Inorg. Chem. **1994**, *33*, 1502–1505

Destructive or Cooperative Attack of Iodide Anions on Alkyltriiodophosphonium Cations: Elimination of Iodine in Solution and Layer Structures in the Solid State

Wolf-Walther du Mont,[*,†] Volkmar Stenzel,[†] Jörg Jeske,[†] Peter G. Jones,[*,†] Angelika Sebald,[*,‡] Siegfried Pohl,[*,§] Wolfgang Saak,[§] and Michael Bätcher[†]

Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, Postfach 3329, D-38023 Braunschweig, Germany, Bayerisches Geoinstitut, Universität Bayreuth, Postfach 101251, D-95444 Bayreuth, Germany, and Fachbereich Chemie der Universität, Carl von Ossietzky-Strasse 9-11, D-26129 Oldenburg, Germany

Received May 18, 1993[⊗]

Solid-state and solution ^{31}P NMR shifts of *t*-BuPI$_4$ and crystal structure determinations of *t*-BuPI$_4$, *i*-PrPI$_4$, and MePI$_4$ reveal that alkyltetraiodophosphorus compounds RPI$_4$ (R = *t*-Bu (**1**), *i*-Pr (**2**), Me$_3$SiCH$_2$ (**3**), Me (**4**)) in the solid state involve μ_3-bridging I···I interactions between RPI$_3^+$ cations and I$^-$ anions (leading to the formation of layer structures (**2**, **4**) or a 3-dimensional network (**1**)) whereas, in CS$_2$/CD$_2$Cl$_2$ solutions, deiodination by nucleophilic I$^-$ anions causes all RPI$_4$ compounds and PI$_5$ to decompose into the iodophosphanes RPI$_2$ or PI$_3$ and molecular iodine. **1** crystallizes in the cubic space group $I2_13$, with $a = 13.613(2)$ Å, $V = 2522.7(6)$ Å^3, and $Z = 8$. **2** crystallizes in the monoclinic space group $P2_1/c$, with $a = 6.686(2)$ Å, $b = 19.918(5)$ Å, $c = 8.961(3)$ Å, $\beta = 97.41(2)°$, $V = 1183.4(6)$ Å^3, and $Z = 4$. **4** crystallizes in the orthorhombic space group *Pbcm*, with $a = 6.031(2)$ Å, $b = 18.426(7)$ Å, $c = 8.741(3)$ Å, $V = 971.4(3)$ Å^3, and $Z = 4$. Cation–anion I···I interactions of solid RPI$_4$ are stronger than molecule–ion interactions within the related anion network of solid PhCH$_2$NMe$_3^+$HCI$_4^-$ (**5**), which crystallizes in the monoclinic space group $P2_1/c$, with $a = 8.200(1)$ Å, $b = 13.723(1)$ Å, $c = 16.216(1)$ Å, $\beta = 91.32(2)°$, $V = 1824.3(3)$ Å^3, and $Z = 4$.

Introduction

The existence of phosphorus pentaiodide has been the subject of contradictory reports,[1-3] and little is known about the nature of the related alkylphosphorus tetraiodides RPI$_4$.[4,5] Recently it was recognized that phosphane and arsane diiodides R$_3$EI$_2$ (R$_3$E = Ph$_3$As,[6] *t*-Bu$_3$P,[7] Ph$_3$P[8]), containing linear moieties E–I–I, may equivalently be described either as molecular adducts of R$_3$E donor molecules with molecular iodine or as iodophosphonium or iodoarsonium iodides with appreciable cation–anion I–I interactions.[9-11] In each case, the tertiary phosphane or arsane and iodide anions compete for coordination with the central iodine atom. Increasing donor strength of R$_3$E toward iodine leads to stronger E–I and weaker I–I bonds (Ph$_3$As < Ph$_3$P < *t*-Bu$_3$P). Likewise, P–I bond strengths increase with decreasing donor properties of the anions. (I$^-$ [6,7] $<$ I$_3^-$ [12] $\approx$ IML$_n$[10,11,13,14]).

$$R_3P \rightarrow I^+ \leftarrow X^-$$

Compared with tertiary phosphanes, phosphorus triiodide is expected to be a much poorer donor toward iodine, but with the help of the weakly donating AlI$_4^-$ or AsF$_6^-$ anions, even the PI$_4^+$ cation has been stabilized.[3,13] In PI$_5$, weakly donating PI$_3$ has to compete with the I$^-$ anion; this leads to the intrinsically low stability of the pentaiodide. Compared with PI$_3$, alkyldiiodophosphanes RPI$_2$ should be slightly better donors toward iodine. Indeed, reports on the preparation of alkylphosphorus tetraiodides RPI$_4$ have appeared, but structures of these compounds are not known. While the existence of PI$_5$ still appears doubtful, alkylphosphorus tetraiodides might exhibit properties similar to those of PI$_5$ in solution and in the solid state.[5] Their investigation should allow a new approach to understanding contradictory previous reports on the PI$_5$ question.

Experimental Section

All ^{13}C and ^{31}P CP MAS spectra were obtained on a Bruker MSL 300 FT-NMR spectrometer, operating at 75.47 MHz (^{13}C) and 121.50 MHz (^{31}P), respectively. Chemical shifts are given with respect to external TMS (^{13}C) and to external H$_3$PO$_4$ (^{31}P). The ^{1}H 90° pulse length was set to 5 μs; the Hartmann–Hahn matching condition was optimized using adamantane (^{13}C) and brushite (^{31}P). Contact times for the CP experiments were 1 ms for both ^{13}C and ^{31}P. Relaxation delays of 5 s were sufficient; between 48 and 800 transients had to be accumulated.

Alkylphosphorus tetraiodides RPI$_4$ (**1**–**4**) were prepared as red solids by addition of iodine in CH$_2$Cl$_2$ to CH$_2$Cl$_2$ solutions of RPI$_2$; PI$_5$ (a solid of this composition) was isolated by evaporation of a PI$_3$/I$_2$ CS$_2$ solution.[15] PhCH$_2$NMe$_3^+$CHI$_4^-$ (**5**) was obtained by addition of PhCH$_2$NMe$_3^+$I$^-$ to CHI$_3$ in CH$_3$OH solution.

[†] Institut für Anorganische und Analytische Chemie der Technischen Universität.

[‡] Universität Bayreuth.

[§] Fachbereich Chemie der Universität.

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1994.

(1) *Gmelins Handbuch der anorganischen Chemie*, 8th ed.; Verlag Chemie: Weinheim, 1965; Phosphor Teil C, p 525.

(2) Feshenko, N. G.; Kostina, V. G.; Kirsanov, A. *Zh. Obshch. Khim.* **1978**, *48*, 222.

(3) Tornieporth-Oetting, I.; Klapötke, T. *J. Chem. Soc., Chem. Commun.* **1990**, 132.

(4) Ginsburg, V. A.; Privezentsva, N. F. *Zh. Obshch. Khim.* **1958**, *28*, 736.

(5) Feshchenko, N. G.; Mel'nichuk, E. A. *Zh. Obshch. Khim.* **1978**, *48*, 365. Kudryavtseva, L. I.; Feshchenko, N. G.; Povolotskii, M. I. *Zh. Obshch. Khim.* **1983**, *53*, 2684.

(6) Mc Auliffe, C. A.; Beagley, B.; Gott, G. A.; Mackie, A. G.; Mac Rory, P. P.; Pritchard, R. G. *Angew. Chem.* **1987**, *99*, 237; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 264. Beagley, B.; Colburn, C. B.; Elsayraf, O.; Gott, G. A.; Kelly, D. G.; Meakie, A. G.; Mc Auliffe, C. A.; Mac Rory, P. P.; Pritchard, R. G. *Acta Crystallogr.* **1988**, *C44*, 38.

(7) du Mont, W.-W.; Bätcher, M.; Pohl, S.; Saak, W. *Angew. Chem.* **1987**, *99*, 912.

(8) Godfrey, S. M.; Kelly, D. G.; Mc Auliffe, C. A.; Mackie, A. G.; Pritchard, R. G.; Watson, S. M. *J. Chem. Soc., Chem. Commun.* **1991**, 1163.

(9) du Mont, W.-W.; Kroth, H. J. *J. Organomet. Chem.* **1976**, *113*, C35.

(10) Kuhn, N.; Jüschke, R.; du Mont, W.-W.; Bätcher, M.; Bläser, D.; Böse, R. *Z. Naturforsch.* **1989**, *B44*, 9.

(11) Bätcher, M.; du Mont, W.-W.; Pohl, S.; Saak, W. *Phosphorus. Sulfur Silicon* **1990**, *49/50*, 147.

(12) Cotton, F. A.; Kibala, P. A. *J. Am. Chem. Soc.* **1987**, *109*, 3308.

(13) Pohl, S. *Z. Anorg. Allg. Chem.* **1983**, *498*, 15, 20.

(14) Mc Auliffe, C. A.; Stephen, M. G.; Mackie, A. G.; Pritchard, R. G. *Angew. Chem.* **1992**, *104*, 992.

(15) van Arkel, A. F. *Research* **1949**, *2*, 312 (cited in ref 1).

0020-1669/94/1333-1502$04.50/0

Table 1. Crystallographic Data for **1**, **2**, **4**, and **5**

	t-BuPI$_4$ (**1**)	*i*-PrPI$_4$ (**2**)	MePI$_4$ (**4**)	PhCH$_2$NMe$_3$$^+CHI_4$$^-$ (**5**)
formula	C$_4$H$_9$I$_4$P	C$_3$H$_7$I$_4$P	CH$_3$I$_4$P	C$_{11}$H$_{17}$I$_4$N
fw	595.68	581.66	553.60	670.88
space group	$I2_13$	$P2_1/c$	$Pbcm$	$P2_1/c$
a, Å	13.613(2)	6.686(2)	6.031(1)	8.200(1)
b, Å	13.613(2)	19.918(5)	18.426(4)	13.723(1)
c, Å	13.613(2)	8.961(3)	8.741(2)	16.216(1)
β, deg		97.41(2)		91.32(2)
V, Å^3	2522.7(6)	1183.4(6)	971.4(3)	1824.3(3)
Z	8	4	4	4
T, °C	−100	−95	−95	23
μ, mm^{-1}	9.952	10.603	12.907	6.745
d_{calcd}, Mg/m^3	3.137	3.265	3.786	2.443
R[a]	0.0235	0.0343	0.0284	0.0408
R_w[b]				0.0484[c]
$R_w(F^2)$[d]	0.0530	0.1033	0.0726	

[a] $R = \sum \| F_o| - |F_c\| / \sum |F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2}$. [c] $w^{-1} = \sigma^2(F) + 0.0002F^2$. [d] $R_w(F^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$; all reflections.

1–5 and PI$_5$ gave satisfactory elemental analyses. **1–4** are moderately soluble in CS$_2$ and slightly soluble in CH$_2$Cl$_2$, which is suitable for recrystallizations.

1. Mp: 112 °C.[5] Anal. Calcd for C$_4$H$_9$I$_4$P (M_r = 595.71): C, 8.1; H, 1.5; P, 5.2. Found: C, 8.0; H, 1.4; I, 85.1; P, 5.2. ^{31}P NMR (CS$_2$/CD$_2$Cl$_2$): δ 165.4. ^{1}H NMR: δ 1.1 (d), ^3J(PH) 14 Hz[≡*t*-BuPI$_2$].

2. Mp: 95 °C dec. Anal. Calcd for C$_3$H$_7$I$_4$P (M_r 581.68): C, 6.19; H, 1.20; P, 5.33. Found: C, 5.92; H, 1.20; P, 5.43. ^{31}P NMR (CS$_2$/CDCl$_3$): δ 156.9. ^{1}H NMR: δ 1.39 (dd), ^3J(PH) = 14.48 Hz, ^3J(HH) = 6.74 Hz (CH_3); δ 2.13 (qd), ^2J(PH) = 20.27 Hz, ^3J(HH) = 6.74 Hz (C*H*).

3. Mp: 119 °C dec. Anal. Calcd for C$_4$H$_{11}$I$_4$PSi (M_r 625.81): C, 7.7; H, 1.76. Found: C, 7.6; H, 1.75. ^{31}P NMR (CS$_2$/CDCl$_3$): δ 143.5. ^{1}H NMR: δ 0.25 ((CH$_3$)$_3$Si); δ 3.04 (d), ^2J(PH) = 18 Hz (CH$_2$).

4. Mp: 157 °C (ref 4: 156 °C). Anal. Calcd for CH$_3$I$_4$P (M_r 553.63): C, 2.17; H, 0.54. Found: C, 2.08; H, 0.50. ^{31}P NMR (CS$_2$/CDCl$_3$): δ 121.7. ^{1}H NMR: δ 3.27 (d), ^2J(PH) = 20.7 Hz.

5. Mp: 132 °C dec. Anal. Calcd for C$_{11}$H$_{17}$I$_4$N (M_r = 670.88): C, 19.69; H, 2.55. Found: C, 20.13; H, 2.65.

X-ray Structure Determinations. X-ray data sets for **1**, **2**, and **4** were collected to 2θ 50° with monochromated Mo Kα radiation (λ = 0.710 73 Å) on a Siemens R3 four-circle diffractometer fitted with an LT-2 low-temperature device. Orientation matrices were refined from setting angles of 50 reflections in the 2θ range 20–23°. Absorption corrections were based on ψ-scans. Structures were solved by the heavy-atom method (**2**, **4**) or direct methods (**1**) and refined using the program SHELXL-93 (G. M. Sheldrick, University of Göttingen) anisotropically on F^2. H atoms were included using rigid methyl groups or a riding model. X-ray data for **5** were collected to 2θ 47° with monochromated Mo Kα radiation on a Stoe Siemens AED-2 four-circle diffractometer. Absorption corrections were based on ψ scans. The structure was solved by direct methods and refined anisotropically on F, using the program Siemens SHELXTL PLUS. H atoms were included using a riding model.

Crystallographic data for **1**, **2**, **4**, and **5** are collected in Table 1.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **1**, **2**, **4**, and **5**

	x	y	z	U(eq)[a]
		t-BuPI$_4$ (**1**)		
I(1)	3807.4(4)	1310.2(4)	6664.8(4)	32.1(2)
I(2)	5038.9(4)	38.9(4)	4961.1(4)	29.2(2)
P	2734.2(14)	2265.8(14)	7734.2(14)	26.4(8)
C(1)	1921(6)	3079(6)	6921(6)	24(3)
C(2)	1377(6)	2396(6)	6215(5)	34(2)
		i-PrPI$_4$ (**2**)		
I(1)	6823.0(7)	2528.2(3)	2449.8(5)	28.9(2)
I(2)	2594.3(7)	3561.3(3)	4389.5(5)	28.4(2)
I(3)	2690.0(7)	3626.2(3)	34.0(5)	27.3(2)
I(4)	9415.8(7)	1146.9(3)	1918.3(5)	28.5(2)
P	4799(3)	3540.0(10)	2438(2)	24.4(4)
C(1)	6450(10)	4274(4)	2684(9)	30(2)
C(3)	5249(13)	4925(4)	2722(10)	39(2)
C(2)	7843(11)	4298(5)	1470(10)	41(2)
		MePI$_4$ (**4**)		
I(1)	12726.7(8)	1189.6(2)	268.9(5)	26.1(2)
I(2)	8442.6(11)	2454.6(3)	2500	25.7(2)
I(3)	6394.3(10)	4116.6(3)	2500	25.7(2)
P	10366(4)	1299.2(12)	2500	23.5(5)
C	8378(16)	549(5)	2500	32(2)
		PhCH$_2$NMe$_3$$^+CHI_4$$^-$ (**5**)		
I(1)	5045(1)	750(1)	3416(1)	55(1)
I(2)	2177(1)	1109(1)	4997(1)	65(1)
I(3)	2073(1)	2641(1)	3175(1)	65(1)
I(4)	1075(1)	4788(1)	2083(1)	58(1)
C(1)	2627(10)	1225(7)	3706(6)	55(3)
N	7344(9)	2494(5)	1153(5)	60(3)
C(2)	7383(14)	3224(7)	486(8)	85(5)
C(3)	9029(14)	2122(8)	1308(8)	88(5)
C(4)	6812(19)	2983(10)	1926(8)	120(6)
C(5)	6166(12)	1665(8)	967(7)	72(4)
C(6)	6609(10)	1023(6)	230(6)	52(3)
C(7)	7486(12)	192(7)	370(7)	72(4)
C(8)	7847(15)	−412(9)	−263(10)	93(5)
C(9)	7379(17)	−184(12)	−1027(9)	102(6)
C(10)	6494(22)	643(13)	−1197(8)	120(7)
C(11)	6087(15)	1233(9)	−568(7)	90(5)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Comparison of Solution and Solid-State NMR Data for *t*-Bu$_3$PI$_2$ and *t*-BuPI$_4$

solution		solid	
δ(^{31}P)	δ(^{13}C)	δ(^{31}P)	δ(^{13}C)
	t-Bu$_3$PI$_2$		
+82.0 (CD$_2$Cl$_2$)	+30.9 (d) (CD$_2$Cl$_2$) +43.5 ^1J(^{31}P,^{13}C) ±6.9 Hz ^2J(^{31}P,^{13}C) not resolved	[a] +93.4	31.7 (*C*H$_3$) 44.9 (*C*C)$_3$[b]
+115 (D$_2$O)			
	t-BuPI$_4$		
+165 (CS$_2$/CD$_2$Cl$_2$) (≡*t*-BuPI$_2$)	+25.9 (d) (CD$_2$Cl$_2$) (≡*t*-BuPI$_2$) ^2J(^{31}P,^{13}C) ±19.6 Hz [d]	−49.2[c]	28.9 (*C*H$_3$) 45.9 (*C*C$_3$)[b]

[a] Fairly broad resonance; $\nu_{1/2} \approx 400$ Hz; no spinning sidebands with ν_{rot} = 3.75 kHz. [b] Broad resonance; ^1J(^{31}P,^{13}C) not resolved. [c] Sharp resonance; substantial chemical shift anisotropy; close to axially symmetric tensor pattern with $\sigma_\perp - \sigma_\parallel \approx 300$ ppm. [d] *C*C$_3$ not resolved (low concentration). [*t*-BuPI$_2$ in CD$_2$Cl$_2$: δ 27.1 (d), ^2J(^{31}P,^{13}C) ±19.6 Hz; δ 32.5 (d), ^1J(^{31}P,^{13}C) ±57 Hz].

Results

Dissolving PI$_5$ (a solid of this analytical composition, made by evaporation of a CS$_2$ solution containing equivalent amounts of PI$_3$ and I$_2$[15]) in CS$_2$/C$_6$D$_6$ leads to a dark red solution which contains PI$_3$ (the slightly broadened ^{31}P NMR signal appears at +173 ppm) and I$_2$ (in toluene, UV/vis absorptions at 497 and 307 nm). Thus, in this solvent PI$_5$ undergoes almost complete dissociation into the starting materials. The ^{31}P NMR signal previously assigned to PI$_4$$^+I^-$ (δ + 182 ppm in CH$_3$I solution[2]) might also be due to PI$_3$; for the PI$_4$$^+$ cation (even with some I–I cation–anion interaction) a ^{31}P NMR resonance far upfield would be expected. In the case of *t*-Bu$_3$P–I–I, cation–anion interactions lead to *slight upfield* shifts (*t*-Bu$_3$PI$^+$BF$_4$$^-$ in CD$_2$Cl$_2$, δ(^{31}P) 114.9 ppm; *t*-Bu$_3$PI$_2$ in CD$_2$Cl$_2$, δ(^{31}P) 82 ppm; see Table 3). A solid-state CP MAS ^{31}P NMR spectrum obtained at 121.50 MHz from powdered *t*-Bu$_3$PI$_2$ (δ(^{31}P) 93.4 ppm) confirms that the I–I interactions of this compound in polar aprotic solvents are similar to those in the solid state (Table 3).

Solid-state ^{31}P NMR spectroscopy is even more informative for *t*-BuPI$_4$ (**1**),[5] a red solid that could be a model for the PI$_5$ system. Red crystalline **1** is easily obtained from *t*-BuPI$_2$ and I$_2$

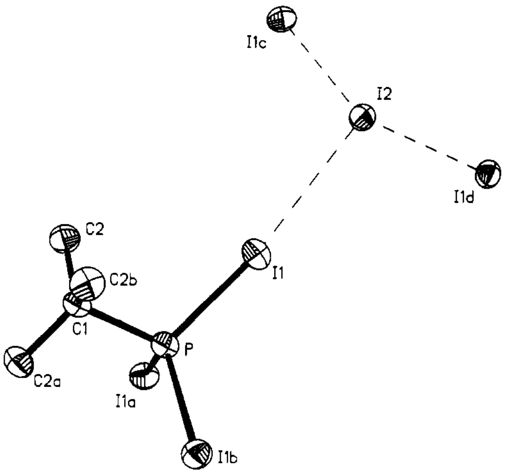
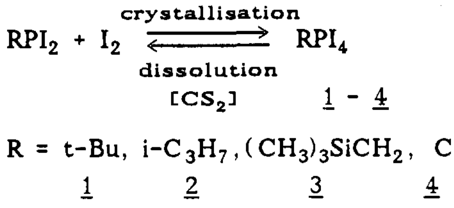


Figure 1. ORTEP plot (50% probability ellipsoids) of **1**. H atoms are omitted for clarity. The atoms I(2), P, and C(1) lie along crystallographic 3-fold axes. Selected bond lengths and angles: I(1)–P, 2.4384(12) Å; I(2)–I(1), 3.3443(8) Å; P–C(1), 1.918(14) Å; P–I(1)–I(2), 172.07(7)°; I(1c)–I(2)–I(1), 105.70(2)°; I(1a)–P–I(1), 110.89(7)°.

in CH_2Cl_2 solution. In the solid state, the ^{31}P NMR resonance of **1** (δ –49.2 ppm) appears far upfield ($\Delta\delta$ –215 ppm) from the educt *t*-$BuPI_2$. Considering the NMR properties of ^{127}I ($I = {}^5/_2$, 100% natural abundance), one might expect a major effect of the adjacent iodine nuclei on the appearance of the ^{31}P CP MAS spectra of *t*-$BuPI_4$ (**1**) and *t*-Bu_3PI_2, such as line-broadening effects and/or splitting patterns[12] due to scalar and quadrupolar interactions ^{127}I–^{31}P, if ^{127}I relaxation is sufficiently slow. This is apparently not the case; in both cases, fairly sharp (*t*-Bu_3PI_2) and even very sharp (*t*-$BuPI_4$) ^{31}P resonances are obtained, despite the fact that line-broadening effects or complex splitting patterns arising from such interactions have been widely observed for a number of combinations of (observed) spin $-{}^1/_2$ nuclei adjacent to nuclei with $I > {}^1/_2$.[16] A remarkable feature of **1** is its decomposition in CS_2/CD_2Cl_2 solution into the P(III) compound *t*-$BuPI_2$ ($\delta(^{31}P)$ +165 ppm) and molecular iodine. Similar to PI_3, alkyldiiodophosphanes RPI_2 (R = Me, *i*-Pr, *t*-Bu, Me_3SiCH_2) are weak donors toward iodine. The corresponding alkylphosphorus tetraiodides RPI_4 (**1**, R = *t*-C_4H_9; **2**, R = *i*-C_3H_7; **3**, R = Me_3SiCH_2; **4**, R = CH_3[4]) exist obviously only in the solid state. Like PI_5, all these red solids give solutions that contain essentially only the P(III) compounds (*t*-$BuPI_2$, $\delta(^{31}P)$ 165; *i*-$PrPI_2$, $\delta(^{31}P)$ +157; $Me_3SiCH_2PI_2$, $\delta(^{31}P)$ +144; $MePI_2$, $\delta(^{31}P)$ +122) and molecular iodine; evaporation of the solvents allows recovery of the "iodine adducts" **1–4**.



$$RPI_2 + I_2 \underset{\text{dissolution} \atop [CS_2]}{\overset{\text{crystallisation}}{\rightleftharpoons}} \underset{\underline{1} - \underline{4}}{RPI_4}$$

$$R = \underset{\underline{1}}{\text{t-Bu}},\ \underset{\underline{2}}{\text{i-}C_3H_7},\ \underset{\underline{3}}{(CH_3)_3SiCH_2},\ \underset{\underline{4}}{CH_3}$$

X-ray crystal structure determinations of *t*-$BuPI_4$ (**1**), *i*-$PrPI_4$ (**2**), and $MePI_4$ (**4**) (Figures 1–3) reveal I···I interactions between RPI_3^+ cations and I^- anions, leading to the formation of extended networks.

Each iodide anion forms three approximately orthogonal short contacts, one to each iodine atom of the cation, with I···I = 3.3443(8) Å (**1**), 3.3189(9)–3.3513(11) Å (**2**), or 3.3022(10), 3.3270(8) Å (**4**). The P–I bond lengths are closely similar, 2.4384(12) Å for **1**, 2.424(2)–2.428(2) Å for **2**, and 2.423(2), 2.424(2) Å for **4**, and the P–I···I angles are all within 10° of linear. Figure 3 (middle) shows that the connectivity of 12-membered $(CH_3P)_3I_9$ rings (of which every second member is a linearly two-coordinate iodine atom) forming a layer of **4** is related to the connectivity of chairlike P_6 rings within the layer structure of black phosphorus. The layers of **2** and **4** are topologically similar despite differences in their formal symmetry. The structure determination of **1** allows the assignment of the observed ^{31}P NMR upfield shift of **1** in the solid state unambiguously to *t*-$BuPI_3^+$ cations triply coordinated by pyramidal μ_3-bridging I^- anions within a three-dimensional network.[17]

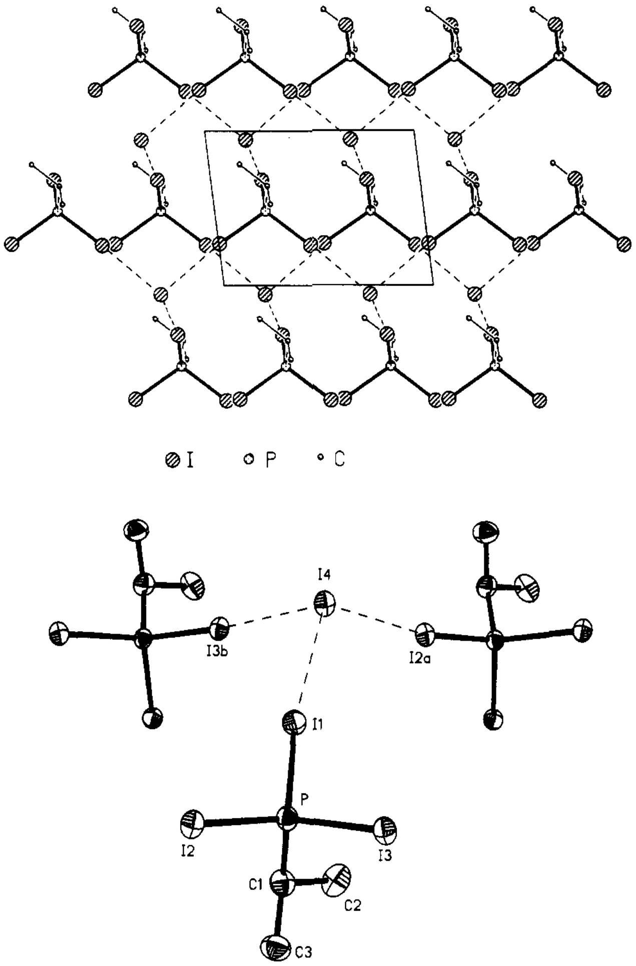


Figure 2. Top: Packing diagram of **2** projected down the *b* axis. Radii are arbitrary; H atoms are omitted for clarity. There are two such layers per cell. Bottom: Bridging interaction of an iodide anion with cations of **2** shown by an ORTEP plot (50% probability ellipsoids). Selected bond lengths and angles: I(1)–P, 2.427(2) Å; P–C(1), 1.828(8) Å; I(1)–I(4), 3.3189(9) Å; I(4)–I(3b), 3.3490(12) Å; I(4)–I(2a), 3.3513(11) Å; I(1)–I(4)–I(3b), 93.77(2)°; I(1)–I(4)–I(2a), 109.98(2)°; I(3b)–I(4)–I(2a), 97.87(3)°; P–I(1)–I(4), 171.55(5)°; I(1)–P–I(2), 113.67(8)°.

The I···I distances in solid **1**, **2**, and **4** are similar to the I···I bond length in solid *t*-Bu_3P–I···I, which, as has been pointed out previously, can be regarded as an iodophosphonium iodide with significant I···I interaction or as a phosphane diiodide charge-transfer complex.[7,9] For a rough estimation of the amount of polar cation–anion attraction to the I–I interaction in the layer structure of **1**, **2**, and **4**, a comparison of the cationic tripod acceptors RPI_3^+ with the uncharged tripod acceptor CHI_3 is useful. With benzyltrimethylammonium iodide, CHI_3 gives a solid adduct **5**, in which CHI_3 acts as an acceptor toward three different I^- ions and each I^- anion coordinates I atoms of three

---

(16) See for example: (a) Lycka, A.; Holecek, J.; Sebald, A.; Tkac, I. *J. Organomet. Chem.* **1991**, *409*, 331. (b) Harris, R. K.; Sebald, A.; Furlani, D.; Tagliavivi, G. *Organometallics* **1988**, *7*, 388. (c) Harris, R. K. *J. Magn. Reson.* **1988**, *78*, 389. (d) Apperley, D. C.; Haiping, B.; Harris, R. K. *Mol. Phys.* **1989**, *68*, 1277 (and references therein).

(17) Bätcher, M. Ph.D. Thesis, Universität Oldenburg, 1989.

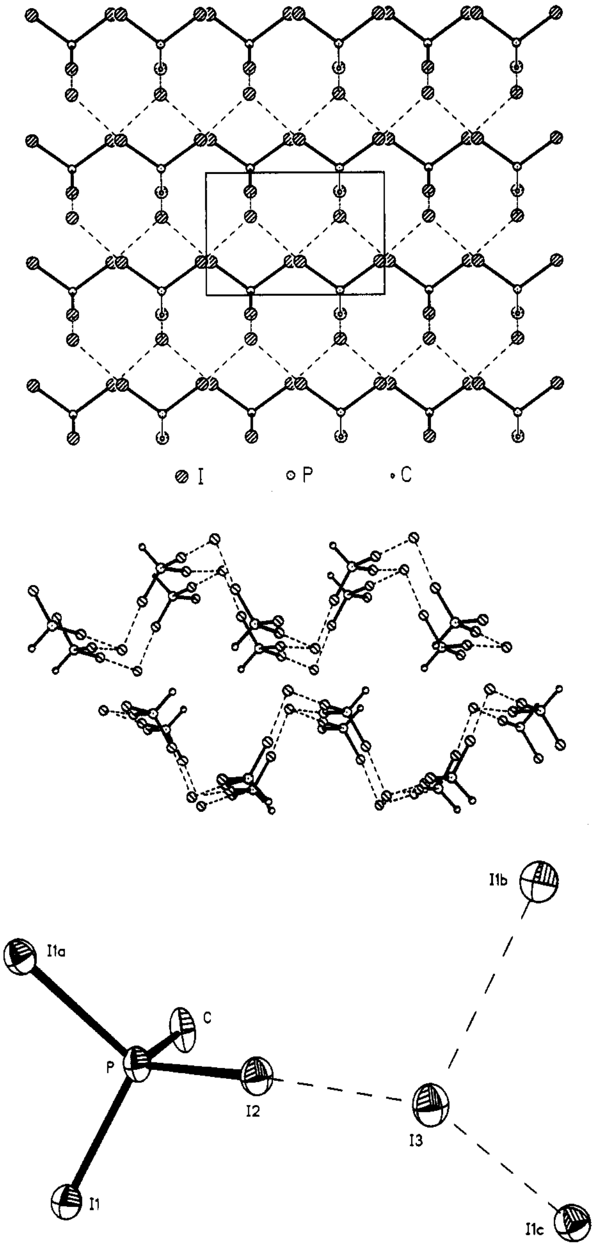


Figure 3. Top: Packing diagram of **4** projected down the *b* axis. Radii are arbitrary; H atoms are omitted for clarity. There are two such layers per cell. Middle: Part of the packing diagram of **4** projected down the *c* axis. Bottom: ORTEP plot (50% probability ellipsoids) of **4**. H atoms are omitted for clarity. The atoms P, C, I(2), and I(3) lie in a crystallographic mirror plane. Selected bond lengths and angles: I(1)–P, 2.423(2) Å; P–C, 1.830(9) Å; I(2)–I(3), 3.3022(10) Å; I(3)–I(1b), 3.3270(8) Å; P–I(2)–I(3), 173.38(7)°; I(1)–P–I(2), 110.76(6)°; I(2)–I(3)–I(1b), 95.25(2)°.

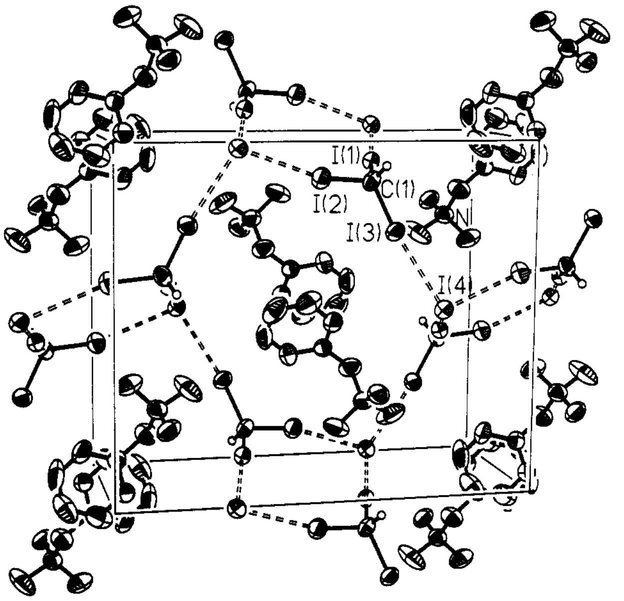


Figure 4. ORTEP plot (50% probability ellipsoids) of **5**. Only the H atom at CHI_3 is shown. Selected bond lengths and angles: I(1)–C(1), 2.150(8) Å; I(3)–I(4), 3.525(1) Å; I(1)–I(4A), 3.555(1) Å; I(2)–I(4B), 3.730(1) Å; I(4)–I(3)–C(1), 173.0(2)°; I(1)–C–I(2), 111.9(4)°.

different CHI_3 molecules (Figure 4). The CHI_4^- anion network of **5** is also related to the polymeric anion of $PPh_4^+CBr_5^-$ (triply bridging Br^- anions).[18] Compared with the I–I distances in the anion network of **5** (3.525, 3.555, and 3.730 Å; see also CI_4[19]), the I–I distances between cations and anions of RPI_4 (3.30–3.36 Å) are significantly shorter. Iodine atoms in iodophosphonium cations are more susceptible to I^- attack than iodine atoms of uncharged iodomethanes. Appreciable I–I interaction was also found in the salt $Ph_3P^+–CH_2–I\cdots I^-$, which contains a "cationic iodomethane".[20] Our results for the RPI_4 compounds allow us to predict that—although PI_5, like RPI_4, decomposes in solution due to I–I bond formation—solid PI_5[1,15] should also exhibit I–I interactions at the expense of some P–I bond strength compared with the known $PI_4^+AlI_4^-$.[13]

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (Germany). Crystal mounting oil (type RS3000) was kindly donated by Fa. Riedel de Haën.

Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (11 pages). Ordering information is given on any current masthead page.

---

(18) Lindner, H. J.; Kitschke-von Gross, B. *Chem. Ber.* **1976**, *109*, 314. Effenberger, F.; Podszum, W.; Schoeller, W. W.; Seufert, W. G.; Stohrer, E. D. *Chem. Ber.* **1976**, *109*, 306.

(19) Pohl, S. *Z. Kristallogr.* **1982**, *159*, 211.

(20) Lauritsen, K.; Vogt, H.; Riesel, L. *Proc. Int. Conf. Phosphorus Chem., 12th* **1992**, Abstract I-92; *Phosphorus, Sulfur Silicon* **1993**, *77*, 211. Vogt, H.; Lauritsen, L.; Riesel, L.; von Löwis, M.; Reck, G. *Z. Naturforsch.* **1994**, *49B*, in press.