

Substituent effect on low coordination phosphorus chemistry

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Abstract

It has been shown by means of computational chemistry that the successful synthesis of some of the most remarkable phosphorus containing molecules in the last decades (e.g., 1,3,5-triphosphinine or 1,3-isodiphosphinine) was greatly facilitated by the presence of the bulky *t*Bu group. This substituent is needed to stabilize *t*BuCP, which is used to be the starting material in many reactions. In a six-membered ring the repulsion of the neighboring *t*Bu substituents brings a destabilization of about 22–25 kcal/mol for each *t*Bu unit, this amount of energy is comparable to the aromatic stabilization in benzene. The minimization of this steric repulsion between neighboring *t*Bu moieties in the possible isomers plays a crucial role in determining the stability of the product. The effect of the steric repulsion on the kinetics of the cycloaddition reaction between *t*BuCP and diazomethane has also been shown to be important, accounting for the observed regioselectivity in the reaction.

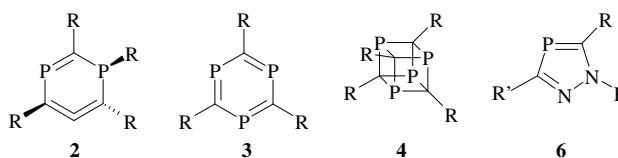
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1. Introduction

In the last few decades there has been an unprecedentedly fast development in the field of low coordination phosphorus chemistry, as it has been shown by the appearance of recent books and review papers [1–3]. Many of the low coordinated phosphorus compounds are aromatic [4], the five-membered ring heterophosphole family, the (poly)phospholide ions and the six-membered ring phosphinine family being perhaps the most representative cases. Cycloaddition products from the low coordinated species are also of commonplace. The most widely used compound in the cycloaddition reactions is *t*BuC≡P (**1**) [5], which is indefinitely stable at ambient conditions. Many of the most remarkable and often highly symmetric structures such as the 1,3-isodiphosphinine (**2**) [6], 1,3,5-triphosphinine (**3**) [7,8] and tetraphosphacubane (**4**) [9] – all of them bearing

the R: *t*Bu substituents – were obtained by using (**1**) as starting material.



In the understanding of the electronic structure of these compounds the substituent alkyl group (R: *t*Bu) is usually considered to play a minor role. Especially in case of quantum chemical calculations this moiety is often replaced by H, in order to reduce the computational costs. In the present work we want to present some examples proving the crucial effect of the *t*Bu substituent on the relative stability of the possible isomers (like **2** and **3**). Also we investigate the effect of alkyl substituents on the cycloaddition reaction between **1** and diazomethane (**5**) leading to the 1,2,4-diazaphosphole (**6**) [10].

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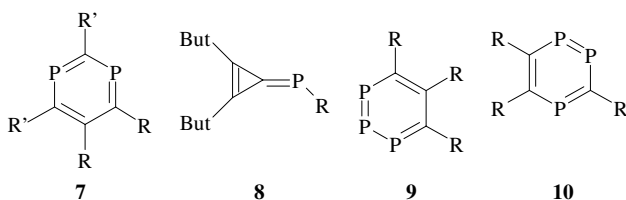
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2. Calculations

For the quantum chemical calculations the GAUSSIAN 98 suite of programs [11] has been used. Geometry optimizations were carried out at the B3LYP/6-31+G* level. Second derivatives were calculated at the optimized structures. For the minima no negative eigenvalues of the Hessian matrix were obtained. Further MP2/6-31G*//B3LYP/6-31+G* calculations were also carried out, to test the applicability of the density functional [12] used in the calculations. The molecular structures were plotted by the MOLDEN program [13]. The transition structures were optimized at the B3LYP/6-311+G** level, and their nature was proved by a single negative eigenvalue of the Hessian matrix and by subsequent IRC calculations.

3. Results and discussion

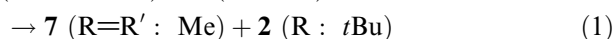
1,3-Diphosphinine **7** (R': *t*Bu, R: H) has been synthesized first by Zenneck and coworkers [14] by a transition metal catalyzed cycloaddition reaction of *t*BuCP and acetylene. **7** (R=R': *t*Bu), the *tert*-butylated system is not yet known. Studies on the relative stabilities of some diphosphinine isomers (all carbons bearing H-s) were carried out by Colombet et al. [15]. Surprisingly, an isomer of **7** (R=R': *t*Bu), a cyclic allene structure (**2**, R: *t*Bu) has been synthesized in the Regitz group [6] in a cycloaddition reaction of **1** with phosphatriafulvene (**8**, R: *t*Bu). Density functional calculations showed [6] that **2** (R: *t*Bu) is somewhat more stable than **7** (R=R': *t*Bu). This result was rather surprising, since **7** has an aromatic electronic structure, while the necessary distortion of the linearity at the allenic unit in the six-membered ring of **2** is expected to cause severe ring strain.



The above considerations about the relative stabilities of **2** and **7** are already confirmed [6] if we compare the parent **2** (R: H) and **7** (R=R': H). The B3LYP/6-31+G* optimized structure of **7** (R=R': H) is planar, while **2** (R: H) exhibits a distorted, non-planar six-membered ring, the tricoordinate phosphorus atom being pyramidal. In accordance with the expectations, **7** (R=R': H) is less stable than **2** (R: H) by about 60 kcal/mol (Table 1). The MP2/6-31G*//B3LYP/6-31+G* relative energies predict somewhat more stabilization for the aromatic system **7**, than the B3LYP/6-31+G* results, but the main conclusion remains unaltered

(Table 1). When all hydrogens are replaced by a methyl group, the energy difference between **2** (R: Me) and **7** (R=R': Me) is somewhat decreased (Table 1) to 45.4 and 52.7 kcal/mol at the B3LYP/6-31+G* and MP2/6-31G*//B3LYP/6-31+G* levels, respectively. This effect can partly be attributed to the differences of the inductive and hyperconjugative effects of the alkyl groups on P and C. Furthermore, the differences between the PH, CH, PC and CC bond strengths should also affect the relative stabilities [16]. Thus, to judge the steric effect of the *t*Bu groups the methyl substituted systems will be used for comparison (see below).

The effect of the *t*Bu group on the relative stabilities of **2** and **7** is dramatic. The B3LYP/6-31+G* optimized structures are shown in Fig. 1. Not only **2** (R: *t*Bu), but also **7** (R=R': *t*Bu) is non-planar. The bulky alkyl groups try to avoid each other being placed above and below the ring. This can be successfully realized in **2**, where the pyramidal phosphorus places the substituent in one direction far above the ring, but causes severe ring strain in case of **7**. As a consequence **7** (R=R': *t*Bu) remains no more stable than **2** (R: *t*Bu). At the B3LYP/6-31+G* level **2** (R: *t*Bu) is somewhat more stable than **7** (R=R': *t*Bu), while at the MP2/6-31G*//B3LYP/6-31+G* level **7** (R=R': *t*Bu) is predicted to be slightly more stable. The relative stabilities of the *tert*-butylated systems can be compared to those of the methylated systems [16], in the isodesmic reaction (1). Depending on the level of the theory used a destabilization of about 45–50 kcal/mol is obtained. (At the B3LYP/6-31+G* 49.6 kcal/mol, while at MP2/6-31G*//B3LYP/6-31+G* 45.8 kcal/mol has been obtained, showing that the B3LYP functional predicts somewhat larger interaction [17] between the bulky alkyl



groups than MP2.) It is worthy to note that from the relative stabilities of **2** (R: *t*Bu) and **7** (R=R': *t*Bu) alone

Table 1
B3LYP/6-31+G* and MP2/6-31G*//B3LYP/6-31+G* relative energies of the substituted diphosphabenzene isomers in kcal/mol

	B3LYP ^a	MP2 ^b	B3LYP ^a	MP2 ^b
R: H	56.6	62.7	0.0	0.0
R: Me	45.4	52.7	0.0	0.0
R: <i>t</i> Bu	0.0	6.9	4.2	0.0

^a B3LYP/6-31+G*.

^b MP2/6-31G*//B3LYP/6-31+G*.

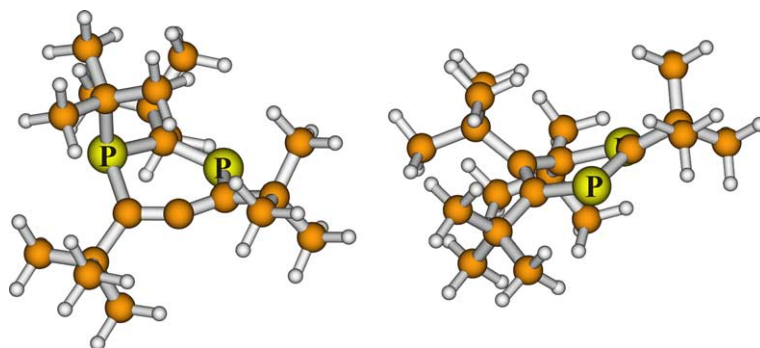


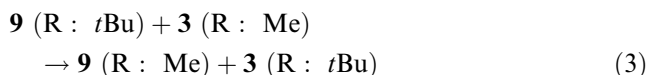
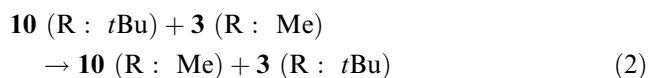
Fig. 1. B3LYP/6-31+G* optimized structures of **2** (R: *t*Bu) and **7** (R=R': *t*Bu).

the success of the synthesis of **2** (R: *t*Bu) cannot be explained. Apparently, kinetic effects play here an important role as can be shown by a detailed analysis of the reaction mechanism which will be published elsewhere [18].

1,3,5-Triphosphinine 3 (R: *t*Bu) has been synthesized by a metal catalyzed cycloaddition of **1** [7,8]. The stabilities of the possible isomers of **3** (R: H) have been investigated computationally in the Schleyer group [19]. According to their [19] MP2/6-31G* calculations the most stable isomer was **9** (R: H), followed by **10** (R: H at +8.0 kcal/mol) and **3** (R: H at +11.0 kcal/mol) [19]. All other possible isomers were by 10–60 kcal/mol less stable than **9** (R: H). Our B3LYP/6-31+G* results (Table 2) are similar to those obtained before, **3** being somewhat even more destabilized. The replacement of the hydrogen by a methyl group has a small effect on the relative energies in case of the triphosphinines, since – unlike in case of diphosphinines **2** and **7** – the CH and CC bond strength differences cancel out in this comparison. **3** (R: Me), **9** (R: Me) and **10** (R: Me) remain planar.

The optimized structures of **3** (R: *t*Bu), **9** (R: *t*Bu) and **10** (R: *t*Bu) are shown in Fig. 2. The effect of the *t*Bu substitution is apparent at first sight in case of **9** (R: *t*Bu) and **10** (R: *t*Bu), the two structures are non-planar, apparently to release some of the strain resulting from the repulsion of the neighboring *t*Bu groups. To

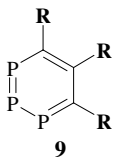
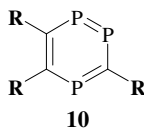
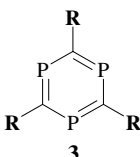
the contrary **3** (R: *t*Bu) is planar, in accordance with its published crystal structure [20]. The B3LYP/6-31+G* relative energies collected in Table 2 also reflect the above considerations. **3** (R: *t*Bu) is the most stable structure among the isomers investigated, reversing the stability ordering obtained for the parent systems (**9**, **10** and **3**; R: H). In isodesmic reaction (2) and (3) the stabilization amounts 21.6 and 45.0 kcal/mol, respectively.



In case of **10** one, while for **9** two pairs of *t*Bu moieties are in neighboring positions. Accordingly, the energy of isodesmic reaction (3) is about twice that of reaction (2). Also in **7** two pairs of *t*Bu–*t*Bu interactions act destabilizing, and the energy of reaction (3) is close to the 49.6 and 45.8 kcal/mol obtained for reaction (1) at the B3LYP/6-31+G* and MP2/6-31G*//B3LYP/6-31+G* levels, respectively (see above). Thus, the effect between two neighboring *t*Bu groups can be estimated to be about 22–25 kcal/mol in a six-membered ring.

It is worthy to note that this (ca. 45–50 kcal/mol) destabilization energy, resulting from two *t*Bu–*t*Bu interactions modifies considerably the relative energies of all the possible isomers. This energy exceeds the 20 kcal/mol aromatic stabilization in 1,3,5-triphosphabenzene [21], and has also a large impact on the relative stabilities of the possible other isomers. Among the possible triphosphabenzene isomers investigated by Hofmann et al. [19] three benzvalene structures (**11**–**13**) were close in energy to **3**, the rest of the isomers were less stable by at least 10 kcal/mol. **12** and **13** (the parent compounds being somewhat less stable than **3**) exhibit one pair of neighboring *t*Bu groups, while in **11** (which was slightly more stable than **3**) two such interactions act destabilizing, while in **3** there is no such destabilizing interaction.

Table 2
B3LYP/6-31+G* relative energies of substituted triphosphabenzene isomers in kcal/mol

			
R: H	0.0	10.2	15.9
R: Me	0.0	7.9	15.5
R: <i>t</i> Bu	29.5	14.1	0.0

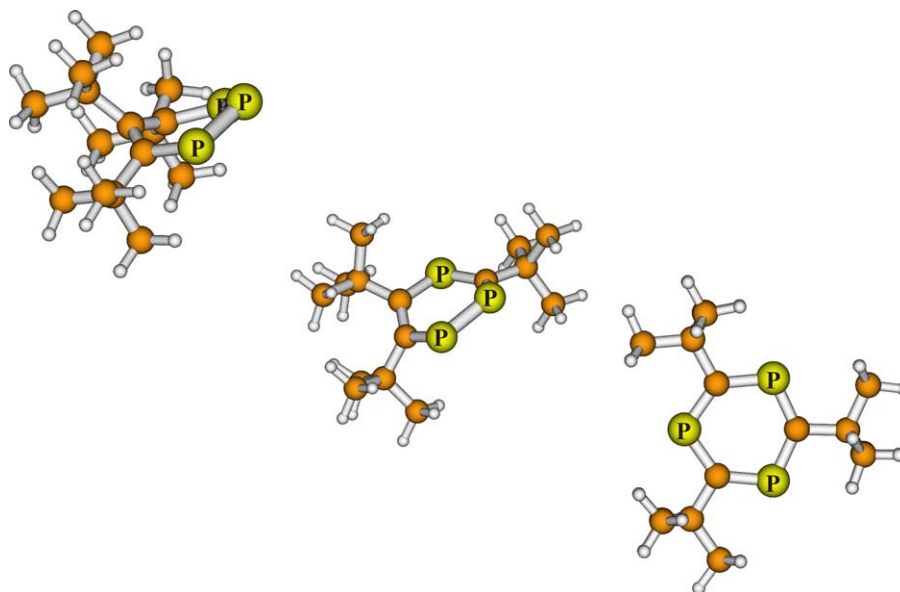
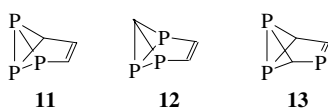
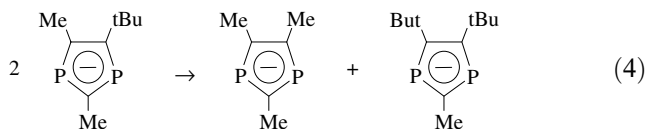


Fig. 2. B3LYP/6-31+G* optimized structures of **9**, **10** and **3** (R: *t*Bu).

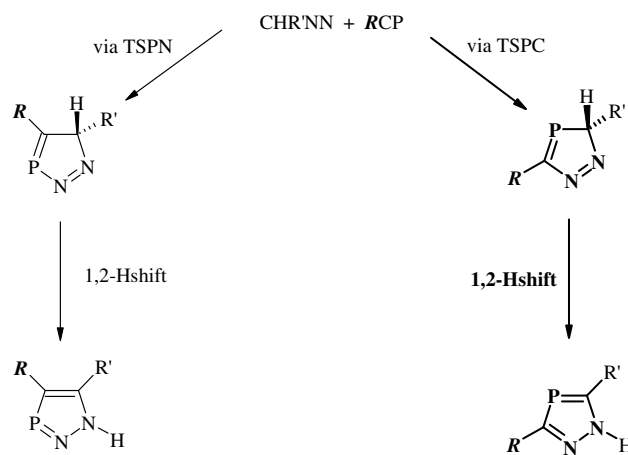


It should be noted, however, that the strain between the two neighboring bulky *t*Bu substituents should depend on the bonding angle in the ring. In a five-membered ring (like **11–13**) the strain arising from the repulsion of the substituents is likely to be smaller than in a six-membered ring, since the narrower bonding angle leaves more space for the bulky groups attached to the ring. To estimate the repulsion of the two neighboring *t*Bu groups in a five-membered ring we used reaction (4).



At the B3LYP/6-31+G* level the destabilization in reaction (4) is 10.2 kcal/mol. Although, this is smaller than in case of the six-membered ring, in accordance with the expectations, but it still has a significant contribution to the stability. Thus, we can conclude rather safely, even without calculating the great number of possible isomeric structures, that in case of the *t*Bu substituted series the symmetric 1,3,5-triphosphabenzene (**3**) is the most stable structure of the possible isomers.

1*H*-1,2,4-diazaphosphole (**6**) can easily be obtained in a cycloaddition reaction between **1** and diazomethane (and many of its derivatives). Among the two possible regioisomers the 1*H*-1,2,4-diazaphosphole (**6**) was obtained exclusively as is shown in Scheme 1 [10]. Consid-



Scheme 1.

ering that some kind of electronic factors should be responsible for this high regioselectivity observed, some time ago we have investigated computationally the cycloaddition reaction between HCP and diazomethane [22]. Computing the two possible transition structures (see Scheme 1) in the rate determining 2+3 cycloaddition steps at various levels of the theory up to CCSD(T)/6-311+G**//MP2/6-311+G** including counterpoise correction for BSSE, the relative energies did not differ by more than 1 kcal/mol in any of the calculations. This implied that there is no significant difference in the kinetic control between the two reaction pathways leading to the different regioisomers formed from HCP and CH₂NN. This result was not in accordance with the observed high regioselectivity in the reaction between *t*BuCP (**1**) and CH₂NN.

Here we present the results for the RCP + CH₂NN reaction (R: H, Me and *t*Bu). Since the relative energies of the two transition structures were shown to vary only slightly at different levels of the theory, we carried out the calculations at B3LYP/6-311+G** only, without using counterpoise correction. In Fig. 3 the two transition structures leading to the two regioisomers are shown (for the R: *t*Bu case). The reaction barriers and the relative energies between the two transition structures are collected in Table 3. For the parent HCP the present data are in agreement with our previous results. The presence of the alkyl groups increases somewhat the reaction barriers, in agreement with the previous results of Löber and coworkers [23]. While the methyl moiety exhibits some effect on the relative stabilities of the two transition structures, substitution of the phosphalkyne with the *t*Bu group increases the energy difference between the two transition structures to 4.5 kcal/mol. By using the Arrhenius equation the 0.9 kcal/mol energy difference results in a 1:7 ratio of the rates of the reactions, while the 4.5 kcal/mol energy difference corresponds to a 1:8000 ratio, provided that the entropy dependent pre-exponential factor is the same in the two competing reaction. We have shown before [22] that the entropy contribution plays only a minor role in case of the parent system. Any further substitution of the diazomethane reactant (R' is different from H in Scheme 1) results in an increase of the steric repulsion in case of TSPN, while the effect on

the energy of TSPC should be much smaller as it is apparent from the geometries of the two transition structures (shown in Fig. 3). Thus, the preference of **6** as a sole product is further confirmed. This conclusion is now in full accordance with the observations [10], showing the crucial effect of the *t*Bu group in the understanding of the the kinetics in a reaction with *t*BuCP.

4. Conclusions

The effect of the steric repulsion caused by the *t*Bu group clearly has non-negligible effects on the reaction kinetics and also on the thermodynamic stability of the isomeric systems. On some selected examples we have shown by computational means that the *tertiary*-butyl substituent has a crucial effect on the stability and thus on the formation of the most beautiful phosphorus heterocyclic systems. This observation is of importance, since this bulky alkyl moiety in *t*BuCP is used to stabilize the phosphorus carbon triple bond, an important reactant in organophosphorus chemistry. The repulsion of the *t*Bu groups at neighboring carbon atoms might amount 22–25 kcal/mol, which is comparable to the aromatic stabilization in a six-membered ring. Thus, the presence of an increasing number of *t*Bu groups affects considerably the relative stabilities of the possible isomers. The repulsion between the interacting *t*Bu groups becomes less important for the smaller rings, since the narrow bond angles in the ring leave more space for the substituent. With the *t*Bu substituent attached the formation of highly symmetric structures such as **3** or **4** is preferred, since the repulsion of the bulky groups is minimized in these cases. (Note that in case of **3** the three *t*Bu groups have a *trigonal-planar* arrangement, while in case of **4** the four *t*Bu groups have a *tetrahedral* arrangement about the center of the molecule.)

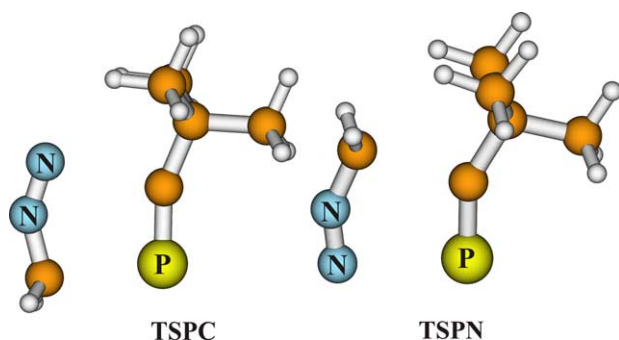


Fig. 3. B3LYP/6-311+G** optimized structures of the two possible concerted 3 + 2 cycloaddition transition structures in the CH₂NN + *t*BuCP reaction.

Table 3
B3LYP/6-311+G** relative energies with respect to RCP + CH₂NN of the TSPC and TSPN transition structures with different R substituents at the phosphalkyne RCP

R	E_{TSPC}	E_{TSPN}	$\Delta E_{\text{TSPC-TSPN}}$
H	8.0	8.9	0.9
Me	11.0	13.9	2.9
<i>t</i> Bu	12.0	16.5	4.5

$\Delta E_{\text{TSPC-TSPN}}$ is the difference between the energies of the two transition structures. All data are in kcal/mol.

Acknowledgement

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