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HEXAORGANO-SUBSTITUTED TRIATOMICS R_3XYZR_3: THE CONFIGURATION OF $(R_3PNPR_3)^+$ AND THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIPHENYL(*P,P,P*-TRIPHENYLPHOSPHINE IMIDATO-*N*)PHOSPHORUS(I) THIOCYANATE

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Summary

Crystals of $(Ph_3P)_2N^+$ SCN^- are monoclinic, *a* 10.836(3), *b* 12.744(5), *c* 24.051(4) Å, β 103.33(2)°; space group $P2_1/c$. In the cation the angle PNP is 136.3(6)°, and despite the virtual identity of their ESCA chemical shifts the salts $(Ph_3PNPPh_3)X$ for X = NCS^- and $V(CO)_6^-$ are not isomorphous, nor are the cations in them isostructural. The anion exhibits both positional and orientational disorder. MNDO calculations on simple analogues of the cation are reported and discussed.

Introduction

The cation $(Ph_3P)_2N^+$ exhibits a wide range both of phenyl group conformation and of PNP angle [1,2]. It would be desirable, in view of the wide range of PNP angles known, to have a non-crystallographic means for the determination of this angle in crystalline salts: Ruff [3] measured the ESCA spectra of a series of simple salts $(Ph_3P)_2N^+ X^-$ (X^- = F^-, Cl^-, Br^-, I^-, NO_3^-, NCO^-, NCS^-, N_3^- and $V(CO)_6^-$) and found that the N(1*s*) and P(2*p*) binding energies were essentially independent of the counter ion. This observation implies either that the cation geometry is the same in these salts, with a linear PNP fragment as found when X^- = $V(CO)_6^-$ [4], or that the binding energies are independent of the PNP angle, when no conclusion could be reached about the angle from the ESCA data.

In this paper we report a further study, by X-ray methods, of the simple salts $(Ph_3P)_2N^+ X^-$, including a single crystal structure analysis for X^- = SCN^-, which

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shows that none of the other salts is isostructural with the hexacarbonylvanadate(—I), and that they are not isostructural with one another. In particular the thiocyanate salt has a PNP angle of 136.3(6)°, compared to the value of 180° found when $X = V(CO)_6^-$.

We report also the results of MNDO calculations on some simple analogues of $(Ph_3P)_2N^+$: conformation analyses of simple ions $(X_3P)_2N^+$ for X = H, F, Cl, and CH_3 made by the PCILO method have been reported previously [5].

Experimental

Salts $(Ph_3P)_2N^+ X^-$ were prepared from $(Ph_3P)_2N^+ Cl^-$ by metathesis [6]. X-ray powder diffraction patterns were recorded for $(Ph_3P)_2N^+ X^-$ ($X^- = Cl^-$, Br^-, I^-, NO_2^-, NO_3^-, NCO^-, NCS^-, and N_3^-) using a Philips powder diffractometer: no satisfactory preparation of $(Ph_3P)_2N^+ F^-$ was achieved, as this salt is extremely hygroscopic, and hence no powder diffraction was recorded in this case. Crystals of $(Ph_3P)_2N^+ NCS^-$ suitable for single crystal diffractometry were grown from aqueous ethanol solution.

Data collection

Data were collected using a Stoe Stadi-2 diffractometer with graphite-monochromatised Mo-K_α radiation, in the ω—2θ scan made with a scan speed of 0.0167° s^{-1} in ω. The intensities of 4627 reflections were measured; standard reflections measured every 50 reflections showed only small random deviations about their mean intensities: backgrounds were measured at each end of the peak scan for a time equal to (scan time/2). Lorentz and polarisation corrections were applied but no absorption corrections were made.

Crystal data

$C_{37}H_{30}P_2N_2S$, mol.wt. 596.66; monoclinic, space group $P2_1/c$ (C_{2h}^5; No. 14); a 10.836(3), b 12.744(5), c 24.051(4) Å; $\beta = 103.33(2)°$; U 3231.7 Å^3. $Z = 4$, D_c 1.226 mg m^{-3}; $F(000) = 1248.00$; Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 1.85 cm^{-1}. Systematic absences $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$ defined the space group $P2_1/c$ uniquely.

Structure solution and refinement

X-ray calculations were made using SHELX-76 [7]. The structure was solved by direct methods using the general multisolution tangent refinement option, TANG. The best E-map yielded positions for the P—N—P fragment and for 12 carbon atoms of the cation, and a subsequent difference map revealed the remaining carbon atoms of the cation. Blocked full-matrix least-squares refinement with P and N anisotropic and C isotropic yielded $R (= \Sigma\Delta/\Sigma F_0;\ \Delta = |F_0 - F_c|) = 0.1822$ and $R_G (= (\Sigma w\Delta^2/\Sigma w|F_0|^2)^{1/2}) = 0.2111$. At this stage, a difference map revealed acceptable positions for the majority of the hydrogen atoms, and in addition showed clearly that the thiocyanate anion was disordered: the difference map showed two orientations of an almost linear ion in which the position of the sulphur atom was common to both orientations, and in which the two alternative S—C vectors were approximately normal to one another. The disorder was initially investigated by refining the site occupation factors (s.o.f.) of the carbon and nitrogen atoms in the anion such that the s.o.f.s of the C and N atoms in each orientation were held to be equal, and the total s.o.f. for each atom was constrained to be unity: this refinement indicated equal population of the two orientations. However when the s.o.f.s of C and N were allowed to refine independently that for nitrogen refined to 0.95 ± 0.01, rather than 0.5, indicative of a higher electron density than would be accounted for by nitrogen alone, and suggesting in fact a second form of disorder in which the thiocyanate ions are not only in two independent sites, but also suffer orientational disorder within each site such that sometimes the sulphur atom is common to the two sites but sometimes the nitrogen is the common atom. A difference map calculated on the basis of a single disordering with equal population of the two sites confirms the existence of the double disorder, since because of the unequal C—N and S—C distance in the anion, and its slight departure from linearity, the carbon positions for the two orientations are not coincident.

All refinements which included the double disorder proved to be unstable and gave unreasonable values of the site occupation factors, irrespective of the particular constraints applied to the s.o.f.s. Such phenomena in the presence of double disorder have been observed previously, as for example, in $Si(NCS)_4$ [8], and may be perhaps traced to the severe correlation between positional parameters, thermal parameters, and s.o.f.s which occurs in these circumstances. Further refinement therefore proceeded on the basis of single disorder only, even though this is known to be an imperfect description of the structure, with S, P and cationic N anisotropic and anionic N, C, and H isotropic. Because of the problem of the disorder, it was not felt to be worthwhile to refine the phenyl rings anisotropically, and it was not possible, because of the correlation referred to above, to refine the carbon and nitrogen of the anion anisotropically. In the final cycles of refinement, with H atoms in calculated positions having a common isotropic temperature parameter, 198 parameters were varied, comprising 132 positional parameters, 24 anisotropic temperature factor components, 41 isotropic temperature parameters, and one overall scale factor, to yield R = 0.1308 and R_G = 0.1431, at which point refinement was discontinued for the reasons discussed earlier. A final difference map revealed no electron density >0.2 Å^{-3}, except around the disordered anion. Final atom coordinates are given in Table 1, and thermal parameters in Table 2: the geometry of the cation is given in Table 3, and that of the anion in Table 4. Least-square planes for the phenyl groups are given in Table 5. The structure of the cation, with the numbering scheme for its atoms, is shown in Fig. 1, and the singly disordered structure of the anion is shown in Fig. 2: the unit-cell contents are shown in Fig. 3.

Molecular energy calculations

There is at the present time no feasible way of undertaking molecular energy calculations, with geometry optimisation, by the molecular orbital method for a cation as large as $(Ph_3P)_2N^+$: even using valence electrons only, with no *d*-orbitals on phosphorus, this ion has 188 electrons in 186 orbitals, and its structure requires 201 geometrical variables for complete definition. Accordingly we have restricted our calculations to the simple analogues $(H_3P)_2N^+$ and $(Me_3P)_2N^+$. Calculations were made using the PCILO [9] and MNDO [10,11]

TABLE 1

FRACTIONAL ATOMIC COORDINATES (Å $\times 10^4$)

Atom	x	y	z
S(1)	7347(4)	995(4)	4100(2)
C(1)	8892(28)	1371(27)	4415(12)
N(1)	10033(20)	2026(19)	4671(9)
C(2)	7693(27)	—81(26)	4633(12)
N(2)	7690(12)	—1070(11)	4878(5)
P(1)	4389(2)	3629(2)	6394(1)
P(2)	2414(2)	3565(3)	7052(1)
N(3)	3670(7)	3254(8)	6866(3)
C(11)	4919(8)	2467(8)	6079(4)
C(12)	4958(9)	1523(9)	6358(4)
C(13)	5407(10)	631(10)	6128(5)
C(14)	5788(11)	705(11)	5620(5)
C(15)	5745(10)	1669(10)	5344(5)
C(16)	5314(10)	2548(10)	5565(5)
C(21)	3458(10)	4410(9)	5824(4)
C(22)	2556(11)	3874(11)	5398(5)
C(23)	1755(13)	4481(12)	4987(6)
C(24)	1841(13)	5556(13)	4989(6)
C(25)	2704(13)	6064(13)	5395(6)
C(26)	3527(11)	5487(11)	5829(5)
C(31)	5785(9)	4351(9)	6713(4)
C(32)	6564(11)	4795(10)	6482(5)
C(33)	7672(12)	5320(11)	6639(6)
C(34)	8028(13)	5423(12)	7220(6)
C(35)	7279(13)	4948(12)	7556(6)
C(36)	6136(11)	4463(10)	7306(5)
C(41)	2675(9)	3287(8)	7807(4)
C(42)	3795(10)	2863(9)	8102(4)
C(43)	4012(12)	2708(11)	8702(5)
C(44)	3063(12)	2999(11)	8978(6)
C(45)	1937(12)	3420(11)	8675(5)
C(46)	1723(11)	3612(10)	8084(5)
C(51)	1093(9)	2776(8)	6683(4)
C(52)	—154(12)	3013(11)	6736(5)
C(53)	—1138(13)	2357(12)	6460(5)
C(54)	—910(13)	1515(12)	6135(6)
C(55)	313(12)	1313(12)	6091(6)
C(56)	1317(10)	1928(9)	6356(4)
C(61)	1987(9)	4920(9)	6968(4)
C(62)	1083(10)	5317(10)	6503(5)
C(63)	864(11)	6389(11)	6441(5)
C(64)	1558(12)	7089(12)	6826(5)
C(65)	2487(14)	6717(13)	7287(6)
C(66)	2699(13)	5637(12)	7350(6)

methods. In the PCILO calculations, all bond lengths and interbond angles were held fixed at values derived from ions and molecules of similar type, as described previously [5]: the minimum energy conformation was determined from conformational energy maps for a series of fixed values of the angle PNP, from which the equilibrium values of angle PNP, and the energy barriers between the equilibrium and linear configurations were found. In the MNDO calculations, all independent geometrical variables were simultaneously opti-

(Continued on p. 179)

TABLE 2

THERMAL PARAMETERS (Å × 10^3)

(a) Anisotropic thermal parameters

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{iso} [a]
S(1)	79(3)	75(3)	68(3)	—1(2)	35(2)	6(2)	68(3)
P(1)	24(1)	35(2)	27(1)	—2(1)	10(1)	—1(1)	26(2)
P(2)	26(1)	38(2)	23(1)	0(1)	9(1)	1(1)	27(2)
N(3)	21(4)	48(6)	27(4)	1(4)	16(3)	—4(4)	25(5)

(b) Isotropic thermal parameters

Atom	U	Atom	U
C(1)	63(8)	C(2)	65(8)
N1(1)	53(6)	N(2)	32(3)
C(11)	29(2)	C(41)	32(2)
C(12)	36(2)	C(42)	40(2)
C(13)	43(3)	C(43)	49(3)
C(14)	46(3)	C(44)	53(3)
C(15)	42(3)	C(45)	56(3)
C(16)	40(3)	C(46)	46(3)
C(21)	31(2)	C(51)	27(2)
C(22)	44(3)	C(52)	52(3)
C(23)	58(4)	C(53)	56(3)
C(24)	60(4)	C(54)	61(4)
C(25)	56(4)	C(55)	59(3)
C(26)	45(3)	C(56)	36(2)
C(31)	29(2)	C(61)	31(2)
C(32)	41(3)	C(62)	42(3)
C(33)	51(3)	C(63)	50(3)
C(34)	57(4)	C(64)	52(3)
C(35)	60(4)	C(65)	67(4)
C(36)	44(3)	C(66)	60(4)

[a] U_{iso} is defined as the geometric mean of the diagonal elements of the diagonalised matrix of U_{ij}. All hydrogen atoms were given a common isotropic thermal parameter which refined to 107(13) × 10^{-3} Å^2. Anisotropic thermal parameters take the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23}$ $2lhc^*a^*U_{31} + 2hka^*b^*U_{12})]$.

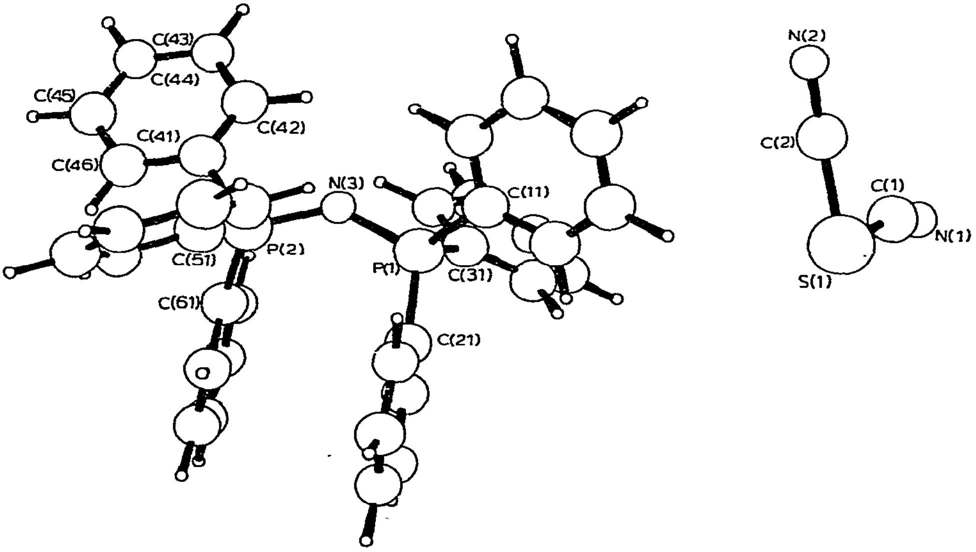

Fig. 1. The structure of the cation $(Ph_3P)_2N^+$ showing the numbering of the atoms.

TABLE 3

GEOMETRY OF THE CATION

(i) Bond distances (Å)

P(1)...P(2)	2.941(9)		
P(1)—N(3)	1.592(9)	P(2)—N(3)	1.579(9)
P(1)—C(11)	1.817(10)	P(2)—C(41)	1.807(10)
P(1)—C(21)	1.802(10)	P(2)—C(51)	1.806(9)
P(1)—C(31)	1.786(10)	P(2)—C(61)	1.787(12)
C(11)—C(12)	1.373(15)	C(41)—C(42)	1.367(13)
C(12)—C(13)	1.399(17)	C(42)—C(43)	1.422(16)
C(13)—C(14)	1.381(18)	C(43)—C(44)	1.397(20)
C(14)—C(15)	1.391(18)	C(44)—C(45)	1.378(17)
C(15)—C(16)	1.367(18)	C(45)—C(46)	1.410(17)
C(16)—C(11)	1.402(15)	C(46)—C(41)	1.412(16)
C(21)—C(22)	1.419(15)	C(51)—C(52)	1.418(17)
C(22)—C(23)	1.390(18)	C(52)—C(53)	1.396(18)
C(23)—C(24)	1.373(22)	C(53)—C(54)	1.382(21)
C(24)—C(25)	1.352(19)	C(54)—C(55)	1.378(20)
C(25)—C(26)	1.413(18)	C(55)—C(56)	1.373(17)
C(26)—C(21)	1.374(18)	C(56)—C(51)	1.392(16)
C(31)—C(32)	1.405(17)	C(61)—C(62)	1.401(14)
C(32)—C(33)	1.388(17)	C(62)—C(63)	1.389(19)
C(33)—C(34)	1.367(18)	C(63)—C(64)	1.379(18)
C(34)—C(35)	1.406(22)	C(64)—C(65)	1.397(18)
C(35)—C(36)	1.391(18)	C(65)—C(66)	1.398(23)
C(36)—C(31)	1.396(15)	C(66)—C(61)	1.395(17)

(ii) Bond angles (°)

P(1)—N(3)—P(2)	136.3(6)		
N(3)—P(1)—C(11)	107.8(5)	N(3)—P(2)—C(41)	106.9(4)
N(3)—P(1)—C(21)	115.4(5)	N(3)—P(2)—C(51)	111.0(5)
N(3)—P(1)—C(31)	110.7(5)	N(3)—P(2)—C(61)	115.4(5)
C(11)—P(1)—C(21)	108.0(5)	C(41)—P(2)—C(51)	107.9(5)
C(11)—P(1)—C(31)	106.3(5)	C(41)—P(2)—C(61)	106.3(5)
C(21)—P(1)—C(31)	108.2(5)	C(51)—P(2)—C(61)	109.1(5)
P(1)—C(11)—C(12)	119.2(8)	P(2)—C(41)—C(42)	120.8(8)
P(1)—C(11)—C(16)	119.9(8)	P(2)—C(41)—C(46)	116.9(7)
C(16)—C(11)—C(12)	120.9(10)	C(46)—C(41)—C(42)	122.0(9)
C(11)—C(12)—C(13)	119.6(10)	C(41)—C(42)—C(43)	120.0(11)
C(12)—C(13)—C(14)	119.7(12)	C(42)—C(43)—C(44)	118.6(11)
C(13)—C(14)—C(15)	119.8(12)	C(43)—C(44)—C(45)	120.7(12)
C(14)—C(15)—C(16)	121.1(12)	C(44)—C(45)—C(46)	121.4(13)
C(15)—C(16)—C(11)	118.8(11)	C(45)—C(46)—C(41)	117.1(10)
P(1)—C(21)—C(22)	117.1(9)	P(2)—C(51)—C(52)	120.1(8)
P(1)—C(21)—C(26)	121.7(8)	P(2)—C(51)—C(56)	119.2(8)
C(26)—C(21)—C(22)	120.9(10)	C(56)—C(51)—C(52)	120.7(9)
C(21)—C(22)—C(23)	117.4(12)	C(51)—C(52)—C(53)	118.8(12)
C(22)—C(23)—C(24)	121.4(12)	C(52)—C(53)—C(54)	121.1(13)
C(23)—C(24)—C(25)	121.1(13)	C(53)—C(54)—C(55)	119.2(13)
C(24)—C(25)—C(26)	119.8(14)	C(54)—C(55)—C(56)	122.1(14)
C(25)—C(26)—C(21)	119.4(11)	C(55)—C(56)—C(51)	118.8(11)
P(1)—C(31)—C(32)	121.6(8)	P(2)—C(61)—C(62)	123.6(8)
P(1)—C(31)—C(36)	119.7(9)	P(2)—C(61)—C(66)	118.0(8)
C(36)—C(31)—C(32)	118.7(10)	C(66)—C(61)—C(62)	118.0(11)
C(31)—C(32)—C(33)	120.8(11)	C(61)—C(62)—C(63)	120.7(10)
C(32)—C(33)—C(34)	120.8(13)	C(62)—C(63)—C(64)	120.8(11)
C(33)—C(34)—C(35)	118.7(12)	C(63)—C(64)—C(65)	119.7(14)
C(34)—C(35)—C(36)	121.2(12)	C(64)—C(65)—C(66)	119.4(13)
C(35)—C(36)—C(31)	119.4(12)	C(65)—C(66)—C(61)	121.4(12)

TABLE 4

GEOMETRY OF THE ANION

(i) Distances (Å)

S(1)—C(1)	1.739(28)	S(1)—C(2)	1.856(32)
C(1)—N(1)	1.501(37)	C(2)—N(2)	1.392(36)
S(1)—N(1)	3.201(25)	S(2)—N(2)	3.202(24)

(ii) Angles (°)

S(1)—C(1)—N(1)	162.1(25)
S(1)—C(2)—N(2)	160.4(21)
C(1)—S(1)—C(2)	83.2(14)

TABLE 5

LEAST-SQUARES PLANES

Planes are defined in orthogonal Ångstrom coordinates by the equation $Ax + By + Cz + D = 0$

Plane	Atoms	*A*	*B*	*C*	*D*
1	C(11)—C(16)	−0.835(2)	−0.202(5)	−0.511(0)	9.553(4)
2	C(21)—C(26)	0.818(6)	−0.048(1)	−0.574(1)	7.667(8)
3	C(31)—C(36)	−0.509(8)	0.859(4)	−0.047(2)	−2.738(26)
4	C(41)—C(46)	−0.377(11)	−0.913(4)	−0.159(1)	6.212(18)
5	C(51)—C(56)	0.048(2)	0.586(2)	−0.809(0)	10.697(5)
6	C(61)—C(66)	0.833(7)	0.054(2)	−0.551(1)	10.064(12)
7	P(1), P(2), N(3)	−0.372	−0.671	−0.641	13.148

Dihedral angles between planes (°)

Plane	2	3	4	5	6	7
1	−67.7(3)	74.0(5)	54.5(7)	75.2(2)	−64.9(4)	39.2(3)
2		−64.4(2)	−80.0(10)	61.6(2)	6.0(4)	84.5(12)
3			−54.2(6)	58.9(2)	−69.4(5)	−69.1(2)
4				−64.9(2)	−74.0(6)	31.2(5)
5					58.8(1)	83.8(1)
6						89.6(2)

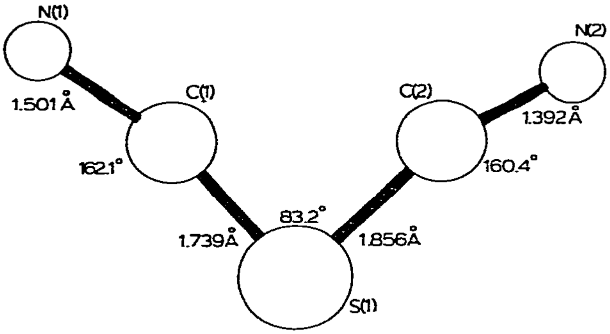

Fig. 2. The singly-disordered structure of the anion.

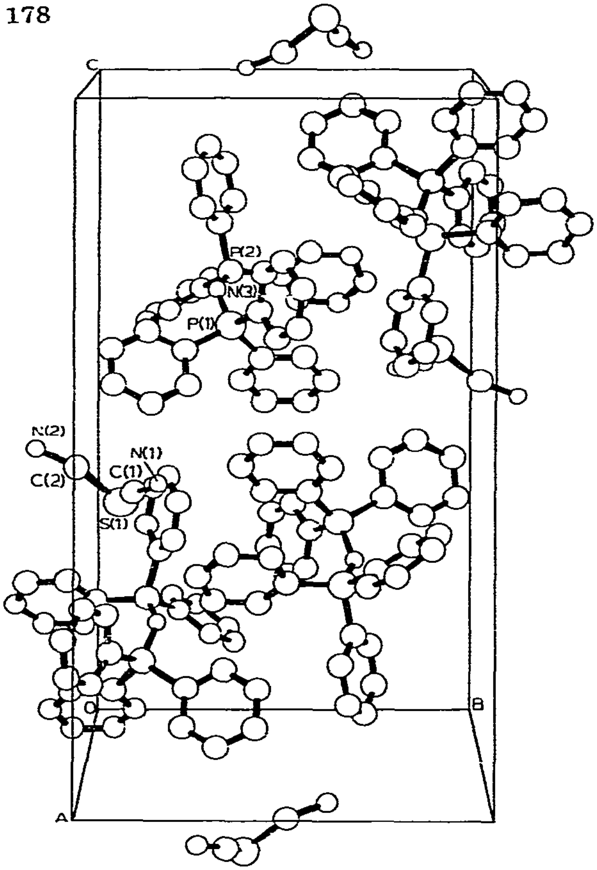

Fig. 3. The contents of the unit cell viewed down *a*.

TABLE 6

CALCULATED STRUCTURES FOR $(H_3P)_2N^+$ AND $(Me_3P)_2N^+$

	PCILO	MNDO	
(i) $(H_3P)_2N^{+a}$			
r(HP) (Å)	1.450	1.360(X2) 1.357(X4)	d_1 0.154 Å d_2 1.349 Å
r(PN) (Å)	1.620	1.636	
angle (HPN) (°)	112.0	104.2(X2) 116.7(X4)	a_1 8.4° a_2 111.8°
angle (PNP) (°)	133.3	121.1	
ΔE (kJ mol^{-1})	78.7	85.7	
(ii) $(Me_3P)_2N^+$			
r(CP) (Å)	1.809	1.816(X2) 1.798(X4)	d_1 0.225 Å d_2 1.789 Å
r(PN) (Å)	1.620	1.646	
angle (CPN) (°)	114.4	100.7(X2) 115.3(X4)	a_1 9.8° a_2 109.4°
angle (PNP) (°)	128.7	128.1	
ΔE (kJ mol^{-1})	101.8	75.8	

[a] In $(H_3P)_2N^+$, $a_5 = -a_6 = 120.3°$; in $(Me_3P)_2N^+$, $a_5 = -a_6 = 120.4°$: for definitions of d_n and a_n see ref. 12.

mised, both for the equilibrium structure and for that constrained to linearity at nitrogen. Structural parameters and barriers to linearity calculated by the two methods are recorded in Table 6. The PCILO geometry specification assumed local C_{3v} symmetry for the R_3PN (R = H, Me) groups, but as usual [12] when attached to a non-axially symmetric skeleton, these groups are found not to exhibit C_{3v} symmetry about the PN vectors when the structures are fully optimised by MNDO (see Table 6).

Results and discussion

The structure consists of cations $(Ph_3P)_2N^+$ which are markedly non-linear at nitrogen, angle PNP 136.3(6)°, and anions SCN^- which exhibit both positional and orientational disorder. In the cation, the PNP angle is towards the lower end of the observed range [2], 134.6(3)° to 180.0(0)°, with only the cations in the $Fe(CO)_4CN^-$ and $H_2Os_4(CO)_{12}{}^{2-}$ salts [13,14] having smaller PNP angles. The wide range of observed angle indicates that this cation exhibits Class 4 behaviour for hexaorgano-substituted triatomics R_3XYZR_3 [15], in which the skeletal bond angle can be changed over a wide range with very little expenditure of energy, since its force constant is close to zero because of the close numerical similarity between the first two terms in the perturbative expansion of the energy [16]. The ease of alteration of the angle is best shown by the existence of cations with angles of 139.1° (× 2) and 180.0° (× 1) in the same unit cell in $[(Ph_3P)_2N]_3\{Na[Mo_3(CO)_6(NO)_3(\mu_2\text{-}OCH_3)_3(\mu_3\text{-}O)]_2\}$ [17].

The mean torsional angle in the cation [2] is 45.4(4)°, and hence this conformation of the cation, with its small PNP angle, lies comfortably on the smooth curve previously established [2] for correlation of angle PNP and torsional angle.

In contrast to the Class 4 behaviour of $(Ph_3P)_2N^+$, both $(H_3P)_2N^+$ and $(Me_3P)_2N^+$ exhibit Class 1 behaviour (Table 6): substantial barriers to linearity are calculated for both these ions, by both PCILO and MNDO, implying large negative force constants for the skeletal bending vibration of the linear ion. The calculated value [12] of this force constant in $(H_3P)_2N^+$ is -87.9 Nm^{-1}, and there is ample evidence [12,18] that in molecules and ions formally isoelectronic with $(H_3P)_2N^+$ there is an exact correspondence between the ordering of the inversion barriers calculated by MNDO and the ordering of the force constants for skeletal bending from linearity, implying a force constant in $(Me_3P)_2N^+$ somewhat less negative than in $(H_3P)_2N^+$ but still substantially more negative than the approximately zero force constant in $(Ph_3P)_2N^+$. In the only other similar series $(R_3Si)_2O$ for R = H, Me or Ph, the same ordering is observed: $(Me_3Si)_2O$ has a negative force constant [19,20] but a slightly wider equilibrium angle SiOSi than $(H_3Si)_2O$ [21], whereas $(Ph_3Si)_2O$ is linear at oxygen [22], implying again an ordering of force constants with R: $H < Me < Ph$. If the analogous species $(R_3M)_2O$ (R = Ph, $PhCH_2$; M = Ge, Sn) are also included [23—26], the ordering of force constants becomes $H < Me < Ph < CH_2Ph$, so that for a given XYZ core, linearity at Y is most likely to be attained with benzyl substituents and least likely with hydrogen substituents.

In an ESCA study of a range of salts $(Ph_3P)_2N^+$ X^- [3] it was found that the phosphorus 2*p* and nitrogen 1*s* binding energies were identical within experimental error for P(2*p*) and very similar for N(1*s*), for $X^- = F^-, Cl^-, Br^-, I^-, NCO^-, NCS^-, NO_3^-, N_3^-$, and $V(CO)_6^-$, and it was concluded that the most appropriate formulation of the cation was as I rather than as II or any other form. The virtual identity of the binding energies in this series implies [4] either that the

$$Ph_3\overset{+}{P}-\overset{-}{N}-\overset{+}{P}Ph_3 \qquad Ph_3P=\overset{+}{N}=PPh_3$$

(I) (II)

cation geometry is the same throughout the series i.e. linear at nitrogen, since $(Ph_3P)_2N^+$ $V(CO)_6^-$ has a cation of exact $\bar{3}$ (S_6) symmetry [4], or that, if the cation geometries differ within this series, then the ESCA binding energies are independent of geometry.

We find here, not only that none of the salts having $X^- = F^-, Cl^-, Br^-, I^-, NCO^-, NCS^-, NO_3^-$ or N_3^- is isomorphous with $X^- = V(CO)_6^-$, although all could in principle contain anions lying on the three-fold axis of a rhombohedral cell, and that in particular for $X = NCS^-$ the cation is markedly non-linear and in the related salt $(Ph_3P)_2N^+$ $NCTe^-$, angle PNP is 143.2(3)° [27]: hence we conclude that no correlation exists between angle PNP in cations $(R_3P)_2N^+$, and the P(2*p*) and N(1*s*) binding energies. We note however for the isolated ions $(H_3P)_2N^+$ and $(Me_3N)_2P^+$, as opposed to $(Ph_3P)_2N^+$ in a crystal and hence influenced both by counter ions X^- and other cations, that at equilibrium the charges on phosphorus and nitrogen respectively are, in $(H_3P)_2N^+$, +0.45*e* and —0.50*e*, and in $(Me_3P)_2N^+$, +0.33*e* and —0.59*e*; while at linearity the corresponding values are in $(H_3P)_2N^+$, +0.94*e* and —1.12*e*, and in $(Me_3P)_2N^+$, +0.79*e* and —1.14*e*. These data support the conclusion that I is the better formulation, but indicate a large change in the electron populations with geometry: in real crystals this is effectively cancelled out in its influence on atomic binding energies by the variations in the electrostatic potential [3].

The thiocyanate anion shows positional disorder, Fig. 2, and orientational disorder also: the precision of the interatomic distances is not high because of the failure in resolving the double disorder. Non-linear thiocyanate ions have been observed in salts of the cations $Cr(en)_3^{3+}$ and $Co(en)_3^{3+}$ [28,29], and the tellurocyanate ion in $(Ph_3P)_2N^+$ $NCTe^-$ has a TeCN angle of 175(1)° [27]: MNDO calculations show that bending of the ion from linearity to an SCN angle of 170° requires the input of 5 kJ mol^{-1}, and bending to an SCN angle of 160° requires 20 kJ mol^{-1}, both of which may be readily compensated for by interionic energies in the crystal.

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