

COMMUNICATION

The first structural characterisation of a phosphonium amide: synthesis, isolation and molecular structure of $(\text{Ph}_3\text{PEt})^+(\text{NPh}_2)^-$

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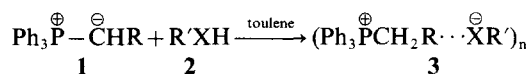
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Abstract—The first isolation of a phosphonium amide, $(\text{Ph}_3\text{PEt})^+(\text{NPh}_2)^-$, obtained via the deprotonation of a secondary amine (diphenylamine) with a phosphorus ylide (triphenylphosphonium ethylide), is described. An X-ray crystal structure provides the first observation of an essentially ion-separated Ph_2N^- anion in the solid state, though weak association with Ph_3PEt^+ cations takes place through $\text{C}\cdots\text{H}\cdots\text{N}$ hydrogen bonding. Cryoscopic and NMR spectroscopic data suggest that this association is not maintained in benzene solution.
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Much effort has been focused on the preparation and structural characterisation of compounds containing 'naked' organic anions. Of particular interest are their reactivity [1], geometry [2,3], and participation in weak intermolecular interactions [3]. A number of strategies have been employed for the synthesis of such ion-separated systems. For example, lithiation of organic acids in the presence of crown ether ligands [2], cleavage of Si—element bonds using fluorosilicate anions, [1(b),3(b)] or deprotonation of organic acids using strong, nitrogen-containing organic bases [4,5]. We recently reported the isolation and characterisation of a phosphonium aryloxide **3a** by deprotonation of a substituted phenol **2a** using a non-stabilised phosphorus ylide **1a** as a strong base [6] which has led us to consider the more general use of (particularly non stabilised) phosphorus ylides as an alternative means of generating organic anions to those strategies outlined above. We herein describe the preliminary results of one such extension of this work: the deprotonation of Ph_2NH (diphenylamine) **2b** using $\text{Ph}_3\text{PC}(\text{Me})\text{H}$ (triphenylphosphonium ethylide) **1b**. The resulting salt, $[(\text{Ph}_3\text{PEt})^+(\text{NPh}_2)^-]_n$, **3b** is,

to our knowledge, the first example of a phosphonium amide to be isolated and characterised structurally. Furthermore, the crystal structure contains the first example of an essentially 'naked' Ph_2N^- anion.



a: R = H; R' = C₆H₂Me₃-2,4,6; X = O

b: R = Me; R' = Ph; X = NPh

Reaction of solid Ph_2NH with a dry toluene solution of $\text{Ph}_3\text{C}(\text{Me})\text{H}$ resulted in the formation of a bright red precipitate which dissolved on gentle warming. Cooling to room temperature yielded a crop of red crystals. Preliminary analyses of this solid were consistent with the expected formation of a phosphonium salt $[(\text{Ph}_3\text{PEt})^+(\text{NPh}_2)^-]_n$.

A crystal structure was determined (Fig. 1) [7] which confirms the identity of **3b** as a phosphonium amide. The phosphonium cation utilises both alkyl and aryl donors in chelating the anion through two moderately strong [8] $\text{C}\cdots\text{H}\cdots\text{N}$ hydrogen bonds [C(1)—H(1b)⋯N(1) $D = 3.543(4)$, $d = 2.49$ Å, $\theta = 164^\circ$ and C(32)—H(32a)⋯N(1), $D = 3.387(5)$, $d = 2.32$ Å, $\theta = 171^\circ$] [9]. This motif of chelating alkyl

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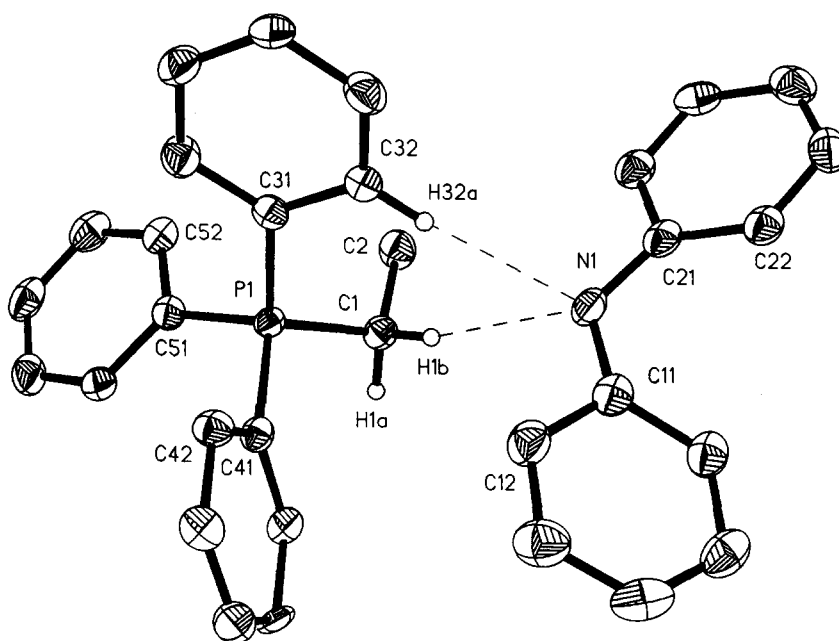


Fig. 1. ORTEP diagram of **3b** (thermal ellipsoids at 50% probability level, all aryl hydrogen atoms, except that involved in hydrogen bonding, omitted for clarity).

and aryl hydrogen bond donor groups is reminiscent of, but less extensive than, that found in **3a** and we suggest that it represents a particularly stable and general mode of association by hydrogen bonding for alkyltriphenylphosphonium salts [10].

While the geometry of the cation is not unusual, that of the $(\text{Ph}_2\text{N})^-$ anion is of considerable interest. Previous attempts to isolate this anion in a crystal have failed. Power *et al.* were able to achieve ion-separation with isoelectronic $(\text{Ph}_2\text{X})^-$ anions (where $\text{X} = \text{CH}, \text{P}, \text{As},$ or Sb) by lithiation of Ph_2XH and crystallisation in the presence of crown ethers to give solvent-separated ion pairs [2]. However, this strategy was unsuccessful in the case of Ph_2NH (due to the strong $\text{Li}-\text{N}$ bond) the result being an ion-contacted monomer $\text{Ph}_2\text{NLi} \cdot 12\text{-crown-4}$ [1(b)]. The structural characterisation of this 'naked' anion has, until now, remained elusive [11]. The geometry of the anion in **3b** does not differ significantly from that found in the ion-contacted lithium amide, which reflects the predominantly ionic nature of the $\text{Li}-\text{N}$ bond in lithium amides [12] [in **3b**; $\text{N}(1)-\text{C}(11)$, 1.380(5) Å; $\text{N}(1)-\text{C}(21)$, 1.365(3) Å; $\text{C}(11)-\text{N}(1)-\text{C}(21)$, $121.5(3)^\circ$: average corresponding values in $\text{Ph}_2\text{NLi} \cdot 12\text{-crown-4}$; 1.388 Å, and 119.1° , respectively]. In the lithium amide, the anionic nitrogen is three coordinate and planar (indicative of sp^2 hybridisation) and, though ion-separation in the case of **3b** precludes a similar definitive analysis, in view of its similar geometry to the lithium amide, we suggest that $\text{N}(1)$ in **3b** is similarly sp^2 hybridised. Significantly, the bisector of the two $\text{C}-\text{H} \cdots \text{N}$ hydrogen bond

vectors completes the trigonal planar geometry of N1 almost perfectly, implying that the $\text{C}-\text{H} \cdots \text{N}$ interactions are both with a lone pair of electrons in an sp^2 orbital of nitrogen. It is well established that weak hydrogen bonds can exhibit such electrostatic directionality [13] and this leaves the other lone pair of electrons in the nitrogen p orbital to interact with the π -system of the phenyl rings. In spite of this proposed interaction, the nitrogen-bound phenyl rings are not coplanar, as would be required for ideal overlap of the nitrogen p orbital with both phenyl π -systems, but are tilted at an angle of 39.9° to each other. This is presumably in order to relieve steric strain between the hydrogen atoms bound to $\text{C}(22)$ and $\text{C}(16)$ rather than for compelling electronic reasons.

Cryoscopic RMM measurements [14] suggest that the ion pairs observed in the solid state are not maintained in benzene solution. ^1H and ^{31}P NMR spectroscopies [15] are consistent with the existence of phosphonium and amide ions in solution though, especially in view of the expected similarity in the pK_a of Ph_3PEt^+ and Ph_2NH [16], the operation of an equilibrium (fast on the NMR time scale) between ionic and molecular species in solution cannot be discounted.

We believe that this work demonstrates that the reaction of basic ylides, not exclusively phosphonium ylides, with acidic compounds, not exclusively alcohols or amines, offers much scope for development, both in terms of the study of weak hydrogen bonds in the absence of other, more dominant intermolecular interactions and in terms of the isolation and util-

isation of 'naked' anions. We are currently investigating further both chemical and structural aspects related to using group 15 ylides and related compounds in the generation of weakly associated ion pairs.

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- Crystal data for **3b**: $C_{32}H_{30}NP$, $M = 459.54$, Monoclinic, space group $P2_1/c$, $a = 9.888(2)$, $b = 14.256(3)$, $c = 17.815(4)$ Å, $\beta = 98.75(3)^\circ$, $U = 2482.0(9)$ Å³, $Z = 4$, $D_c = 1.230$ g cm⁻³, $\lambda(\text{Mo-K}_\alpha) = 0.71073$ Å, $\mu(\text{Mo-K}_\alpha) = 0.132$ mm⁻¹, $T = 153(2)$ K. Data were collected on a Stoe four-circle diffractometer in the range $5 \leq 2\theta \leq 55^\circ$ (3395 reflections were collected of which 3117 were independent, $R_{int} = 0.058$). The structure was solved by direct methods [17] and refinement, based on F^2 , was by full matrix least-squares techniques [17] (all non hydrogen atoms were refined anisotropically; H atoms, except H(1a) and H(1b) which were located and refined freely, were placed in calculated positions) to R [F , for 2558 unique reflections for which $F > 4\sigma(F)$] = 0.0403, wR (F^2 , all data) = 0.1214. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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- Cryoscopic measurement for **3b**: relative molecular mass = 280 ± 10 for 8.0×10^{-3} M benzene solution, corresponding to degree of association, n (relative to monomeric $\text{Ph}_3\text{PEt} \cdot \text{NPh}_2$) = 0.62 ± 0.03 .
- ¹H NMR (200 MHz, C₆D₆, 25°C, TMS): $\delta = 2.1$ (d, 3H, $\text{Ph}_3\text{PCH}_2\text{CHM}_3$, $^3J_{\text{PH}} = 19$ Hz), 3.9 (br.s, 2H, $\text{Ph}_3\text{PCH}_2\text{CH}_3$), 6.8–7.7 (m, 25H, $\text{Ph}_3\text{PCH}_2\text{CH}_3$ and Ph_2N) ppm. ³¹P NMR (101.2 MHz, C₆D₆, 25°C, 85% H₃PO₄): $\delta = 19.4$ ppm.
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