X-Ray Crystal Structure Analysis of Protonated Phenyl-(t-butyl)-phosphinic Amide

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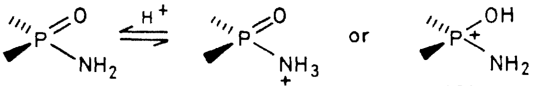
Summary Determination of the crystal and molecular structure of the hydrochloride of phenyl-(t-butyl)-phosphinic amide, $[Ph(Bu^t)P(O)NH_2]_2 \cdot HCl$, shows that the acidic proton is located between the two phosphoryl oxygen atoms, clearly demonstrating preferred *O*-protonation of the amide function.

PROTONATION of P^{IV} amides (**1**) could result in the formation of either *N*-protonated (**2**) or *O*-protonated (**3**) structures. Although the problem of whether (**2**) or (**3**) is formed is closely related to the reactivity of system(**1**) under acidic conditions, direct evidence for the structure of the conjugate acid is still lacking. *N*-Protonation to give (**2**) is favoured on the basis of kinetic[1] and stereochemical[2] studies of the acidic solvolysis of (**1**), as well as n.m.r. measurements.[3] On the other hand, recent MO calculations[4] demonstrate unambiguously the greater stability of the *O*-protonated form. Direct investigation of protonated amides (**1**) is limited by the high susceptibility of these compounds towards nucleophilic displacement. However, Harger has demonstrated[5] that some sterically hindered phosphine amides Ph(R)P(O)NH$_2$ (R = Bu^t, 1-methylcyclopropyl) form stable, crystalline hydrochlorides when dry HCl is passed into their solution in an inert solvent. The i.r. spectra of these salts did not provide clear evidence for either *N*- or *O*-protonation; dimeric structures were suggested as a possibility.[5] In order to gain further insight into the protonation behaviour of system (**1**), we have determined the crystal structure of the hydrochloride of phenyl-(t-butyl)phosphinic amide (**4**) obtained according to Harger's procedure.[5] When dry HCl is passed into a solution of (**4**) in benzene, a crystalline salt of composition (**4**) ·HCl, identical to that described in literature, is formed. However, unless HCl is admitted very slowly, a mass of crystals, analysing for (**4**) ·HCl, but too small for *X*-ray analysis, separates out. At very low rates of HCl admission, a few crystals of *ca.* 0·3 mm maximum dimension were obtained and one of these was transferred to a Lindemann capillary under dry conditions. *X*-Ray crystal analysis showed it not to be the expected simple hydrochloride (**4**) ·HCl, however.



(1) (2) (3)

The crystal size was *ca.* 0·16 × 0·04 × 0·30 mm. *Crystal data:* $(C_{10}H_{16}NPO)_2\cdot HCl$, triclinic, space group $P\bar{1}$; a = 11·816(4), b = 9·115(3), c = 12·654(5) Å, α = 117·05(8), β = 93·2(7), γ = 98·88(7)°; U = 1188·9 Å^3. There was a noticeable discrepancy between the measured density, 1·23 g ml^{-1}, and that calculated for four molecules of (**4**) ·HCl per cell, 1·3 g ml^{-1}. Intensity data were collected on a Canberra-automated Picker four-circle diffractometer using filtered Cu-K_α radiation and a pulse height analyser. 3739 reflections were recorded of which 2134 were taken to be significant on the criterion $F_0 \geqslant 2\sigma(F_0)$. The *E*-distribution indicated space group $P\bar{1}$. Application of direct methods gave no chemically intelligible *E*-maps nor could the Patterson function be interpreted in terms of P . . . Cl vectors arising from (**4**) ·HCl. After a number of attempts at solution the (**4**) ·HCl model was abandoned. The Patterson function could, however, be interpreted in terms of two molecules of (**4**) $_2$·HCl per cell and this model proved correct, refining to a conventional *R* of 0·095. [The calculated density for this material is 1·21 g ml^{-1}. The bulk sample taken for flotation presumably contained some of the more dense (**4**) ·HCl.]†

All hydrogen atoms attached to carbon were located on the ΔF map. For one nitrogen atom N(B) two hydrogen atoms close to those expected for sp^2-hybridization were clearly marked; for the other nitrogen atom only one attached hydrogen was clear and the position of the other was assumed to correspond to sp^2-hybridization also. The remaining proton was clearly established to be between the *oxygen* atoms. The Figure gives the most important bond lengths. After refinement the hydrogen bond was very asymmetric: O(A) . . . H, 0·92, and O(B) . . . H, 1·47 Å. The chloride ion may also be hydrogen bonded to the four N–H hydrogen atoms, with Cl . . . N distances of 2·26—2·75 Å.

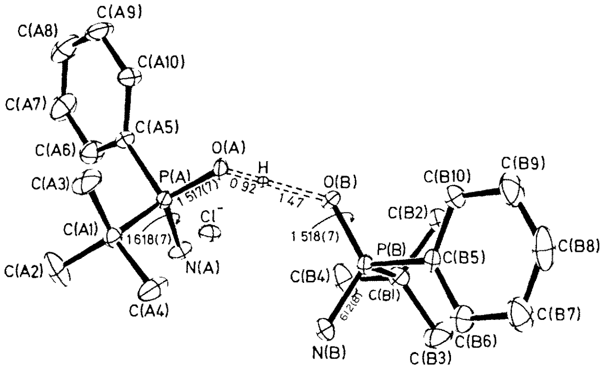


FIGURE. Molecular structure of [Ph(Bu^t)P(O)NH$_2$]$_2$·HCl.

In conclusion, we found that in the crystalline state the structure of the conjugate acid of phosphinic amide corresponds, in agreement with the MO calculations,[4] to the *O*-protonated form (**3**). This structure is further stabilized by the formation of a hydrogen bond to the phosphoryl oxygen of a second amide molecule. There is no reason to expect the stability of (**3**) to be greater than that of (**2**) in solution. The *O*-protonated from (**3**) can still interact *via* hydrogen bonding with a solvent or with another molecule of a substrate. Harger demonstrated[6] that in solution phosphinic amides associate easily with hydrogen bond donors, and suggested the possibility of dimeric structures similar to that shown in the Figure.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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[6] M. J. P. Harger, *J.C.S. Perkin II*, 1978, 326.