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1-(2,4,6-Tri-tertiarybutylphenyl)-3,5-di-*tert*-butyl-1,2,4-triphosphole: a possibly stable, fully aromatic, compound with planar tricoordinate phosphorus

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Abstract

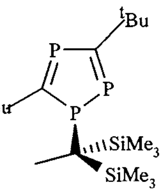
1-(2,4,6-Tri-tertiarybutylphenyl)-3,5-di-*tert*-butyl-1,2,4-triphosphole was found to be planar according to ab initio geometry optimisation at the HF/3-21G(*) level. The reliability of the calculations was shown by evaluations on model compounds and by comparison with available crystal structures of other triphospholes. The planarity of the triphosphole system is due to the steric effects of the bulky substituents. The planar system is highly aromatic according to different aromaticity measures, with a fully delocalised lone pair of the tricoordinate phosphorus. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Planar triphosphole; Aromaticity; Ab initio calculations; Steric effects

1. Introduction

It is well known that the lone pair of tricoordinate phosphorus, which has a high propensity to be pyramidal, has a large 's' character [1], and thus cannot overlap with neighbouring π-systems. It was shown recently, however, [2–7] that aromatic systems can be formed with planarised tricoordinate phosphorus. Even partial planarisation results in some degree of aromatic behaviour [4,7–11], which is reflected both in the chemical reactivity [8,10] and the photoelectron spectra [7] of the compounds investigated.

Several independent effects are known to increase the degree of planarity about phosphorus in ring systems. This is well documented when bulky substituents (e.g. 3,5-di-*tert*-butyl-tolyl, [12] or 2,4,6-tri-tertiary-butylphenyl (supermesityl) groups [9]) are placed at the tricoordinate phosphorus of phosphole. Another possibility is to increase the number of dicoordinate phosphorus atoms in a five-membered phosphole ring [4–6]. In the latter case although di-, tri-, and tetra-phospholes were not planar [4,7], pentaphosphole (P_5H) has C_{2v} symmetry according to ab initio calculations [5,6]. Unfortunately the parent P_5H is known to dimerise [5] and then polymerise further [13] and is unlikely to be a reasonable synthetic target.



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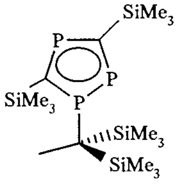

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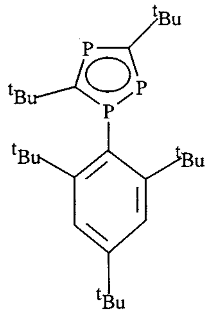

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The stable 1,2,4-triphosphole system (1-(bis-trimethylsilyl-methyl-3,5-di-*tert*-butyl-1,2,4-triphosphole), $P_3C_2Bu^t_2CH(SiMe_3)_2$ (**1**) has been reported recently [14], but it is not completely planar (sum of angles around the tricoordinate phosphorus = 342°). Very recently we have reported triphosphole (**2**), which has a bond angle sum of 359.6° and is highly aromatic

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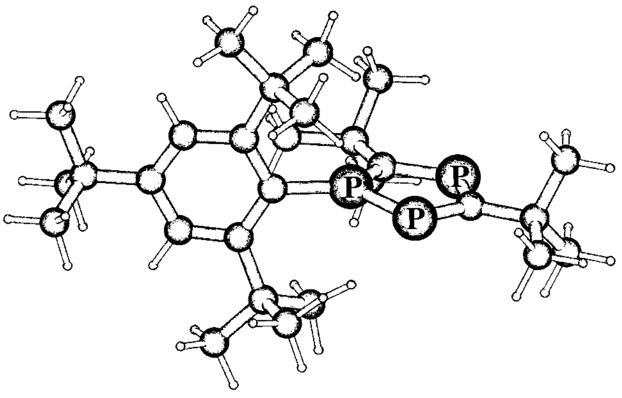


Fig. 1. The HF/3-21G* structure of 1-(2,4,6-tri-tertiarybutylphenyl)-3,5-di-*tert*-butyl-1,2,4-triphosphole, as plotted by the MOLDEN program ([18]).

[15]. It was shown that the presence of the π electron acceptor silyl groups contributed to the planarity of the ring. Would it be possible to obtain a planar triphosphole ring, substituted with alkyl instead of silyl groups, while increasing the steric effect on the tricoordinate phosphorus?

2. Results and discussion

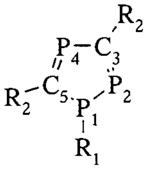
We anticipated that a combination of the different factors that planarise phospholes was likely to be most effective. The present ab initio quantum chemical calculations [16] show that a bulky alkyl–aryl substituent in 1-position of the 1,2,4-triphosphole ring leads to a planar tricoordinate phosphorus. In aryl-substituted phospholes the two rings are perpendicular to each other [8,9,12,17] (according to the present HF/3-21G(*) calculations this is the case for 1-phenyl-1,2,4-triphosphole too). Any substituents in the 2- and 6-position of the phenyl ring force the phosphorus ring to be planar, as it has been shown previously on phosphole [8,9,12,17]. Preliminary MNDO calculations indicated that only the supermesityl but not the mesityl and di-*tert*-butyl-tolyl resulted in a planar triphosphole system. Furthermore, neither omission of the tertiary-butyl group on the triphosphole ring in the 3-position, nor the *para*-substituents on the phenyl ring, has any significant effect on the optimised structures. However, the tertiary-butyl group in the 5-position of the phosphole ring, turned out to be important, since in its absence the supermesityl substituent bends away, towards the C_5 atom, and only has a smaller flattening effect. On the basis of the above preliminary results it was decided to optimise the structure of the 1-(2,4,6-tri-tertiarybutylphenyl) - 3,5 - diertiarybutyl - 1,2,4 - triphosphole (**3**).

The HF/3-21G(*) optimised structure of the 1-supermesityl-3,5-di-tertiarybutyl-1,2,4-triphosphole (**3**) is shown in Fig. 1. Neither the exocyclic carbon atom attached to the tricoordinate phosphorus, nor the other ring atoms (within the phosphole system) deviate more than 0.5° from the planes formed by any three other ring atoms in the optimised structure. Since the optimisation started from a non-planar structure and the second derivative calculation [16] showed that the structure is a real minimum on the potential-energy surface, it seems quite likely that only a planar stationary point exists for the supermesityl-substituted 1,2,4-triphosphole.

Further calculations at the HF/6-31G* and B3LYP/3-21G(*) levels for a model compound, containing no tertiary-butyl groups in the *para* position of the phenyl ring and in the 3-position of the 1,2,4-triphosphole ring, again resulted in a planar structure, with minor structural differences in comparison to the fully tertiary-butyl-substituted structure. In order to check the reliability of the calculations, the geometry of **1** has also been optimised at the HF/3-21G(*) level, and the structural parameters were compared with those of the recent single crystal X-ray structure [14]. The data in Table 1 show that the degree of bond length equalisation and thus the planarity (cf. the calculated 327.2° vs. 342° measured bond angle sum) are somewhat underestimated at the HF level. Also, the barrier for the planarization of phosphole and 1,2,4-triphosphole was overestimated at the HF level, relative to the values obtained at any correlated levels [19]. Thus, the calculated planarity of the tricoordinate phosphorus in **3** is unlikely to be attributed to an artifact of the calculation method employed, since higher levels of the theory would even favour the planar structure more. Also the planarity of **2** was properly predicted at the HF/3-21G(*) level [15].

The important structural data for **3** and those of **1** are given in Table 1. The optimised structure of the 1-supermesityl-3,5-di-*tert*-butyl-1,2,4-triphosphole (**3**) shows equalised bond lengths, and similar geometrical parameters to those of planar 1,2,4-triphosphole [4,7] (which is a first-order saddle point on the potential-energy hypersurface). However, the structure of the non-planar 1,2,4-triphosphole [4,7] (see Table 1) differs significantly from that of **3**. The Bird aromaticity index (a measure of bond length equalisation) [20] for 1-supermesityl-3,5-di-tertiarybutyl-1,2,4-triphosphole is 83 on the 0–100 scale, which is among the largest yet obtained for five-membered heterocycles (furan 43 [20], pyrrole 59 [20], thiophene 66 [20], pyrazole 73 [20], pentazole 89 [20] and pentaphosphole (P_5H) 77 [5]. The bond-shortening index [20] is 0.63 for 1-supermesityl-3,5-di-tertiarybutyl-1,2,4-triphosphole, while for benzene, pyrrole, thiophene, pyrazole and pentaphosphole the values of 0.68 [21], 0.62 [21], 0.63 [21], 0.65 [21] and 0.60 [5], respectively were reported. The NICS value [22] of **3** is − 14.7 ppm, for thiophene − 13.6; a value of − 15.1 was reported for pyrrole [22] by using the same basis set.

Table 1
HF/3-21G(*) bond lengths of substituted 1,2,4-triphospholes (Å)

	$R_1 = H$; $R_2 = t$-Bu	$R_1 = R_2 = H$		R_1 = SUME [c]; $R_2 = t$-Bu	R_1 = DISI [d]; $R_2 = t$-Bu; X-ray [14]	R_1 = DISI [d]; $R_2 = t$-Bu
		OPT [a]	PLANAR [b]	**3**	**1**	**1**
P_1P_2	2.165	2.170	2.061	2.061	2.098	2.135
P_2C_3	1.674	1.668	1.717	1.727	1.718	1.683
C_3P_4	1.819	1.797	1.735	1.736	1.763	1.794
P_4C_5	1.670	1.663	1.722	1.747	1.720	1.691
C_5P_1	1.808	1.786	1.692	1.699	1.734	1.786

[a] Non-planar structure, minimum on the potential-energy surface.

[b] Planar structure, first order saddle point on the potential-energy surface.

[c] SUME, supermesityl group.

[d] DISI, bis-trimethylsilyl-methyl group.

Since the planar triphosphole is highly aromatic, it can be expected that the chemical reactivity will be different from those of the common phospholes. Also **1**, which was not entirely planar, has formed η^5-complexes with different metals [15]. Nevertheless, despite the aromatic electronic structure no inertness in the chemical reactivity can be expected in the case of the 1,2,4-triphosphole system. The energy needed to make the tricoordinate phosphorus planar compensates for the aromatic stabilisation. Thus, if the destruction of the aromatic system in any chemical reaction can be accompanied by the pyramidalization of the tricoordinate phosphorus, the loss of the aromaticity will not raise the reaction barrier. It has been shown [1] that **1** (which has built a complex characteristic for aromatic systems) rearranges slowly under the influence of light to 1,3,5-triphosphabicyclo[2,1,0]pent-2-ene, which in turn undergoes [1,3]-sigmatropic rearrangement with a low barrier [23].

Acknowledgements

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