ of the acyclic phosphenium ion **15** and ethylene **16** (-10.7 ppm cgs) with that for **2**: -45.0 ppm cgs. The large enhancement for the combination (34.3 ppm cgs) is consistent with cyclic delocalization in **2**. Both **3** and **4** also show large negative $\Delta\chi_{anis}$ as expected for aromatic systems.

In summary, calculated energetic comparisons, structural evidence, natural orbital analysis, electronic charge distributions, and magnetic properties for 1,3,2-diazaphospholenium ion **2** and molecules **3**, and **4** are consistent with generally accepted criteria for aromaticity.[1] In a broader context, these results also speak to the importance of π overlap between adjacent 2p/3p orbitals. Despite common misconceptions that overlap between p orbitals on elements in different rows is ineffective, phosphorus sustains cyclic delocalization

around the carbon 2p system quite well in these systems. These results are consistent with the recent conclusions of Schleyer et al.[18] who recently defined *inherent* π donor ability in terms of the π-stabilization energy between cationic centers and planarized donors. It was concluded that the π-donating capabilities of heavier elements are as large or larger than those of second row counterparts. In this context, the planar structures of the systems studied herein are expected to benefit optimally from 2p/3p overlap.

Computational Methodology. All calculations were carried out using the *Gaussian 94* suite of programs.[10a] Full geometry optimizations were carried out on all molecules using default convergence criteria and the MP2(FC)/6-31G(d,p) basis set. Frequency calculations established that each structure was an energy minimum (no negative frequencies). Magnetic anisotropy data was derived from structures optimized at the Becke3LYP/6-31G(d,p) level using a 6-311+G(d,p) basis set and the IGAIM method.[15]

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