

Phosphindolizine: a compound with planar phosphorus

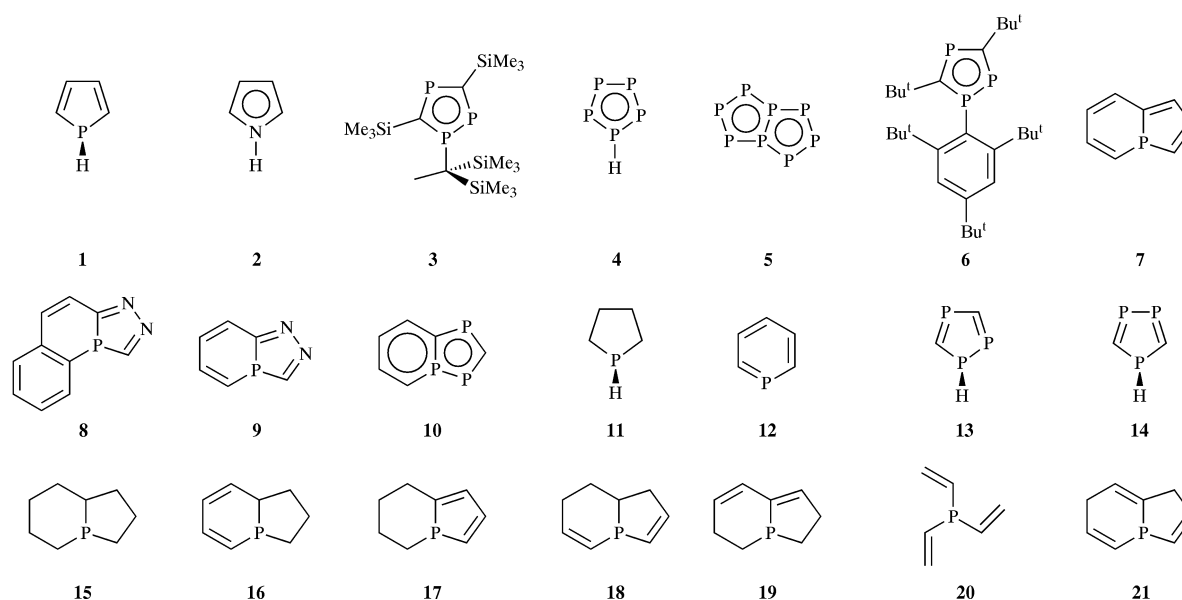
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Letter

Phosphindolizine, a fused ring with a bridgehead tricoordinated phosphorus, is nearly planar, with an inversion barrier of 3.5 kcal mol⁻¹ at the B3LYP/6-311 + G** level of theory. Diphosphaphosphindolizine is planar. Both the six- and the five-membered rings exhibit significant aromatic character, even in phosphindolizine, which is not entirely planar. The lone pair of the tricoordinate phosphorus is delocalized. The estimated aromatic stabilization in the two rings is 40 kcal mol⁻¹.



Tricoordinate phosphorus is inherently non planar;¹ the inversion barrier of phosphine is 35 kcal mol⁻¹.² As a consequence, phosphorus compounds do not mimic the rich chemistry of unsaturated aromatic nitrogen heterocycles. Phosphole (1) is essentially non-aromatic,^{3–5} in contrast to pyrrole (2), since the bending of the phosphorus lone pair (having large 's' character) precludes effective overlap with the carbon p-orbitals.

On the contrary, tricoordinate phosphorus is now established to be a good π -electron-pair donor when planar,^{6–8} and can serve as an excellent building block in aromatic systems.^{4c–f,9} Recent computational^{4f,10} and experimental¹¹ evidence shows that compounds with partially planarized (*i.e.* less pyramidal) tricoordinate phosphorus arrangements have structural, spectroscopic, magnetic, and chemical behavior characteristic of aromatic compounds. The first planar triphosphole derivative (3)¹² was reported very recently. Pentaphosphole, (P₅H, 4),^{4e,13} P₈ (5)^{4e} and an alkyl-aryl substituted triphosphole (6)¹⁴ were shown computationally to have planar tricoordinate phosphorus arrangements. However, 4–6 and their derivatives have not been synthesized.¹⁵ Since compounds with planar tricoordinate phosphorus can have delocalized lone electron pairs, their chemistry should be different from the common phosphines. Hence the search for new syn-

thesizeable systems with planar tricoordinate phosphorus is an intriguing challenge.

Our *ab initio* quantum chemical calculations now demonstrate that the fused phosphindolizine ring system (7), of which a derivative (8) has recently been prepared,¹⁶ is nearly planar and exhibits aromatic characteristics.

The calculated¹⁷ barriers to planarization for compounds 1 and 7, 9 and 10 are compiled in Table 1. The planar and the non-planar structures of 7, as well as the geometry of 10 are shown in Fig. 1. The decrease of the barrier in 1, with respect to its saturated analog, phospholane (11), was attributed tentatively^{9a} to the aromatic stabilization in the planar form. This has been verified recently by *ab initio* calculations.^{4c–f,9} The inversion barriers at phosphorus in 7 and 9 are reduced further, in comparison with phosphole (1) (Table 1). Replacement of a CH group by P in five-membered rings is known to decrease the tricoordinate phosphorus inversion barrier,^{4f,10} and pentaphosphole (4) is planar.^{4e,13} In the phosphindolizine system, replacement of two CH units by P results in 10, which is found by second-derivative calculations to have a planar minimum (Fig. 1) at the B3LYP/6-311 + G** and at the HF/6-31G* levels of theory.¹⁹ While the attempted synthesis of 4 was unsuccessful¹⁵ due to subsequent polymerization reactions, substituted 1,2,4-triphospholes are reported in the literature.^{12,20} Thus, it seems reasonable that 10—a new heterocycle with planar tricoordinate phosphorus—might be synthesized.

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Table 1 The B3LYP/6-311+G** inversion barriers (ΔE in kcal mol⁻¹) of different compounds containing tricoordinate phosphorus

PH ₃		33.7
11		39.4
20		29.1
21		45.9
1		18.0
7		3.5
9		2.8
10		0.0

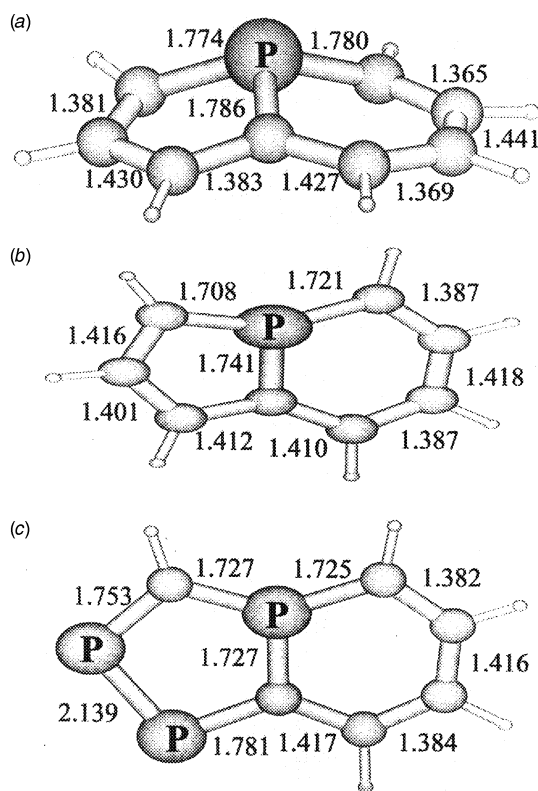


Fig. 1 The B3LYP/6-311+G** optimized structures of **7** [non-planar (a), planar (b)] and **10** (c), as shown by the MOLDEN program¹⁸

Consistent with the small inversion barrier, the tricoordinate phosphorus environment in the phosphindolizines **7** and **9** are substantially flattened. The bond angle sums about the tricoordinate phosphorus are 325 and 320° in **7** and **9**, respectively. These are somewhat lower than the sums obtained for 3,5-di-*tert*-butyl-1-(bis-trimethylsilylmethyl)-1,2,4-triphosphole (342),²⁰ for 1-(2,4,6-tri-*tert*-butylphenyl)phosphole (332),^{11c} or for 3,5-diphosphonio-1,2-diphospholes (339°).²¹ The range for the tetraphospholes (CP₄H₂) are 325–329° at the same level of theory.^{4f} Such bond angle sums allow the phosphorus lone-pair orbital to interact with the π -system, *e.g.* as shown by the HOMO of **7** (Fig. 2).

The decrease in the inversion barrier of **7**, **9** and **10** (with respect to **1**), is due to aromatic stabilization of the planar forms both by the five- and six-membered ring moieties. This is shown by aromaticity criteria (Table 2), *e.g.* geometric (Bird²² and bond shortening²³ indices, BI and BDSHRT, respectively) and magnetic [NICS,^{24,25} NICS(π)²⁵] and diamagnetic susceptibility exaltation (see below) for **7**, **9** and **10**, for both their planar and their non-planar forms. Owing to the shielding effect of the σ -ring bonds, the NICS(π) values are higher than the NICS values.²⁵ The various aromaticity measures in the six- and five-membered rings comprising the planar forms are comparable to the values in the six- (**12**) and (planar) five-membered ring (**4**) models (Table 2). The aromaticity of planar **7**, **9** and **10** is appreciable. The geometric and the NICS(π) aromaticity criteria for the **7** and **9** minima are only 20–30% lower than those in the planar structures both in the six- and five-membered rings. However, in the five-membered ring moiety these values are larger than those for 1,2,4-triphosphole (**13**) or 1,3,4-triphosphole (**14**),^{4f} (These are non-planar compounds with considerable aromatic character).

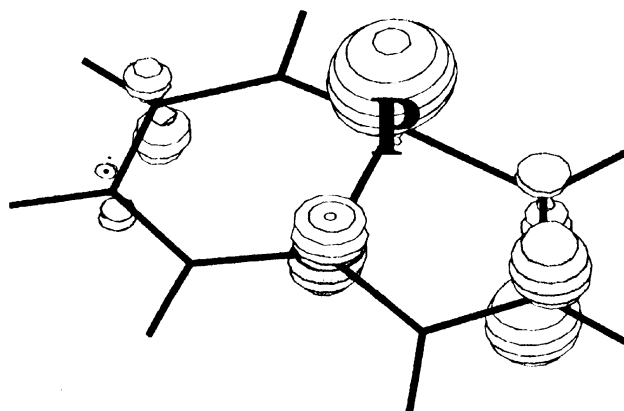


Fig. 2 The (HF/6-31G*) HOMO of **7**, plotted by the MOLDEN program¹⁸

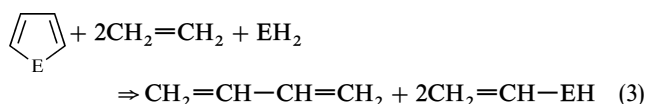
Table 2 Geometric [BDSHRT and Bird index (BI)] and magnetic [NICS and NICS(π) in the ring centers (in ppm)] aromaticity criteria and B3LYP/6-311+G** total energies (E_{tot} in a.u.) for **7**, **9** and **10** as well as reference five- and six-membered rings containing phosphorus

	BDSHRT		BI		NICS[NICS(π)]		$-E_{\text{tot}}$
	5-Ring	6-Ring	5-Ring	6-Ring	5-Ring	6-Ring	
12 ^a C _{2v}	—	62	—	96	—	−8.4(−19.1)	534.95528
1C _s	50	—	46	—	−5.0(−12.0)	—	496.81005
1 ^a C _{2v}	64	—	87	—	−17.4(−21.1)	—	496.78394
13C ₁	56	—	63	—	−7.9(−13.0)	—	1102.13576
14C _s	56	—	56	—	−5.5(−13.0)	—	1102.13213
4 ^a C _{2v}	68	—	87	—	−17.2(−18.8)	—	1707.49698
7C ₁	53	53	75	66	−10.8(−17.8)	−2.6(−13.4)	650.45681
7 ^a C _s	61	61	89	87	−20.0(−23.5)	−11.4(−19.1)	650.45125
9	51	54	67	66	−9.1(−18.2)	−3.2(−13.6)	682.51875
9 ^a C _s	59	62	93	86	−19.9(−24.0)	−11.2(−18.5)	682.51430
10 ^a	62	63	73	77	−16.7(−19.8)	−9.8(−18.9)	1255.79461

^a Planar structures.

The NICS values in the six-membered rings of **7** and **9** are quite small and negative, since the σ components have positive (deshielding) contributions.

The aromatic stabilization energy in phosphindolizine (**7**) is complicated to estimate, since the gain in cyclic delocalization is counterbalanced by the energy consumed to planarize tricoordinate phosphorus.^{4,6} Similar conclusions have been drawn from the related investigation of phospholes $\text{PH}(\text{CH})_n\text{P}_{(4-n)}$ ($n = 1-4$).^{4d-4f} The homodesmotic reaction (1), in which the reference molecules on the right-hand side are stabilized by the butadienic conjugation (both in the six-membered ring and in the phosphole moiety), is exothermic by 3.5 kcal mol⁻¹. Reaction (2), which does not consider the butadienic stabilization of the reference molecules, is endothermic by 3.1 kcal mol⁻¹.



The exaltation of the diamagnetic susceptibility, a unique criterion of aromaticity,^{2,6} is estimated to be -12.5 by using homodesmotic reaction (1) and -18.0 from reaction (2).²⁷ The exaltations deduced from isodesmic reactions of type (3) for five-membered aromatic heterocycles (E = O, S or NH) are all -11.8 or less;^{4f} the value is only -2.2 for phosphole (**1**).^{4f} A good correlation with other aromaticity measures was obtained for these systems.^{5d} Like the stabilization energies, equation (2) gives a larger exaltation of the magnetic susceptibility of **7** than given by equation (1).

Comparison of the inversion barriers (Table 1) of related systems helps to understand the planarity of **7**, **9** and **10**. The barrier to planarization in phosphine (33.7 kcal mol⁻¹) is smaller than in phospholane (**11**) (39.4 kcal mol⁻¹), since ring strain increases upon planarization of the tricoordinate phosphorus. Similarly, the planarization barrier of trivinylphosphine (**20**) (29.1 kcal mol⁻¹)²⁸ is smaller than that of **21** (45.9 kcal mol⁻¹), despite the similar conjugation, indicating an even more pronounced ring-strain effect in the latter fused cycle. The inversion barrier of phospholane (**11**) is calculated to be 20 kcal mol⁻¹ larger than that of phosphole (**1**) due to the aromaticity of the latter in the planar transition state.⁹ (This value has been taken as a measure of the aromatic stabilization in the planar system.⁹) The further decrease of the inversion barrier in **7**, despite the increased ring strain, is thus due primarily to the even greater delocalization in the bicyclic system. Using the planarization energy of the related system **21** as the basis of comparison, the aromatic stabilization of **7** is estimated to be 40 kcal mol⁻¹ (twice as much as in **1**) due to the combined effects of the two rings. That the bond angle sum about the tricoordinate phosphorus in **7** (325°) is much larger than in **15-19** and **21** [the values are between 292 (**15**) and 298° (**18**) in these partially saturated systems], also indicates the decisive effect of the uninterrupted cyclic delocalization in the fused ring **7**.

The phosphindolizine ring system (**7**) contains a substantially flattened phosphorus arrangement, with the lone pair incorporated into the π -system. Both **7** and **9** are aromatic even in their non-planar minima. Replacement of two =CH groups by =P units in the five-membered ring (**10**) results in a planar albeit an unusually floppy system. The planarization of the trivalent phosphorus in these fused-ring systems is due to the inherent planar preference of the conjugated bicyclic ring system, and also to the aromatic stabilization in both the five- and six-membered rings. It is likely that the chemistry of the phosphindolizine ring system will differ considerably from that of phosphines or from non-planar phospholes.

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