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UNEXPECTED LINEAR P—N—P FRAGMENT IN THE ANION $[SPh_2PNPPh_2S]^-$: CRYSTAL STRUCTURE OF BIS(TRIPHENYLPHOSPHINE)IMINIUM DITHIOTETRAPHENYLIMIDODIPHOSPHINATE, $[Ph_3PNPPh_3]^+[SPh_2PNPPh_2S]^-$

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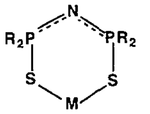
Abstract—The structure of $[Ph_3PNPPh_3]^+[SPh_2PNPPh_2S]^-$ was determined by single crystal X-ray diffraction. The cation displays the usual bent conformation [P—N—P 143.0(5)°] and long P—N bonds (1.577(3) Å). This salt represents the first example of a linear $SPh_2PNPPh_2S^-$ anion (P—N—P 180°) with short P—N bonds [1.554(2) Å]. The structures of the bent and linear forms of the $[Ph_3PNPPh_3]^+$ cation and $[SPh_2PNPPh_2S]^-$ anion can be rationalized in terms of P—N single and double bond contributions to the resonance structures describing them.

The tetra(alkyl,aryl)dithioimidodiphosphinate anion $[SR_2PNPR_2S]^-$ is a versatile ligand, able to form inorganic (carbon-free) chelate rings, **1**.[1] It is derived from bis(thiophosphinyl)amine, $R_2(S)PNHP(S)R_2$, **2**, which can be readily deprotonated with alkali metals,[2] metal alkoxides (e.g. KOBut[2] NaOEt[3]) or even ammonia[2] to give the corresponding metal or ammonium salts.

While the molecular structures of the parent, neutral bis(thiophosphinyl)amines, **2** (R = Ph[4a–c] and Me[4d]), have been determined independently by various laboratories, few structural investigations of their salts have been performed. The potassium salt was recently found to display a supramolecular structure, as a ladder polymer consisting of chelate ring $K(SPPh_2)_2N$ units, connected through K ··· S interactions.[5] The only compound containing a discrete, free dithioimidiodiphosphinato anion, $[SPh_2PNPPh_2S]^-$ **3**, investigated by X-ray diffraction, is the potassium crown ether salt $[K(18\text{-crown-}6)]^+[SPh_2PNPPh_2S]^-$.[6]

Both in the bis(thiophosphinyl)amine **2** and in the anion of **3** the P—N—P fragment is bent, with an *anti* orientation of the sulphur atoms. In **2** there are distinct single P—N and double P═S bonds, while in **3** the pi electrons are delocalized.



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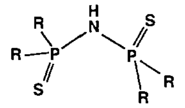

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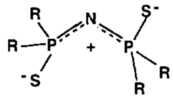

3

The P—N—P fragment is also present in cationic species, $[R_3PNPR_3]^+$, **4** (R = Ph) commonly known as PPN^+. In this cation, the P—N—P fragment is usually bent (P—N—P bond angle in the range 134–142°), e.g. in salts of metal carbonyl[7] and hydroborate[8] anions, but a linear structure has been found in some compounds. There are now well over 100 structures containing the PPN^+ cation determined by X-ray diffraction, but apparently only five contain a linear PNP sequence.[9a] These are: $PPN^+[Fe(CN)_2Pc]^-$ (where Pc = phtalo-

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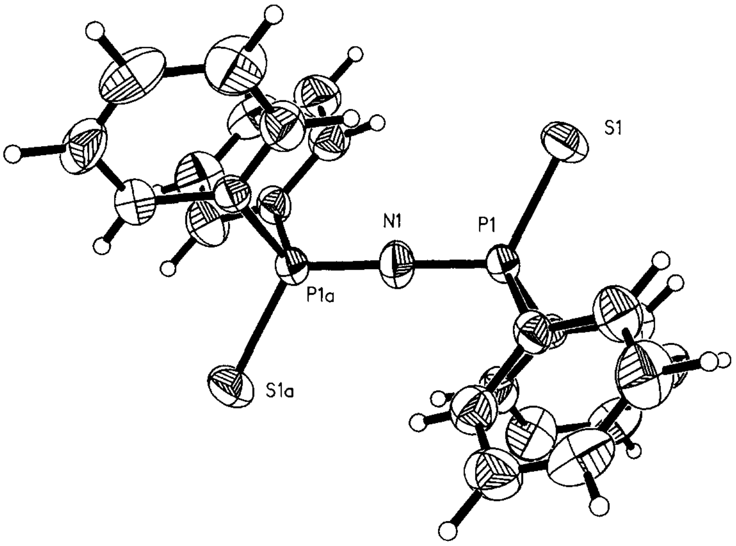


Fig. 1. Structure of linear $[SPh_2PNPPh_2S]^-$ anion with the atom numbering scheme.

cyaninato),[9a] $PPN^+[V(CO)_6]^-$,[9b] $PPN^+[Nb(CO)_6]^-$,[9c] $PPN^+[Au\{Co(CO)_4\}_2]^-$,[9d] and $PPN^+[Ni_2(CO)_6H]^-$.[9e] Both bent and linear PPN^+ cations have been found in the same crystal of the compound $[PPN]_3[NaMo_3(CO)_6(NO)_3(\mu_2\text{-}OMe)_3(\mu_3\text{-}O)_2]$ complex.[10] The energy barrier between the bent and linear forms of PPN^+ (calculated with the CNDO2-SCF method) is small[11] and packing forces seem to be enough to influence the molecular geometry in various crystals.

We considered it of interest to combine the cation **4** with the anion **3** in a single compound and to determine the crystal structure of the resulting salt. It has been recognized already that the PPN^+ species is a very valuable counter-ion for the stabilization of various organometallic anions in the solid state[12] and it has been frequently used in crystal structure determinations. It was expected and experimentally confirmed that such a salt will also contain independent $[SPh_2PNPPh_2S]^-$ anions.

RESULTS AND DISCUSSION

Preparation of $[Ph_3PNPPh_3]^+[SPh_2PNPPh_2S]^-$

The synthesis of this compound was first described in a Ph.D. thesis[13] which has never been published. We used a similar procedure, based upon the double exchange reaction:

$$[Ph_3PNPh_3]^+Cl^- + K^+[SPh_2PNPPh_2S]^- \longrightarrow$$
$$[Ph_3PNPPh_3]^+[SPh_2PNPPh_2S]^- + K^+Cl^-. \quad (1)$$

The salt crystallizes as a colourless solid, m.p. 234–235°C, and can be recrystallized from acetonitrile.

Structure analysis

The crystal structure of the salt was established by X-ray diffraction, using a crystal grown from acetonitrile. The anion is shown in Fig. 1 and the cation in Fig. 2. The anion–cation packing in the unit cell is presented in Fig. 3. Important interatomic distances and bond angles are listed in Table 1. Refined atomic coordinates and temperature factors for both the cation and anion, and other data are available as supplementary material.

The most surprising result was the linear structure of the P—N—P fragment in the anion $[SPh_2PNPPh_2S]^-$. This is clearly illustrated by Fig. 1, which shows a view of the anion along an axis perpendicular to the P—N—P bond sequence. By

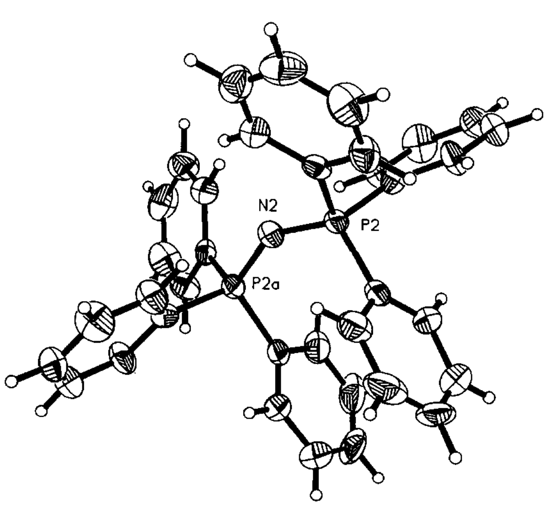


Fig. 2. Structure of the bent $[Ph_3PNPPh_3]^+$ cation with the atom numbering scheme.

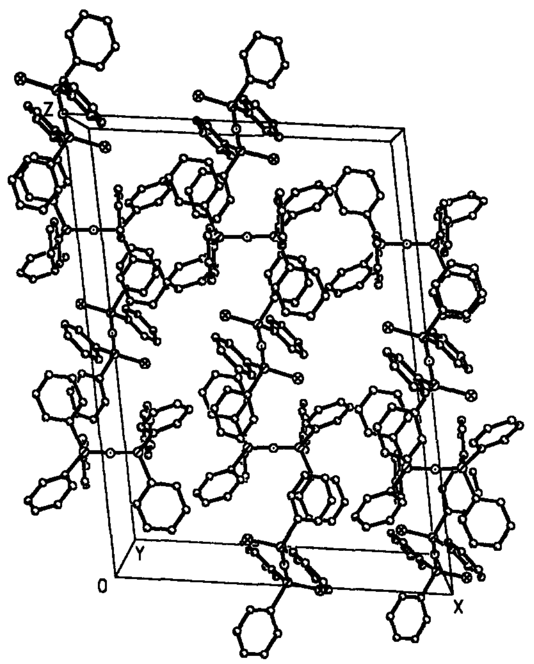


Fig. 3. Unit cell packing. Note the rows of cations alternating with rows of anions.

contrast, in the cation, the P—N—P sequence is bent, and the value of this bond angle (143.0°) is near the upper limit of the bent bond angle values observed in various PPN^+ salts.[9a]

A comparison of essential interatomic distances and bond angles in the neutral **2** (R = Ph), anionic **3** (R = Ph) in three different salts (including the one described here) and the bent and linear cation $[Ph_3PNPPh_3]^+$ is presented in Table 2. In the parent $Ph_2(S)PNHP(S)Ph_2$ (**2**) the interatomic distances clearly indicate P═S double and P—N single bond character. In the $[SPh_2PNPPh_2S]^-$ anions a length of the P—S bonds intermediate between single and double bond values[14] and the shortening of the P—N interatomic distances, indicate partial double bond character, i.e. charge and π-electron delocalization all over the SPNPS fragment. The values of P—N bond lengths are in the range observed in cyclophosphazenes.[15]

The short P—N bond length (1.554 Å) observed in the linear anion $[SPh_2PNPPh_2S]^-$ is comparable to that observed in the linear cation $[Ph_3PNPPh_3]^+$ (see Table 2) and indicates substantial double bond character, even more than in cyclophosphazenes. According to these molecular dimensions and using classical Lewis structure diagrams, the linear and bent anions and cations discussed here can be intuitively described with the aid of major contributions of canonic forms **a**–**d** to the respective resonance structures.

A space filling representation of the anion and cation (Fig. 4) is a good illustration of the shape of these species. Since the charge is buried well inside

Table 1. Interatomic distances (Å) and bond angles (°) in $[Ph_3PNPPh_3]^+$

Anion $[SPh_2PNPPh_2S]^-$ (Fig. 1)			
P(1)—S(1)	1.975(2)	P(1)—C(1)	1.820(6)
P(1)—N(1)	1.554(2)	P(1)—C(7)	1.820(6)
P(1A)—N(1)	1.554(2)		
P(1)—N(1)—P(1A)	180.0(1)	S(1)—P(1)—C(1)	111.2(2)
S(1)—P(1)—N(1)	117.4(1)	S(1)—P(1)—C(7)	108.5(2)
		N(1)—P(1)—C(1)	107.2(2)
		S(1)—P(1)—C(7)	108.8(2)
		C(1)—P(1)—C(7)	102.7(3)
Cation $[Ph_3PNPh_3]^+$ (Fig. 2)			
P(2)—N(2)	1.577(3)	P(2)—C(13)	1.797(6)
P(2A)—N(2)	1.577(3)	P(2)—C(19)	1.794(6)
		P(2)—C(25)	1.799(6)
P(2)—N(2)—P(2A)	143.0(5)	N(2)—P(2)—C(13)	114.9(3)
		N(2)—P(2)—C(19)	107.5(3)
		N(2)—P(2)—C(25)	111.0(2)
		C(13)—P(2)—C(19)	107.8(3)
		C(13)—P(2)—C(25)	107.1(3)
		C(19)—P(2)—C(25)	108.4(3)

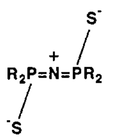
Symmetry operations are: for the anion: $x, y, z \rightarrow 0-x, 0-y, 2-z$; for the cation: $x, y, z \rightarrow 1-x, 0+y, 1.5-z$.

Table 2. Comparison of some interatomic distances (Å) and bond angles (°) in neutral **1**, anionic **2** and cationic **3**

Compound	P—S	P—N	P—N—P	S—P—N	C—P—C	Ref.
$Ph_2(S)P—NH—P(S)Ph_2$	1.936[a]	1.684	132.6	114.7	107.7	4a
	1.950	1.671		115.5		
	1.937	1.683	132.7	114.5		4b
	1.950	1.672		114.6		
$K^+[SPh_2PNPPh_2S]^-$	1.978	1.592	128.6	120.7		5
$[K(18\text{-crown-}6)]^+[SPh_2PNPPh_2S]^-$	1.976	1.599	132.8	120.8	100.2	6
$[Ph_3PNPh_3]^+[SPh_2PNPPh_2S]^-$						
bent cation	—	1.577	143.0	—	107.7	This
linear anion	1.975	1.554	180	117.4	102.7	work
Compare with salts of the linear cation:						
$[Ph_3PNPPh_3]^+[Fe(CN)_2Pc]^-$	—	1.555	180			9a
$[Ph_3PNPPh_3]^+[V(CO)_6]^-$	—	1.539	180			9b
$[Ph_3PNPPh_3]^+[Nb(CO)_6]^-$	—	1.547	180			9c
$[Ph_3PNPPh_3]^+[Au\{Co(CO)_4\}_2]^-$	—	1.547	180			9d
$[Ph_3PNPPh_3]^+[Ni_2(CO)_6H]^-$	—	1.55	175.6			9e

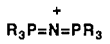
[a] The difference in the P═S bond lengths is due to the participation of one of them (the longest) in P═S ··· H—N hydrogen bonding to form a dimer.

the anion and cation, respectively, the lattice packing does not require alternation of the cations with the anions. Thus, rows of neighbouring cations with the rows of anions are alternating in the crystal lattice (Fig. 3).



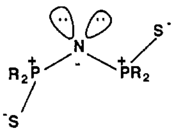
a

linear anion



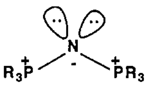
b

linear cation



c

bent anion



d

bent cation

If the values observed experimentally in various P—N—P compounds discussed are compared with those expected for double P═N bonds (1.56 Å) and single P—N bonds (1.77 Å)[16] these formulations seem sustainable. It should be noted that even in neutral $Ph_2(S)P—NH—P(S)Ph_2$ a small degree of P—N—P π-electron delocalization is suggested by the P—N bond lengths and by the near planarity (sp^2 hybridization) of the three bonds (2 P—N and N—H) around nitrogen (sum of bond angles 358.7°).[4b]

Alternatively, the differences observed in the P—N bond lengths can be simply interpreted as hybridization effects. Thus, in the absence of any π interactions, the carbon–carbon bond distances differ by a methyl group attached to a carbon atom in various states of hybridization: $H_3C—C(sp^3)$ 1.53–1.54 Å, $H_3C—C(sp^2)$ 1.50 Å and $H_3C—C(sp)$ 1.47 Å.[17] In our pairs of compounds the hybridization of nitrogen is sp^3 in the bent fragments and sp in the linear fragments, and thus may produce similar bond length effects.

EXPERIMENTAL

Preparation of $[Ph_3PNPPh_3]^+[SPh_2PNPPh_2S]^-$

The compound was prepared as described by Dillard.[13] Thus, a slurry of 2 g $K^+[SPh_2PNPPh_2S]^-$ in 30 cm^3 methylene chloride was treated with 2.35 g PPN^+Cl^- in 20 cm^3 methylene chloride, the mixture was stirred for 3 h at room temperature, then diethyl ether was added to precipitate the salt. The white solid was filtered and recrystallized from acetonitrile. M.p. 234–235°C (lit. 235–236°C).[13] Found: C, 72.8; H, 5.2; N, 2.4%. $C_{60}H_{50}N_2P_4S_2$ (M 987) requires: C, 73.0; H, 5.1; N, 2.8%. The compound displays two ^{31}P NMR signals at 36.77 ppm (anion) and 21.02 ppm (cation).[13]

Table 3. Crystal data and refinement results for $[Ph_3PNPPh_3]^+$ $[SPh_2PNPPh_2S]^-$

Empirical formula	$C_{60}H_{50}N_2P_4S_2$
Formula weight	987.0
Crystal size (mm)	0.28 × 0.24 × 0.20
Space group	C2/c (monoclinic)
Unit cell dimensions	a = 17.687(4) Å b = 12.681(2) Å c = 23.955(5) Å β = 98.750°
Unit cell volume (Å^3)	5310(2)
d_{calc} (g cm^{-3})	1.235
Radiation used	Mo-K_α (λ = 0.71073 Å)
Absorption coefficient (mm^{-1})	0.261
2θ range (°)	3.0–50
Scan type	omega
Index range	$0 < h < 20$ $0 < k < 15$ $-29 < l < 28$
Reflections collected	4828
Independent reflections	4664
Observed reflections (with $F > 4.0\ \sigma(F)^2$)	2172 (R_{int} = 3.19%)
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0003F^2$
No. of parameters refined	310
Final R indices (obsd data) (%)	R = 6.14; wR = 5.46
R indices (all data)	R = 14.21; wR = 7.51
Goodness-of-fit	1.23

R defined as: $R = \dfrac{\Sigma[|F_o| - |F_c|]}{\Sigma|F_o|}$

wR defined as: $wR = \left[\dfrac{\Sigma[w|F_o - F_c|]^2}{\Sigma w|F_o|^2}\right]^{1/2}$.

X-ray data collection and structure analysis

A single crystal of the title compound, grown from acetonitrile, was selected for X-ray diffraction analysis. The crystal data and refinement results are listed in Table 3. All data were collected at room temperature (293 K) using a Siemens P4 PC diffractometer and graphite monochromated Mo-K_α radiation (λ = 0.71073 Å), with variable scan speed (4–30° min^{-1}) in the ω = 0–60° range. Three standard reflections were measured after every 97 reflections. No absorption correction was applied in view of the small absorption coefficient. The data were refined using the Siemens SHELXTL PLUS (PC version) set of programs and the structure was solved by direct methods and refined by the full-matrix least-squares method. The hydrogen atoms were introduced at fixed positions but not refined.

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Supplementary material available. Structure determination summary (crystal data, data collection, solution and refinement details), complete listings of atomic coordinates with equivalent isotropic displacement coefficients, bond lengths and angles, anisotropic displacement coefficients and H-atom coordinates with iso-

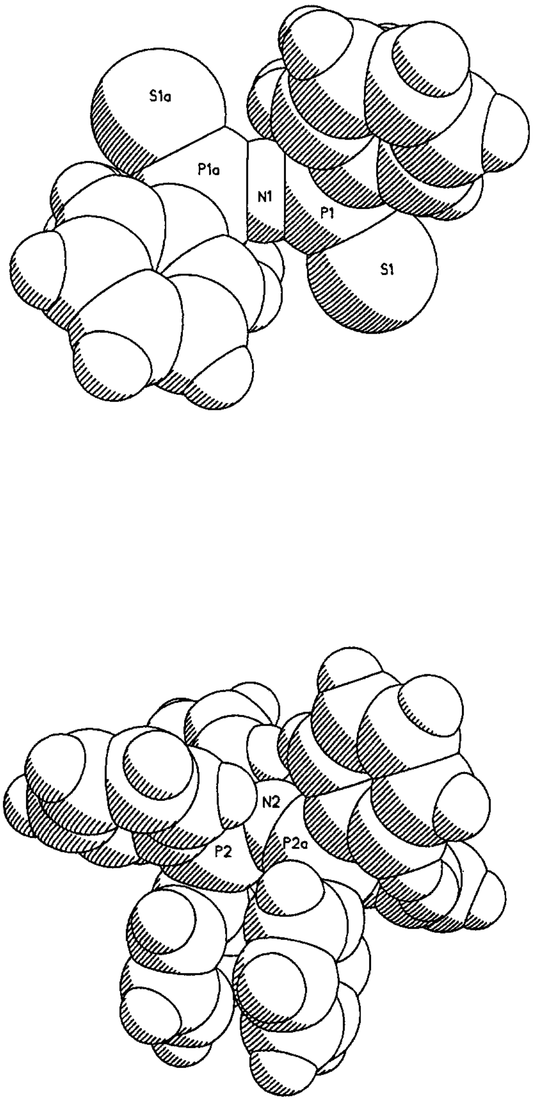

Fig. 4. Space filling models of the anion and cation.

tropic displacement coefficients (8 pages) were deposited with the editor at Cambridge Crystallographic Data Centre.

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