Crystal and Molecular Structure of Nonamethylcyclotetraphosphonitrilium Pentacarbonyliodochromate(0)

By **Harry P. Calhoun** and **James Trotter**,* Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia, Canada

Crystals of the title compound are triclinic, $a = 14{\cdot}632(21)$, $b = 10{\cdot}364(10)$, $c = 10{\cdot}765(9)$ Å, $\alpha = 89{\cdot}65(9)$, $\beta = 106{\cdot}98(13)$, $\gamma = 63{\cdot}72(7)°$, $Z = 2$, space group $P\bar{1}$. The structure was determined from diffractometer data by Patterson and electron-density maps, and was refined by full-matrix least-squares methods to R 0·053 for 2112 observed reflexions. The anion has approximate C_{4v} symmetry. Mean Cr–C bond lengths *cis* to I are 1·893 Å and the *trans* Cr–C bond length is 1·859 Å. Mean C–O is 1·135, and the Cr–I 2·790 Å. The phosphonitrilic ring has an unusual distorted tub conformation, probably as a result of steric requirements. Bond length inequalities in the phosphonitrilic ring are discussed and compared with the P–N bond lengths in the $[N_4P_4Me_8H^+]$ion.

THE reaction of nonamethylcyclotetraphosphonitrilium iodide with hexacarbonylchromium to give $[N_4P_4Me_9{}^+]$-$[Cr(CO)_5I^-]$ has recently been investigated.[1] N.m.r. studies on the product show that there is a donor–acceptor interaction between the anion and cation in solution, and the observed i.r. activity of the B_1 carbonyl stretching mode is also of interest. Although the structures of several protonated phosphonitrilium ions have

[1] N. L. Paddock, T. N. Ranganathan, and J. N. Wingfield, *J.C.S. Dalton*, 1972, 1579.

been investigated,[2-5] those of methylphosphonitrilium ions have not yet been studied. The crystal structure of $[N_4P_4Me_9][Cr(CO)_5I]$ was thus undertaken to gain further insight into the interaction between the anion and cation and to determine the structure of the $[N_4P_4Me_9]^+$ ion.

EXPERIMENTAL

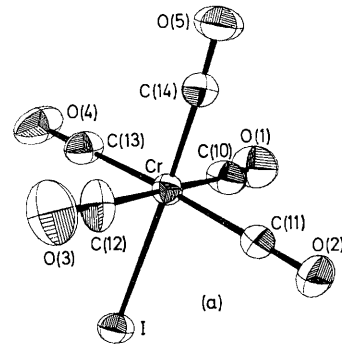
Only a few of the dark brown crystals had distinct crystal faces, and many were hollow. The crystal chosen for intensity measurement was a plate-like fragment with no crystal faces well developed, and of dimensions *ca.* $0.14 \times 0.11 \times 0.06$ mm. It was sealed in a glass capillary as the compound is slightly air sensitive.

Crystal Data.—$C_{14}H_{27}CrIN_4O_5P_4$, $M = 634.19$, Triclinic, $a = 14.632(21)$, $b = 10.364(10)$, $c = 10.765(9)$ Å, $\alpha = 89.65(9)$, $\beta = 106.98(13)$, $\gamma = 63.72(7)°$, $U = 1382$ Å^3, $D_m = 1.533$ g cm^{-3} (flotation), $Z = 2$, $D_c = 1.523$ g cm^{-3}, $F(000) = 632$. No systematically absent reflexions. Space group $P\bar{1}$ from the distribution of the normalized structure factors and the structure analysis. Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 18.2 cm^{-1}.

Space group and initial unit-cell parameters were determined from precession and Weissenberg films. Accurate unit-cell parameters were obtained by least-squares refinement of $\sin^2\theta$ values for 30 reflexions measured on a General Electric XRD 6 diffractometer.

Intensity data were collected on a Datex-automated General Electric XRD 6 diffractometer with a scintillation counter, Mo-K_α radiation (zirconium filter and pulse-height analyser) and a θ—2θ scan. The scan width in 2θ was $(1.80 + 0.86 \tan\theta)°$, and 20 s background counts were taken on either side of every scan. All reflexions with 2θ(Mo-K_α) $\leq 45°$ were measured. A check reflexion was monitored every 30 reflexions and its intensity varied only slightly throughout the data collection. The intensity of this reflexion was used to scale the data to the same relative scale. Lorentz and polarization corrections were applied and the structure amplitudes derived. No corrections were made for absorption. Of 3377 independent reflexions measured, 2112 (62.5%) had $I > 3\sigma(I)$ above background, where $\sigma^2(I) = S + B + (0.03S)^2$ with S = scan count and B = background count. These reflexions were classified as observed.

Structure Analysis.—The positions of the chromium and iodine atoms were obtained from a three-dimensional Patterson map. A structure-factor calculation with B 4.0 Å^2 for both atoms gave R 0.372. The positions of 4P, 4N, 4O, and 5C atoms were obtained from an electron-density map, and with these atoms included R was reduced to 0.216. A difference map gave the positions of the remaining 10 non-hydrogen atoms. One cycle of full-matrix least-squares refinement with chromium and iodine having anisotropic thermal parameters and all other atoms isotropic thermal parameters reduced R to 0.088. Three cycles of refinement with all atoms having anisotropic thermal parameters and a weighting scheme added reduced R to 0.057. At this point it became apparent that the thermal parameters were quite large, corresponding to a large amount of anisotropic thermal motion. In addition, the parameters for one atom, N(3), had not converged. The thermal parameters for this atom are particularly large, corresponding to a root-mean-square amplitude of vibration of 0.6 Å, so it is possible that there is disorder in the phosphonitrilic ring. Attempts to solve for the disorder by using a split-atom model for N(3) did not give a reasonable solution. The disorder may involve other atoms in addition to N(3), the most likely being P(3), C(6), C(7), C(8), and C(9) on the basis of their large anisotropic thermal motion (Table 1 and Figure 1). A difference map at this stage showed peaks of up to only ± 0.78 eÅ^{-3}. Refinement was continued, and convergence was reached after two additional cycles. On the last two cycles of refinement methyl hydrogen atoms for C(2)—(9) were included in calculated positions (staggered with respect to the other atoms bonded to the phosphorus atom) with B 10.0 Å^2, but the parameters for these atoms were not refined. On the last cycles of refinement no parameter shift was $> 0.37\sigma$. The final R was 0.053 for 2112 observed reflexions.



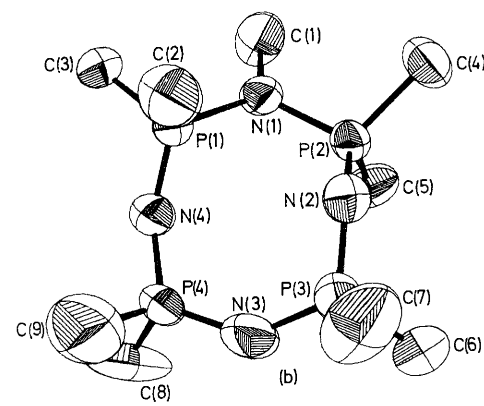


FIGURE 1 General view of (a) the $Cr(CO)_5I^-$ anion and (b) the $N_4P_4Me_9^+$ cation, with 25 and 50% probability thermal ellipsoids respectively

The least-squares refinement was based on the minimization of $\Sigma w(|F_o| - |F_c|)^2$. The anisotropic thermal parameters are U_{ij} in the expression: $f = f_o \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$. Scattering factors, f_o, were obtained from ref. 6 for all non-hydrogen atoms, and for hydrogen atoms from ref. 7. Correction for anomalous dispersion was included for Cr and I. By use of the weighting scheme: $w = [A + B|F_o| + C|F_o|^2 + D|F_o|^3]^{-1}$, approximately constant average values

[2] J. Trotter and S. H. Whitlow, *J. Chem. Soc.* (*A*), 1970, 455.
[3] J. Trotter and S. H. Whitlow, *J. Chem. Soc.* (*A*), 1970, 460.
[4] N. V. Mani and A. J. Wagner, *Acta Cryst.*, 1971, **B27**, 51.
[5] H. P. Calhoun and J. Trotter, following paper.
[6] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.
[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

of $w(|F_o| - |F_c|)^2$ over ranges of $|F_o|$ could be obtained. The coefficients A, B, C, and D were adjusted before each cycle, the values used in the final cycle of refinement being 10·70, 0·495, 0·0061, and 0·00003 respectively. Unobserved reflexions were not included in the refinement.

The crystals of the compound were of poor quality, as mentioned earlier, and this, together with the lack of correction for absorption, could explain the rather large thermal motion. Because of possible slight disorder, the geometrical parameters associated with atoms N(3) and C(6)—(9) may be less accurate than the estimated standard deviations indicate.

Final atomic positions and thermal parameters are given in Table 1. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 20873 (6 pp.).*

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. Items less than 10 pp. are sent as full size copies.

[8] S. F. A. Kettle and I. Paul, *Inorg. Chim. Acta*, 1968, 15.

DISCUSSION

The structure consists of a $Cr(CO)_5I^-$ anion and a $N_4P_4Me_9^+$ cation. Bond lengths and angles are given in Table 2. The anion is shown in Figure 1(a), the cation in Figure 1(b), and a view of the unit cell contents in Figure 2.

TABLE 1

Final positional parameters (fractional $\times 10^4$) and anisotropic thermal parameters (U_{ij}, Å^2 $\times 10^4$) with standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
I	1356(1)	1177(1)	−0012(1)	C(1)	0362(12)	5540(15)	8034(16)
Cr	3360(1)	0415(2)	1868(2)	C(2)	3250(12)	3355(15)	7733(14)
P(1)	1876(3)	4463(3)	6758(3)	C(3)	1265(14)	3285(15)	6470(14)
P(2)	1546(2)	6994(3)	8118(3)	C(4)	1716(11)	7004(14)	9838(11)
P(3)	2926(4)	7374(5)	6780(4)	C(5)	0349(11)	8635(14)	7260(14)
P(4)	2285(3)	5873(4)	4727(3)	C(6)	2405(16)	9306(19)	6654(16)
O(1)	3707(11)	−2588(15)	2703(14)	C(7)	4349(15)	6672(21)	7430(24)
O(2)	2223(8)	1612(13)	3867(10)	C(8)	1393(16)	6667(25)	3096(17)
O(3)	3094(12)	3384(14)	1074(12)	C(9)	3400(19)	4482(25)	4481(24)
O(4)	4339(9)	−0809(15)	−0247(12)	C(10)	3533(12)	−1446(18)	2396(16)
O(5)	5532(9)	−0256(13)	3794(11)	C(11)	2655(10)	1129(15)	3112(13)
N(1)	1268(7)	5607(9)	7697(8)	C(12)	3162(13)	2307(19)	1339(13)
N(2)	2597(8)	6754(10)	7844(9)	C(13)	3976(11)	−0321(16)	0549(15)
N(3)	2547(17)	7036(21)	5331(14)	C(14)	4697(12)	−0013(14)	3077(14)
N(4)	1700(8)	5216(11)	5388(9)				

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I	610(6)	804(7)	687(6)	−238(5)	160(4)	−178(4)
Cr	602(12)	607(13)	534(11)	−251(10)	192(9)	−98(9)
P(1)	800(23)	463(18)	551(19)	−281(16)	344(16)	−127(14)
P(2)	605(20)	472(19)	504(17)	−209(15)	258(15)	−129(14)
P(3)	1174(34)	1157(33)	869(26)	−880(29)	638(25)	−523(24)
P(4)	937(26)	855(25)	533(19)	−582(22)	404(18)	−261(17)
O(1)	1404(108)	934(90)	1852(129)	−616(84)	368(92)	203(86)
O(2)	921(74)	1594(108)	781(66)	−457(71)	435(60)	−320(68)
O(3)	1922(132)	912(88)	1322(103)	−793(93)	481(89)	−74(75)
O(4)	1049(86)	1949(133)	1241(93)	−752(88)	676(77)	−848(95)
O(5)	643(65)	1445(99)	972(75)	−395(65)	109(58)	−274(67)
N(1)	641(62)	503(56)	630(57)	−267(47)	344(49)	−117(44)
N(2)	797(73)	617(65)	690(63)	−344(55)	332(55)	−187(51)
N(3)	2974(223)	2460(190)	1094(104)	−2390(191)	1327(134)	−997(120)
N(4)	837(71)	740(69)	531(58)	−479(59)	253(51)	−140(49)
C(1)	944(109)	871(101)	1321(128)	−523(86)	797(102)	−444(91)
C(2)	945(106)	677(91)	931(103)	−19(78)	391(86)	−33(76)
C(3)	1614(148)	676(91)	933(101)	−678(97)	783(104)	−261(76)
C(4)	949(100)	781(92)	524(73)	−306(77)	276(70)	−161(65)
C(5)	763(89)	579(79)	1019(102)	−243(68)	300(76)	55(70)
C(6)	1786(176)	1065(128)	1051(117)	−1011(131)	670(119)	−290(97)
C(7)	1170(148)	1186(145)	2369(241)	−699(119)	1138(163)	−675(152)
C(8)	1540(171)	2232(224)	935(118)	−1135(167)	482(115)	300(127)
C(9)	1859(206)	1412(176)	1987(214)	−686(157)	1322(184)	−450(154)
C(10)	824(104)	719(103)	1121(120)	−410(88)	132(88)	84(92)
C(11)	626(84)	911(103)	623(82)	−276(74)	183(68)	−60(73)
C(12)	1395(136)	866(112)	610(87)	−757(107)	357(85)	−210(80)
C(13)	727(95)	962(108)	840(98)	−392(82)	295(78)	−329(84)
C(14)	651(94)	776(93)	745(89)	−302(74)	202(77)	−40(71)

The $Cr(CO)_5I^-$ anion does not show large deviations from C_{4v} symmetry, those which are significant being always less than 2·8° in the 90° angles and less than 5·0° in the 180° angles. The close approximation of the anion to C_{4v} symmetry gives evidence that the observation of the B_1 carbonyl stretching mode in the i.r. spectrum [1] is probably due to coupling with the formally allowed A_1 transitions,[8] which does not depend upon a reduction of symmetry of the equilibrium molecular geometry. The Cr–C bonds *cis* to I [mean 1·893(16) Å] are longer than the *trans* Cr–C bond [1·859(15) Å], indicating greater Cr→CO back donation into the *trans*-bond. The mean C–O bond length is 1·135(22) Å. These bond lengths can be compared with those found in

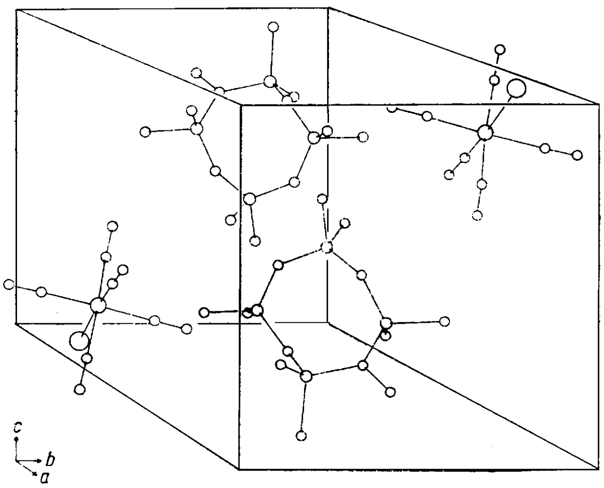


FIGURE 2 View of the unit-cell contents

hexacarbonylchromium [9] [Cr–C 1·909(3), C–O 1·137(4) Å] and in the $Ph_3PCr(CO)_5$ (1) and $(PhO)_3PCr(CO)_5$ (2) complexes [10] [(1): mean *cis* Cr–C 1·880(11), *trans* Cr–C 1·844(4), mean *cis* C–O 1·147(5), *trans* C–O 1·154(5) Å; (2): mean *cis* Cr–C 1·896(6), *trans* Cr–C 1·861(4), mean *cis* C–O 1·131(6), *trans* C–O 1·136(6) Å]. The shorter Cr–C length over that found in hexacarbonylchromium indicates greater overall Cr–C π bonding, since I^- is not a competitive π acceptor.

The phosphonitrilic cation is distorted from the usual tub and saddle [11] conformations found for tetrameric phosphonitrilic derivatives. The parent molecule, $N_4P_4Me_8$,[12] exists in a near-tub conformation, with four atoms above and four below the mean plane through the ring atoms, the nitrogen atoms showing larger deviations (0·54 Å) from the mean plane than the phosphorus atoms (0·21 Å). In the present structure five atoms lie below and three above the mean plane through all ring atoms [Table 3(*a*)]. The conformation can roughly be described as a distorted tub, derived from the tub conformation by twisting of the N(4)–P(1) bond, N(4) being below instead of above the mean plane, and by bringing N(2) in toward the centre of the ring. The conformation is probably influenced by the necessity to minimize methyl–methyl contacts between the N–Me group and adjacent P–Me groups, while at the same time keeping the angle between CPC and local NPN planes close to 90° (these angles average 88·2° in the present structure). Close contacts are C(1) ··· C(3) 2·94, C(1) ··· C(4) 3·23, and C(1) ··· C(5) 3·30 Å; C(1) ··· C(3) is especially short. Thus there is a considerable amount of steric

TABLE 2

Bond lengths (Å) and angles (deg.) with standard deviations in parentheses (σ for a mean value is the root-mean-square deviation from the mean)

(*a*) Distances

Cr–I	2·790(2)	P(1)–N(1)	1·681(9)
		N(1)–P(2)	1·689(9)
Cr–C(10)	1·892(16)	P(2)–N(2)	1·562(11)
Cr–C(11)	1·884(15)	N(2)–P(3)	1·596(11)
Cr–C(12)	1·908(17)	P(3)–N(3)	1·592(13)
Cr–C(13)	1·888(15)	N(3)–P(4)	1·516(13)
Cr–C(14)	1·859(15)	P(4)–N(4)	1·602(10)
		N(4)–P(1)	1·560(10)
C(10)–O(1)	1·120(16)		
C(11)–O(2)	1·155(14)	N(1)–C(1)	1·502(16)
C(12)–O(3)	1·104(15)		
C(13)–O(4)	1·142(15)		
C(14)–O(5)	1·152(15)		
Mean C–O	1·135(22)		

P(1)–C(2)	1·781(15) [1·812(15)] *
P(1)–C(3)	1·787(14) [1·812(14)]
P(2)–C(4)	1·796(12) [1·817(12)]
P(2)–C(5)	1·792(13) [1·814(13)]
P(3)–C(6)	1·788(17) [1·812(17)]
P(3)–C(7)	1·776(20) [1·817(20)]
P(4)–C(8)	1·777(18) [1·835(19)]
P(4)–C(9)	1·728(20) [1·801(21)]
Mean P–C	1·778(21) [1·815(10)]

(*b*) Angles

I–Cr–C(10)	91·7(4)	Cr–C(10)–O(1)	175·1(15)
I–Cr–C(11)	88·8(4)	Cr–C(11)–O(2)	177·7(13)
I–Cr–C(12)	87·7(5)	Cr–C(12)–O(3)	176·8(15)
I–Cr–C(13)	87·2(4)	Cr–C(13)–O(4)	177·4(14)
I–Cr–C(14)	177·0(4)	Cr–C(14)–O(5)	177·7(12)
C(10)–Cr–C(11)	88·5(7)		
C(10)–Cr–C(12)	179·0(7)	P(1)–N(1)–P(2)	120·9(5)
C(10)–Cr–C(13)	89·9(7)	P(2)–N(2)–P(3)	138·3(7)
C(10)–Cr–C(14)	91·1(6)	P(3)–N(3)–P(4)	136·0(10)
C(11)–Cr–C(12)	90·8(6)	P(4)–N(4)–P(1)	138·9(7)
C(11)–Cr–C(13)	175·6(6)		
C(11)–Cr–C(14)	92·2(6)	N(1)–P(1)–C(2)	107·5(6)
C(12)–Cr–C(13)	90·8(6)	N(1)–P(1)–C(3)	105·1(5)
C(12)–Cr–C(14)	89·5(6)	N(4)–P(1)–C(2)	115·0(6)
C(13)–Cr–C(14)	91·9(6)	N(4)–P(1)–C(3)	107·4(6)
		N(1)–P(2)–C(4)	106·9(5)
P(1)–N(1)–C(1)	120·5(8)	N(1)–P(2)–C(5)	106·2(6)
P(2)–N(1)–C(1)	118·1(7)	N(2)–P(2)–C(4)	110·8(6)
		N(2)–P(2)–C(5)	116·1(6)
C(2)–P(1)–C(3)	106·5(8)	N(2)–P(3)–C(6)	111·3(6)
C(4)–P(2)–C(5)	106·5(6)	N(2)–P(3)–C(7)	105·9(8)
C(6)–P(3)–C(7)	104·6(9)	N(3)–P(3)–C(6)	106·9(9)
C(8)–P(4)–C(9)	102·6(11)	N(3)–P(3)–C(7)	112·2(10)
		N(3)–P(4)–C(8)	106·7(11)
N(4)–P(1)–N(1)	114·6(5)	N(3)–P(4)–C(9)	111·1(11)
N(1)–P(2)–N(2)	109·8(5)	N(4)–P(4)–C(8)	105·6(7)
N(2)–P(3)–N(3)	115·5(6)	N(4)–P(4)–C(9)	110·3(8)
N(3)–P(4)–N(4)	118·9(6)		

* Values in square brackets have been corrected for thermal libration.

TABLE 3

(*a*) Mean plane through the phosphonitrilic ring atoms

(i) Equation of plane through P(1)—(4), N(1)—(4):

$$-0·5919X + 0·5731Y - 0·5668Z = -2·1615$$

X, *Y*, *Z* are orthogonal co-ordinates (Å) with respect to axes *a*, *b*′, and *c**.

(ii) Distances (Å) of ring atoms from plane [negative value considered to be above the plane, as in Figure 1(b)]:

P(1) −0·31, N(1) 0·24, P(2) 0·24, N(2) −0·65, P(3) −0·46, N(3) 0·21, P(4) 0·31, N(4) 0·45

(*b*) Dihedral angles (deg.) in the phosphonitrilic ring

P(1)N(1)–P(2)N(2)	15·0	P(3)N(3)–P(4)N(4)	−36·0
N(1)P(2)–N(2)P(3)	−103·8	N(3)P(4)–N(4)P(1)	55·3
P(2)N(2)–P(3)N(3)	65·2	P(4)N(4)–P(1)N(1)	−93·1
N(2)P(3)–N(3)P(4)	26·2	N(4)P(1)–N(1)P(2)	58·1

[9] A. Whitaker and J. W. Jeffery, *Acta Cryst.*, 1967, **23**, 977.
[10] H. J. Plastas, J. M. Stewart, and S. O. Grim, *Inorg. Chem.*, 1973, **12**, 265.
[11] D. P. Craig and N. L. Paddock, in 'Nonbenzenoid Aromatics,' vol. 2, Academic Press, New York, 1971, p. 273.
[12] M. W. Dougill, *J. Chem. Soc.*, 1961, 5471.

strain, and this influences the conformation of the ring greatly. The distorted ring conformation can also be seen from the dihedral angles in the ring [Table 3(*b*)]. The inequality of dihedral angles is not expected to affect π bond-orders in the ring, however, since the total π overlap in a P–N bond is expected to be independent of dihedral angle if the π_a and π_s systems [11] are equivalent. This flexibility of phosphonitrilic molecules can be seen in the related structure $[N_4P_4Me_8H]_2[CoCl_4]$,[3] where two $N_4P_4Me_8H^+$ ions are found in the asymmetric unit, one with the tub and one with the saddle conformation.

The bond lengths in the phosphonitrilic ring are not equal, as they are in $N_4P_4Me_8$ [mean 1·596(5) Å], but show the same qualitative pattern of long and short bonds alternating in pairs from N(1) as found in the protonated molecule. The mean values of chemically equivalent bonds from N(1) are: 1·685, 1·561, 1·599, and 1·55 Å, and can be compared with the corresponding values in $[N_4P_4Me_8H^+]$ ions in the structure $[N_4P_4Me_8H]_2$-$[CoCl_4]$ (means of four chemically equivalent bonds): 1·695, 1·538, 1·614, and 1·582 Å. The explanation for the bond length variation in the $N_4P_4Me_9^+$ ion is qualitatively the same as for the $N_4P_4Me_8H^+$ ion.[3,13]

The angles at N(1) (120·9, 120·5, 118·1°; sum 359·5°) indicate that the P(1),N(1),[C(1)],P(2) group is nearly planar and that N(1) is sp^2 hybridized. The sum of the covalent radii of sp^2 hybridized nitrogen (*ca.* 0·70 Å) and sp^3 hybridized carbon (0·77 Å) is 1·47 Å, indicating that the N(1)–C(1) bond is perhaps slightly longer (*ca.* 0·03 Å, 2σ) than expected.

The mean P–C bond length is 1·778(21) Å [1·815(10) Å after correction for thermal libration by use of a riding model]. This value can be compared with the P–C bond length in $N_4P_4Me_8$, 1·805(4) Å.

The endocyclic angles at N(2), N(3), and N(4), mean 137·7°, are slightly larger than the P–N–P angle in $N_4P_4Me_8$ (132·0°), whereas the angle at N(1) is much smaller (120·9°). A small endocyclic angle at nitrogen is also found in structures of tetrameric phosphonitrilic derivatives when the nitrogen atom is protonated or donating to a transition metal.[2,3,13] The average N–P–N angle is 114·7°, smaller than in $N_4P_4Me_8$ (119·8°). The corresponding value in the $N_4P_4Me_8H^+$ ion is 115·5°.

As mentioned earlier, n.m.r. data for the compound indicate a donor–acceptor interaction between the anion and cation, similar to the interaction of I^- with $N_4P_4Me_9^+$, the $Cr(CO)_5I^-$ ion being a better donor than I^-. Charge-transfer donor–acceptor complexes generally have short interionic contacts in the crystal, with specific spatial orientation rather than distortion of anion or cation.[14] It is thus surprising that the interionic contacts between anion and cation in the present structure are of the normal van der Waals type, with no close approach of the iodine atom to the ring π system (although the methyl groups on the phosphorus atoms may prevent the anion from getting close to the ring). The orientation of anion and cation in the unit cell is shown in Figure 2 (the lower anion and cation are at x, y, z).* Closest interionic contacts are $C(4) \cdots I^{I}$ 4·13, $C(4^{II}) \cdots I$ 4·10 Å, and $C(8^{III}) \cdots I$ 4·04 Å (for $I \cdots Me$ the sum of the van der Waals radii is 4·15 Å). Closest $I \cdots P$ and $I^{I} \cdots N$ distances are $I^{I} \cdots P(2)$ 4·72 and $I^{I} \cdots N(2)$ 4·98 Å (sum of van der Waals radii 4·05 and 3·65 Å). There is thus no indication in the crystal structure of an interaction between the anion and cation. This interaction may take place only in solution.

The other intermolecular contacts are also of the van der Waals type. The shortest $O \cdots C$ (methyl) contact is 3·40 Å (C(4) at x, y, z to O(3) at $x, y, 1 + z$) and the shortest $Me \cdots Me$ contacts are 3·68 and 3·71 Å.

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* Roman numeral superscripts denote the following translations of atoms, relative to the reference molecule at x, y, z:

I $x, 1 + y, 1 + z$
II $-x, 1 - y, 1 - z$
III $-x, 1 - y, 1 - z$

[13] H. P. Calhoun, N. L. Paddock, and J. Trotter, *J.C.S. Dalton*, 1973, 2708.

[14] C. K. Prout and J. D. Wright, *Angew. Chem. Internat. Edn.*, 1968, **9**, 659.