Non-stoichiometry induced by differential oxygen/lone pair occupation in chiral bicyclic 1,1′-binaphthoxy cyclodiphosphazanes†

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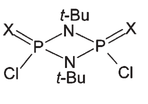
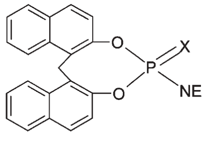
Non-stoichiometry and isostructurality in a set of chiral phosphorus compounds as a result of lone pair/oxygen exchange, substantiated by the combined use of ^{31}P NMR spectroscopy and X-ray crystallography, is described.

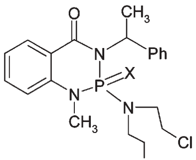
Non-stoichiometry is a very common feature for metal oxides as a result of various defects.[1] However, in molecular chemistry where all molecules should be the same, non-stoichiometry is rare. Phosphorus forms numerous molecular compounds in valence states of three or five. Here exchange of position of a lone pair of electrons with that of an oxygen in a crystal (like that in a P(III) compound and its oxidation product), then leading to non-stoichiometry is possible. Thus if the space occupied by the phosphorus lone pair and (phosphoryl) oxygen atom are nearly the same, interchange of sites by the lone pair and oxygen can lead to isomorphous crystals, provided that the strong hydrogen bond acceptor property of the phosphoryl (P=O) group is not structure-determining. A CSD survey of compounds with at least one P–N bond revealed three pairs **1–3** with X-ray structures (unsolvated) of the P(III) species and its oxidized product determined,[2] but in none of these pairs did the two compounds crystallize in the same space group despite the fact that the difference in volume between the oxygen and the lone pair (on phosphorus) in each set is $\leqslant 5\text{Å}^3$. Although exchange among groups having similar volumes/shapes [Kitaigorodskii's theory: *e.g.* chloro *vs* methyl] is well known in organic chemistry,[3] to our knowledge, similar features involving a lone pair of electrons and an oxygen have not been documented.



X = lone pair (**1a**: *Pbca*)
O (**1b**: *P42/n*)



lone pair (**2a**: *Pbca*)
O (**2b**: *P*$2_12_12_1$)

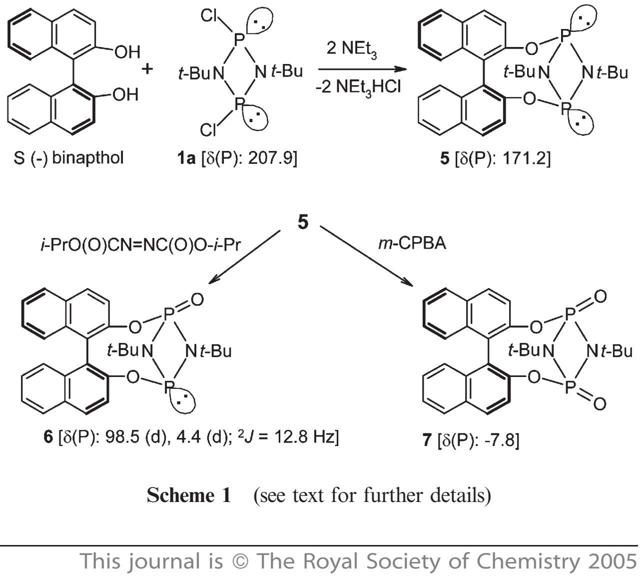


lone pair (**3a**: $P\bar{1}$)
O (**3b**: *P*$2_12_12_1$)

In the above context, cyclodiphosph(III)azanes (with a lone pair on phosphorus) and their oxidized counterparts (with P=O bonds) constitute a convenient class of compounds since (a) most of them tend to crystallize easily, (b) the P–Cl groups in **1a** or its phenyl analogue $[\text{ClPNPh}]_2$ (**4**) can be replaced by other groups, and (c) the products or the reactants can be readily oxidized/complexed.[4,5] The present work is a continuation of our previous studies, and was originally intended for the synthesis of chiral P(III) and P(V) systems for use in asymmetric catalysis. Thus, treatment of **1a** with a di- or polyfunctional reagent can lead monomeric, dimeric or oligomeric products;[6] we wanted to exploit this reaction for the generation of chiral cyclophosphazanes that have two potential phosphorus sites amenable for ligation as soft donors to transition metals for possible use in chiral synthesis.[7] Even the oxidized products with P(O) group/s (hard donors) can act as catalysts in several asymmetric organic transformations (*e.g.* silicon based aldol reactions[8]).

In this communication, we report the synthesis of the bicyclic (*ansa*-type compound) **5** and its oxidized products with emphasis on the crystallization behaviour of **5**, its partially (**6**) and fully oxidized (**7**) products as well as the mixed crystal **8** [**5** + **7**]; all these derivatives [*cf.* Scheme 1] are isomorphous (Table 1; compound **9** is the racemic form of **5**).‡ The powerful hydrogen-bond acceptor property of the phosphoryl (P=O) group is apparently not effective in bringing about any significant change in the crystallization behaviour.[9] The resulting non-stoichiometric nature of partially oxidized and mixed products, as evidenced by the combined use of X-ray and ^{31}P NMR spectroscopy, is also highlighted here.

Synthesis of **5** is straightforward and the yield is very high. The δ(P) value is close to those for the bicyclic phosphazane {[2,2′-$(\text{C}_6\text{H}_4\text{O})_2$][PN-*t*-Bu]$_2$} [$\delta$(P): 167.2][6c] and the bis(aryloxy) derivative *cis*-[(2,6-$\text{Me}_2\text{C}_6\text{H}_3\text{O}$)(PN-*t*-Bu)]$_2$ [δ(P): 156.3][5e] which suggests that the structure is retained in solution. There was no evidence for the formation of the dimer/oligomer. Reactivity at mainly one of the two P(III) centres of cyclodiphosph(III)azanes when treated with diisopropyl azodicarboxylate (DIAD) is a feature that we have described recently although in the present case, **6** is a simple



Scheme 1 (see text for further details)

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† Electronic supplementary information (ESI) available: experimental procedures, ORTEP drawings and further crystal data (CIF files). See DOI: 10.1039/b509327a

Table 1 Crystal data for **5**–**8** and the racemic compound **9**[a]

Compd	Space group	a/Å	b/Å	c/Å	V/Å^3	V per molecule/Å^3	P=O oxygen occupancy at P(1)/P(2)
5	$P2_12_12_1$	9.661(3)	15.095(2)	17.904(4)	2610.8	652.7	0.00/0.00
6	$P2_12_12_1$	9.712(1)	15.188(1)	17.821(1)	2628.9	657.2	0.50/0.60
7	$P2_12_12_1$	9.731(1)	15.256(2)	17.737(3)	2633.0	658.3	1.00/1.00
8	$P2_12_12_1$	9.716(1)	15.191(1)	17.808(1)	2628.2	657.0	0.70/0.70
9[a]	$P2_1/c$	22.838(3)	9.590(3)	23.901(5)	5023.0	627.9	0.00/0.17

[a] Two molecules in the asymmetric unit; β = 106.34(1)°. There is partial oxidation (17%) of one of the phosphorus atoms of each molecule in the asymmetric unit (X-ray structure and NMR). The occupancy factors were first refined and then fixed at a set value. Full crystal data are in the ESI.

oxidized product.[10] More reactive *m*-chloroperbenzoic acid readily oxidizes both phosphorus centres in **5** to yield **7**. As expected for the same stereochemistry at the chiral binaphthoxy centre, compounds **5**–**8** showed essentially identical CD spectra.

The ORTEP drawing of **7** is shown in Fig. 1; the numbering scheme is the same in **5**, **6** and **8** (ESI†). All these structures are isomorphous (*cf.* Table 1). In the case of **6**, lone pair of electrons on P(III) and oxygen on P(V) centre show the same interchangeability as the methyl and chloro groups,[3] and as a result, the refinement of the occupancy factor proceeded satisfactorily. Thus this predominantly mono-oxidized compound **6** does not show full oxygen occupancy on single phosphorus [O(3) 0.5; O(4) 0.6]. This feature leads to apparent molecular non-stoichiometry. The extra occupancy is because some dioxo-compound **7** co-crystallizes with **6**. These observations prompted us to explore the crystallization behaviour of the mixture of **5** and **7** and to our delight, the crystals (**8**) obtained showed partial occupancy of phosphoryl oxygens. This 'compound' contains molecules of both **5** and **7** in a 1 : 2.3 ratio with 0.7 oxygen per phosphorus which is clearly non-stoichiometric and a situation quite similar to solid-state compounds (*e.g.* metal oxides). Crystallographically there is no significant difference between **6** and **8** in terms of basic structure or crystal data, *despite the fact that the former is essentially a mono-oxidized product while the latter is a mixture of P(III)-N-P(III) and P(V)-N-P(V) compounds*. That they are chemically different is readily shown by ^{31}P NMR spectroscopy [Fig. 2]. The presence of the bis-oxidized product [δ(P) −7.8, expected intensity with respect to one of the other peaks ~10%] in the solution made from crystals of **6** is clearly seen. The solution made from the mixed crystal **8** exhibits two peaks corresponding to **5** [δ(P) 171.2] and **7** [δ(P) −7.8] in the ratio ~1 : 2.3, consistent with X-ray structure. The presence of partially oxidized product is also noticed in the structure of the racemic compound **9** (*cf.* Table 1). Interestingly, the packing (>65.9% space filled) in the racemic crystal **9** is more efficient than in the chiral crystal **5** (64.0% space filled).

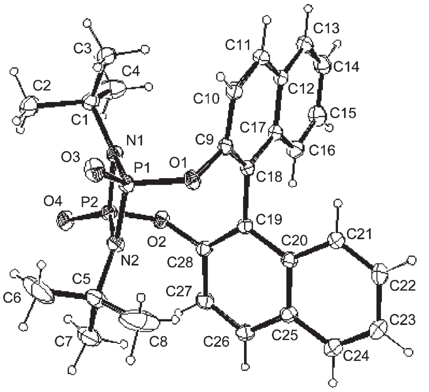

Fig. 1 ORTEP drawing of **7**; only non-hydrogen atoms labelled. Short contacts: O(4)···H(6B) 2.577, O(1)···H(11) 2.677, O(3)···H(13) 2.673, C(3)···H(21) 2.894, C(11)···H(3B) 2.867Å [labelling is similar for **5**, **6** and **8**; short contacts in **5**: O(1)···H(11) 2.658, C(11)···H(3B) 2.872Å].

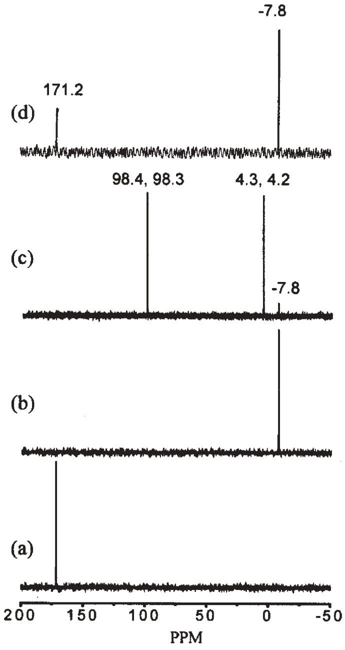

Fig. 2 The ^{31}P NMR spectra of crystals of (a) **5**, (b) **7**, (c) **6** and (d) **8**.

As regards bond parameters, values given in Table 2 can be used as a guide to the general trends. The P–N or P–O distances are longer for the P(III) derivative **5** relative to the P(V) compound **7** with values for the others in between. Noteworthy are the P=O distances in **6**, **8** and **9** which clearly reflect the partial oxygen occupancy; these values are significantly lower than the normal

Table 2 Mean bond distances (Å) in **5**–**9**[a]

Compd	P(III)–N	P(V)–N	P–O	P=O
5	1.701	—	1.664	—
6	1.689		1.630	1.393
7	—	1.673	1.600	1.454
8	1.681		1.620	1.419
9	1.689	1.676	1.638	1.328

[a] Esds are not given because the averaging is done on different numbers of entries; however, all the structures have been determined with a fair degree of accuracy.

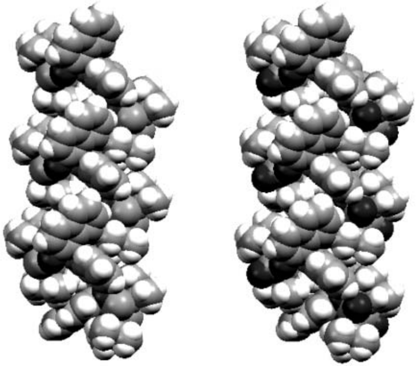

Fig. 3 Packing (space filling model) in **5** (left) and **7** (right).

P=O bond length (*cf.* 1.454Å in **7**)[11] as a result of the unconventional structural features. In this context, it is important to note that because of compositional variation of chloro/oxo groups, varying Mo=O distances were reported in the so called "bond stretch isomers".[12]

The phosphoryl (P=O) oxygen is a strong hydrogen bond acceptor and hence we were curious to see short contacts between **5** and **7** in particular; these are also shown in the caption for Fig. 1. It is strikingly clear that there are more short contacts in **7** when compared to **5**. Of particular interest are the sets (a) C(6)–H(6a)···O(3) [0.96, 2.51, 3.217(4)Å, 130°] and (b) C(6)–H(6B)···O(4′) (symmetry: $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$) [0.96, 2.58, 3.496(4) Å, 160°] in **7** that cannot be there in **5**. While the former may not play a significant role in the packing arrangement, the latter could have, but does not and hence the crystal maintains the same cell dimensions and space group as that of **5**. A space-filling model depicting the packing along the *c*-axis is shown in Fig. 3. Thus the interactions involving the P=O bond are not used as a guiding motif in the present series. This situation is different from that normally observed for other compounds (see the pairs **1a–b–3a–b** above) including Ph_3P and $Ph_3P(O)$.[13]

What we have described here is a set of chiral phosphorus compounds in which interchangeability of the lone pair and oxygen allows them to crystallize in an isostructural manner and leads to non-stoichiometry. It is possible that the molecular pseudo-C_2 symmetry also assisted this phenomenon. Such an exchange has earlier been described primarily for chloro/methyl groups in organic systems, but not for an oxygen/lone pair type of system presented here. The crystals of **6** and **8** are thus indistinguishable by unit cell dimensions/space group (but distinguishable clearly by ^{31}P NMR) although they are entirely different materials.

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Notes and references

‡ Experimental procedures are given in the ESI. X-ray data were collected on an Enraf-Nonius-MACH3 (compounds **5** and **9**) or a Bruker AXS SMART (compounds **6**–**8**) diffractometer using Mo-K_α (λ = 0.71073 Å) radiation. The structures were solved and refined by standard methods.[14] Crystal data are given as supplementary information.† CCDC numbers for **5**–**9** are, respectively, 276373–276377. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b509327a

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