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Iodine−Iodine Interactions in Dialkyldiiodophosphonium Iodides and Triiodides

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Reactions of dialkyldiiodophosphanes R$_2$PI, **1** (**1a**, R = *t*-Bu; **1b**, R = *i*-Pr; **1c**, R = Et) with various molar ratios of iodine were followed by NMR spectroscopy in solution and by X-ray crystal structure determinations of solid compounds R$_2$PI$_n$ (*n* = 3, 4, 5). In solution at room temperature, rapid iodine transfer reactions occur between P^V-compounds R$_2$PI$_3$ (**2a**, R = *t*-Bu; **2b**, R = *i*-Pr; **2c**, R = Et) and the iodophosphanes. With increasing iodine content of R$_2$PI$_3$/I$_2$ systems, decreasing I···I interactions between cations (R$_2$PI$_2^+$) and anions (I$^-$ > I$_3^-$) are indicated by solution NMR data such as ^{31}P downfield shifts and increasing $^3J(^{31}P, ^1H)$. Cation−anion interactions are weakest when I$^-$ anions are trapped as AlI$_4^-$ anions by addition of aluminum triiodide (**5a**, *t*-Bu$_2$PI$_2^+$ AlI$_4^-$). Structure determinations of *t*-Bu$_2$PI$_3$ (**2a**, C$_8$H$_{18}$I$_3$P, orthorhombic, space group *Pmmn*, *a* = 9.208(2) Å, *b* = 11.482(2) Å, *c* = 6.970(2) Å, *Z* = 2; μ_2-bridging I$^-$), (*i*-Pr$_2$PI$_2$)$_2$(I)(I$_3$) (**3b**, C$_{12}$H$_{28}$I$_8$P$_2$, monoclinic, space group *P*2$_1$/*n*, *a* = 11.919(3) Å, *b* = 10.156(3) Å, *c* = 25.214(5) Å; α = 90°, *β* = 98.48(2)°, *γ* = 90°, Z = 4, μ_3-bridging I$^-$, terminal I$_3^-$) and Et$_2$PI$_5$ (**4c**, C$_4$H$_{10}$I$_5$P, monoclinic, space group *P*2$_1$/*n*, *a* = 8.294(4) Å, b = 14.516(5) Å, c = 12.315(5) Å, α = 90°, *β* = 91.73(3)°, *γ* = 90°, Z = 4, bridging I$_3^-$) reveal that within the chain structures of **2a, 3b** and **4c**, R$_2$PI$_2^+$···I$^-$ interactions are significantly stronger than R$_2$PI$_2^+$···I$_3^-$ interactions. In each case, both iodine atoms of the R$_2$PI$_2^+$ cations act as *soft* acceptors *via iodine* toward *soft* I$^-$ and/or I$_3^-$ anions.

Introduction

Tertiary amines, phosphanes and arsanes are known to react with 1 equiv of iodine to give compounds R$_3$E−I−I with linear moieties E−I−I. In each case, the donor molecule competes with an iodide anion for coordination with the central iodine atom.

$$R_3E \rightarrow I^+ \leftarrow I^- \quad R_3E \rightarrow I^+ \leftarrow I^- \rightarrow A \quad I_2(R)P \rightarrow I^+ \leftarrow I^-$$

$$R_3E = \text{donor};\ A = \text{acceptor/electrophile}$$

Increasing donor strengths of R$_3$E molecules toward the *soft* acceptor I$_2$ lead to stronger E−I and weaker I−I bonds (Me$_3$N[1] < Ph$_3$As[2] < Ph$_3$P[3] < *t*-Bu$_3$P[4]). Hydrated I$^-$ anions interact much less with the iodine atoms of *t*-Bu$_3$PI$^+$ cations (*t*-Bu$_3$PI$_2$/H$_2$O) than I$^-$ in aprotic solvents (*t*-Bu$_3$PI$_2$ in CH$_2$Cl$_2$ or CHCl$_3$);[4,5] in iodophosphonium salts with anions other than I$^-$, P−I bond strengths increase with decreasing donor properties of the anions,[6−10] whereas donor properties of the iodide anion can be diminished by coordination with electrophiles A (such as I$_2$ and AlI$_3$). Because of their poor donor properties toward molecular iodine, phosphorus triiodide (PI$_3$) and alkyldiiodophosphanes RPI$_2$ cannot compete *in solution* with iodide anions for coordination with the I$^+$ cation, but alkyltetraiodophosphorus compounds RPI$_4$ are stable *in the solid state* because of cooperative cation−anion I···I interactions leading to layer structures (MePI$_4$, *i*-PrPI$_4$) or a three-dimensional network (*t*-BuPI$_4$).[11] In each case, alkyltriiodophosphonium ions RPI$_3^+$ are tripod acceptors μ_3-bridged by iodide anions. With respect to donor properties toward molecular iodine, iododialkylphosphanes R$_2$PI should be intermediate between tertiary phosphanes and alkyldiiodophosphanes RPI$_2$. Several iododiorganylphosphanes R$_2$PI are known to react with iodine to give stable yellow products of 1:1 stoichiometry (R$_2$PI$_3$) and colored compounds of higher iodine content, but there is still a complete lack of structural evidence for the mode of cation−anion interactions in R$_2$PI$_2^+$ salts,[12] nor has the solution behavior of R$_2$PI/I$_2$ systems been satisfactorily studied. To answer these questions, we studied R$_2$PI/I$_2$ (R = *t*-Bu, *i*-Pr, Et) reactions in solution by NMR and determined the first solid state structures of compounds R$_2$PI$_x$ (*x* = 3, 4, 5).

Experimental Section

The experiments were carried out under dry nitrogen as inert gas and in dry and deoxygenated solvents. All ^{1}H, ^{13}C, ^{27}Al, and ^{31}P NMR spectra were obtained on Bruker AC 200 spectrometers operating at 200.1 MHz (^{1}H), 50.32 MHz (^{13}C), 52 MHz (^{27}Al), and 81 MHz (^{31}P). Chemical shifts are given with respect to TMS (^{1}H, ^{13}C), [Al(H$_2$O)]$_6$]$^{3+}$ and H$_3$PO$_4$. Infrared spectra were obtained on a Bruker FT IR and Raman spectrometer at the Institut für Anorganische and Analytische Chemie, Technische Universität Clausthal. Elemental analyses were carried out on a Calo Erba instrument. For the determination of melting points, sample were heated in sealed glass capillaries in a Büchi 535 instrument. Dialkylphosphorus iodides R$_2$PI$_3$, (R$_2$PI$_2$)$_2^+$ I$^-$, I$_3^-$ and R$_2$PI$_5$ (**2a−c, 3a, 3b,** and **4c**) were prepared by addition of iodine in CH$_2$Cl$_2$ to CH$_2$Cl$_2$ solutions of R$_2$PI. **2−4** gave satisfactory elemental analysis. **2a,b** are slightly soluble, **2c** is nearly insoluble, **3a,b** and **4c**

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Table 1. Crystallographic Data for **2a**, **3b**, and **4c**

	t-Bu_2PI_3 (**2a**)	$(i$-$Pr_2PI_2)^+{}_2I^-,I_3^-$ (**3b**)	Et_2PI_5 (**4c**)
formula	$C_8H_{18}I_3P$	$C_{12}H_{28}I_8P_2$	$C_4H_{10}I_5P$
fw	525.89	1249.48	723.59
space group	*Pmmn*	$P2_1/n$	$P2_1/n$
a, Å	9.208(2)	11.919(3)	8.294(4)
b, Å	11.482(2)	10.156(3)	14.516(5)
c, Å	6.970(2)	25.214(5)	12.315(5)
β, deg		98.48(2)	91.73(3)
V, Å^3	736.9(3)	3018.8(13)	1482.0(11)
Z	2	4	4
T, °C	−130	−95	−100
μ, mm^{-1}	6.433	8.323	10.557
d_{calcd} Mg/m^3	2.370	2.749	3.243
R^a	0.0179	0.0249	0.0458
R^b	0.0454	0.0664	0.1507

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$

are moderately soluble in CH_2Cl_2, which is suitable for recrystallizations. **5a** was prepared by addition of AlI_3 to a CS_2 suspension of t-Bu_2PI_3.

2a. Starting materials: 3.2 g of t-Bu_2PI (11.8 mmol), 3.0 of g I_2 (11.8 mmol). Yield: 1.79 g (29%) of yellow crystals, mp 176 °C dec. Anal. Calcd for $C_8H_{18}I_3P$ (525.9 g/mol): C, 18.3; H, 3.4; I, 72.4; P, 5.9. Found: C, 18.0; H, 3.5. ^{31}P NMR (CD_2Cl_2): δ 61.1. ^1H NMR: δ 1.55 (d), $^3J(PH) = 19.1$ Hz. IR [CsI] (600−120 cm^{-1}): 568 (w), 481 (vs), 465 (m), 222 (vw), 166 (w), 126 (m) cm^{-1}. RE (600−20 cm^{-1}): 567 (vw), 481 (w), 462 (w), 384 (w, b), 372 (m), 299 (w, b), 272 (vw, b), 222 (vs), 148 (vs), 124 (vs), 100 (vs), 79 (vw), 60 (s).

2b. Starting materials: 6.19 g of i-Pr_2PI (25.4 mmol), 6.44 g of I_2 (25.4 mmol). Yield: 8.1 g (64%) of yellow crystals, mp 138 °C dec. Anal. Calcd for $C_6H_{14}I_3P$ (497.9 g/mol): C, 14.5; H, 2.8; I, 76.5; P, 6.2. Found: C, 14.3; H, 2.9. ^{31}P NMR (CH_2Cl_2): δ 35.0. ^1H NMR: δ 1.25 (d,d), $^3J = (PH) = 20.35$ Hz, $^3J(HH) = 6.74$ Hz (CH_3); δ 2.32 (d, sept.) $^2J(PH)$ not resolved, $^3J(HH) = 6.74$ Hz (C*H*). RE (600−20 cm^{-1}): 495 (w), 392 (w), 378 (vw), 364 (m), 303 (w), 265 (w), 223 (s), 135 (s), 92 (vs), 61 (w).

2c. Starting materials: 7.3 g of Et_2PI (31.5 mmol), 8 g of I_2 (31.5 mmol). Yield: 4.3 g (29%) of yellow crystals, mp 145 °C dec. Anal. Calcd for $C_4H_{10}I_3P$ (496.81): C, 10.2; H, 2.1; I, 81.1; P, 6.6. Found: C, 10.2; H, 2.2. RE (600−20 cm^{-1}): 439 (m), 373 (m), 315 (m), 253 (m), 230 (m, b), 170 (w,b), 141 (w), 99 (vs), 90 (s), 68 (m).

3a. Starting materials: 3.99 of g t-Bu_2PI (10.7 mmol), 5.45 g of I_2 (21.4 mmol). Yield: 0.9 g (12.9%) of brown crystals, mp 108 °C dec. Anal. Calcd. for $C_{16}H_{36}I_8P_2$ (1305.7 g/mol): C, 14.7; H, 2.7; I, 77.8; P, 4.7. Found: C, 14.4; H, 2.4. ^{31}P NMR (CH_2Cl_2): δ 80.9. ^1H NMR: δ 1.66 (d), $^3J(PH) = 22.0$ Hz.

3b. Starting materials: 1.5 g of i-Pr_2PI_3 (3.0 mmol), 0.8 g of I_2 (3.0 mmol). Yield: 1.32 g (70.4 %) of violet crystals, mp 151 °C dec. Anal. Calcd for $C_{12}H_{28}I_8$ (1249.6 g/mol): C, 11.5; H, 2.2; I, 81.2; P, 5.0. Found: C, 11.4; H, 2.2. ^{31}P NMR (CH_2Cl_2): δ 33.2. ^1H NMR: δ 1.32 (d,d) $^3J(PH) = 24.4$ Hz, $^3J(HH) = 6.72$ Hz (CH_3); δ 2.80 (d, sept.), (PH) = 0 Hz, $^3J(HH) = 6.72$ Hz (C*H*). RE (600−20 cm^{-1}): 495 (vw), 391 (w), 378 (w), 372 (w), 302 (vw), 268 (w,b), 231 (s), 139 (s), 125 (w), 111 (vs), 95(m), 71 (vw), 65 (vw), 57 (vw).

4c. Starting materials: 2.2 g of Et_2PI_3 (4.68 mmol), 1.19 g of I_2 (4.68 mmol). Yield: 2.78 g (82%) of violet crystals, mp 89 °C dec. Anal. Calcd for $C_4H_{10}I_5P$ (723.6): C, 6.6; H, 1.4; I, 87.7; P, 4.3. Found: C, 6.6; H, 1.4. ^{31}P NMR (CH_2Cl_2): δ −11.6. ^1H NMR: d 1.36 (d, t) $^3J(PH) = 29.2$ Hz, $^3J(HH) = 7.4$ Hz (CH_3); δ 3.31 (d,q); $^2J(PH) = 7$ Hz, $^3J(HH) = 7.4$ Hz (CH_2). RE (600−20 cm^{-1}): 440 (w), 368 (w), 339 (vw, b), 316 (w), 281 (vw), 252 (w), 225 (w, b), 142 (m), 124 (w), 108 (vs), 68 (w).

5a. Starting materials: 1.61 g of AlI_3 (3.94 mmol), 1.54 g of t-Bu_2PI_3 (2.93 mmol). Yield: 1.97 g (72%, related to t-Bu_2PI_3) of light brown crystals, mp 150 °C dec. Anal. Calcd for $C_8H_{18}AlI_6P$ (933.5 g/mol): C, 10.3; H, 1.9; Al, 2.9; I, 81.6; P, 3.3. Found: C, 9.3; H, 1.7. ^{31}P NMR: (CH_2Cl_2) δ 96.6. ^1H NMR: δ 1.64 (d), $^3J(PH) = 24$ Hz. ^{27}Al NMR: δ −26.0.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times$ 10^3) for 2a, 3b, and 4c where U(eq) Is Defined as One-Third of the Trace of the Orthogonalized U_{ij} Tensor

	x	*y*	*z*	*U*(eq)
		2a, t-Bu_2PI_3		
I1	5354.0(3)	2500	6668.1(4)	18.9(1)
I2	2500	2500	9669.8(6)	21.7(2)
P	7500	2500	4603(2)	15.0(6)
C1	7500	3910(3)	3230(6)	19(2)
C(2)	6138(3)	4003(3)	1990(5)	32(2)
C(3)	7500	4890(3)	4723(7)	27(2)
		3b, $(i$-$Pr_2PI_2)_2{}^+I^-,I_3^-$		
I1	6512.5(3)	−2102.3(4)	2942.5(1)	26.6(1)
I2	6031.4(3)	−94.5(4)	1572.5(1)	27.9(1)
I3	3441.1(3)	2996.3(4)	1328.6(1)	28.4(1)
I(4)	2751.7(3)	4677.0(4)	−89.5(1)	26.8(1)
I5	6859.9(3)	2606.3(4)	846.6(1)	28.4(1)
I6	709.2(3)	8129.1(4)	1523.9(2)	32.6(1)
I7	1795.9(4)	7955.4(4)	577.2(2)	36.1(1)
I8	−346.4(4)	8277.0(4)	2504.6(2)	37.0(1)
P1	5451.7(12)	−1975.2(14)	2049.0(5)	22.2(3)
P2	2286.4(12)	2873.0(14)	459.8(5)	21.7(3)
C1	3952(5)	−1833(6)	2100(2)	27.9(13)
C2	3539(5)	−3077(6)	2357(3)	40(2)
C3	3695(5)	−585(6)	2398(3)	39(2)
C4	5731(5)	−3487(6)	1686(2)	27.5(13)
C5	4979(6)	−3521(6)	1135(2)	37.0(15)
C6	6998(5)	−3612(7)	1648(3)	37.8(15)
C7	796(5)	3000(6)	548(2)	28.0(12)
C8	536(6)	4272(6)	816(3)	40(2)
C9	431(5)	1767(6)	834(3)	36.8(15)
C10	2572(5)	1316(6)	148(2)	28.2(13)
C11	1778(5)	1133(6)	−374(2)	38.6(15)
C12	3814(5)	1148(7)	85(3)	39(2)
		4c, Et_2PI_5		
I1	9399.6(9)	6811.6(5)	3534.7(6)	38.6(2)
I2	4816.2(9)	6647.4(5)	3681.1(7)	36.7(2)
I3	2045.6(9)	4890.8(5)	3901.4(6)	37.0(2)
I4	2513.2(8)	4377.8(5)	1593.4(6)	34.4(2)
I5	2923(2)	3893.8(6)	−617.1(8)	63.4(3)
P	7000(3)	7724(2)	3542(2)	31.4(6)
C1	6713(13)	8383(8)	2305(10)	37(2)
C2	8128(17)	9004(9)	2050(12)	51(3)
C3	7077(15)	8469(7)	4720(9)	35(2)
C4	7222(18)	7950(8)	5806(11)	48(3)

Crystal Data. **2a.** A red prism (0.80 × 0.15 × 0.04 mm) was mounted in inert oil. Using Mo Kα radiation on a Stoe STADI4 diffractometer 2851 intensities were measured to $2\theta_{max} = 55°$, of which after absorption corrections 926 were unique (R_{int} 0.0365) and 925 used for all calculations (38 parameters).

3b. A red prism (0.40 × 0.28 × 0.28 mm) was mounted as above on a Siemens R3 diffractometer. Using Mo Kα radiation, 7449 intensities were measured to $2\theta_{max} = 50°$, of which after absorption corrections 5335 were unique (R_{int} 0.0267) and 5328 used for all calculations (60 restraints, 208 parameters).

4c. A black cut needle (0.60 × 0.20 × 0.02 mm) was mounted as above (**3b**). A total of 5666 intensities were measured to $2\theta_{max} = 55°$, of which after absorption corrections 3402 were unique (R_{int} 0.0913) and 3377 used for all calculations (93 parameters). The structures were solved by direct methods (SHELXS-86) and refined anisotropically on F^2 (SHELXL-92). For details see Tables 1 and 2.

Results

NMR Investigation of the Stepwise Iodination of Dialkyliodophosphanes (R_2PI/I_2 Systems). The reactions of iodophosphanes R_2PI, **1a−c** (**a**, R = t-Bu; **b**, R = i-Pr; **c**, R = Et), with iodine was followed by ^{31}P- and ^1H-NMR spectroscopy. Iodine was added stepwise to dichloromethane solutions of the iodophosphanes and to dichloromethane solutions or suspensions of R_2PI_3 compounds (Table 3).

Reactions of Iodine with Di-*tert*-butyliodophosphane (1a). When a very small amount of iodine is added to a solution of

Table 3. NMR Data for R_2PI/I_2 Systems (CH_2Cl_2/CD_2Cl_2 Solvent)

	R_2PI	R_2PI/R_2PI_3	R_2PI_3	$(R_2PI_2)_2^+,I^-,I_3^-$	$R_2PI_3 + I_2$ (satd)
R = *t*-Bu					
$\delta(^{31}P)$	136.7	135[a]	61.1[b]	80.9	87.5
$\delta(^1H)$	1.28 d	1.32 d	1.55 d	1.66 d	1.64 d
$^3J(P,H)$	12.0	12.2	19.1	22.0	23.8
R = *i*-Pr					
$\delta(^{31}P)$	112.0	105.6[a]	35.5[b]	33.2	47.2
$\delta(^1H[CH_3])$	1.15 d, d	1.16 d, d	1.25 d, d	1.32 d, d	1.38 d, d
$^3J(PH)$	13.9	14.1	20.4	24.4	26.7
$\delta(^1H[CH])$	1.86 d, sept	1.91 d, sept	2.32 d, sept	2.80 d, sept	2.81 d, sept
$^2J(PH)$	9.77	8.33	0[c]	0[c]	2
$^3J(HH)$	6.88	7.03	6.74	6.72	6.68
R = Et					
$\delta(^{31}P)$	83.6 (toluene)	84.1[a] (CH_2Cl_2)			−11 (CH_2Cl_2)[d]
$\delta(^1H[CH_3])$	1.14	1.46			1.36
$^3J(PH)$	14.87	14.98			29.19
$\delta(^1H[CH_2])$	1.86	2.30			3.31
$^2J(PH)$	9.05	7.5			7
$^3J(HH)$	7.53	7.5			7.4

[a] Line width 100−250 Hz. [b] Line width 500 Hz (**2a**) and 900 Hz (**2b**). [c] <1 Hz (not resolved). [d] Et_2PI_5 for R = Et.

1a, the ^{31}P-NMR signal broadens considerably whereas the ^1H NMR doublet does not; the ^1H- and ^{31}P-NMR signals are shifted slightly to lower field, compared with **1a**, and the coupling constant $^3J(^{31}P,^1H)$ increases slightly. Separate NMR signals for the reaction product are not observed. Apparently, under these conditions rapid iodine transfer between dialkyliodophosphane molecules occurs; such rapid iodine cation transfer is known to occur in various R_3PI^+/PR_3 or R_3PI_2/PR_3 systems at room temperature in solution.[4−6] Adding about 1/2 equiv of iodine to the dichloromethane solution of **1a** leads to precipitation of yellow *t*-Bu_2PI_3 (**2a**); the ^{31}P-NMR signal of the remaining **1a** in solution again appears broad and slightly shifted to lower field (Table 3); running the spectrum at −60 °C did not lead to decoalescence of the ^{31}P-NMR signal. The 1:1 reaction of **1a** with I_2 furnishes **2a** as a yellow solid that is sparingly souble in tetrahydrofuran, trichloromethane and dichloromethane (solubility in CH_2Cl_2: 0.8 g·L^{-1}). **2a** shows a very broad ^{31}P-NMR signal at +61 ppm (75 ppm upfield from **1a**), the increase of $^3J(^{31}P,^1H)$ from **1a** to **2a** is consistent with four-coordination of phosphorus in **2a**.

The X-ray crystal structure determination of **2a** reveals that di-*tert*-butyldiiodophosphonium ions (containing tetrahedrally coordinated phosphorus) are bridged by two-coordinated iodide anions leading to a zigzag chain polymer (Figure 1). Both iodine atoms adjacent to phosphorus are linearly coordinated (177.5°), whereas the angle at the bridging iodide anions is 102.9°. With help of the rules of VSEPR theory, this geometry within the chains of **2** allows the I···I contacts (3.359 Å) to be assigned to donor−acceptor interactions involving the bridging two-coordinated iodide ions as [8−I−2] donors and the two-coordinated iodine atoms adjacent to phosphorus as [10−I−2] acceptors. The cation−anion I···I interactions are associated with significant elongation of the P−I bonds (2.445 Å), compared with essentially isolated iodophosphonium ions (2.40 ± 0.01 Å).[7−10] The environment of the bridging iodide atoms of **2a** is closely related to that of the central iodide anion of the known cation $[(n\text{-}Bu_3PI)_2I]^+$.[13]

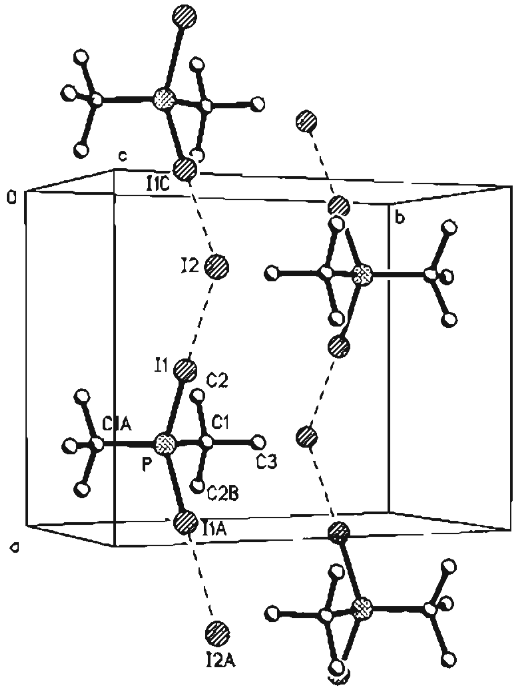

Figure 1. Packing diagram of **2a**. Selected distances (Å) and angles (deg): I1−P 2.4448, I1−I2 3.359, P−C1 1.880; P−I1−I2 177.55, I1−I2−I1C 102.95, I1−P−I1A 107.85. Atoms I1, C1, and C3 occupy special positions of *m* symmetry, and I2 and P, of *mm2* symmetry. Symmetry operations: (A) 1.5 − *x*, 0.5 − *y*, *z*; (B) 1.5 − *x*, *y*, *z*; (C) 0.5 − *x*, 0.5 − *y*, *z*.

Addition of further amounts of iodine to suspensions containing **2a** leads to brown solutions/suspensions, which become darker with increasing amounts of iodine. Such solutions give strong and sharp ^{31}P-NMR singlets that are shifted to lower field, compared with **2a**. ^1H-NMR doublet signals are further shifted downfield and $^3J(^{31}P,^1H)$ increases further, compared with **1a** and **2a**; maximum values ($\delta(^{31}P)$ = + 87.5 ppm $^3J(^{31}P,^1H)$ = 23.8 Hz, see Table 3) were obtained in the presence of a saturated solution of iodine in dichloromethane. Crystallization from 1:2 **1a**/I_2 or 1:1 **2a**/I_2 solutions furnished brown crystals of *t*-Bu_2PI_4 (**3a**), which are moderately soluble in dichloromethane. **3a** is obviously a mixed iodide, triiodide (*t*-$Bu_2PI_2)_2(I)(I_3)$; attempts to isolate crystals of the bis(triiodide) *t*-Bu_2PI_5 (**4a**) failed even in the presence of excess iodine. The fact that all NMR parameters of *t*-Bu_2PI_3/I_2 systems are dependent on the iodine content in solution suggests that iodine addition leads to consumption of iodide anions by triiodide formation. Since triiodide is a weaker donor toward iodophosphonium cations, the overall cation−anion *soft−soft* interactions decrease with increasing addition of iodine. Retrosynthetically,

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(13) Mc Auliffe, C. A.; Godfrey, S. M.; Mackie, A. G.; Pritchard, R. G. *Angew. Chem.* **1992**, *194*, 932.

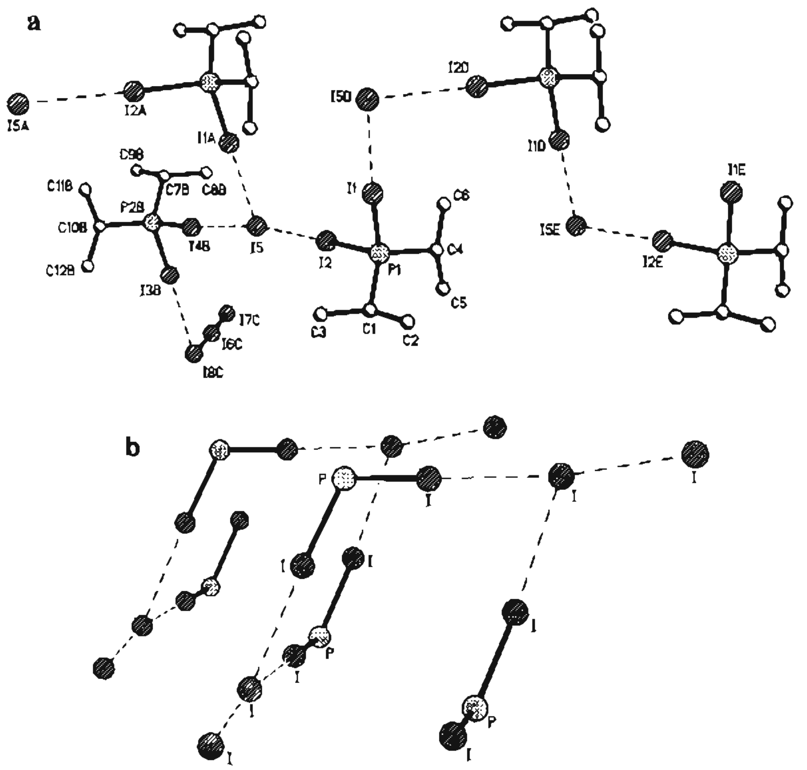

Figure 2. (a) Helical structure of **3b**. The helix is built up via interactions I2···I5···I1. On the bottom left is seen a side chain (see text). Selected distances (Å) and angles (deg): I1–P1 2.419, I2–P1 2.411, I3–P2 2.412, I4–P2 2.410, I1–I5D 3.3803, I2–I5 3.5188, I3B–I8C 3.4531, I5–I4B 3.4251, I6C–I7C 2.8844, I6C–I8C 2.9388; P–I–I 173–176, I1A–I5–I4B 109.03, I2–I5–I4B 171.57, I1A–I5–I2 76.46, I7C–I6C–I8C 178.54. Symmetry operations: (A) 1.5 − *x*, 0.5 + *y*, 0.5 − *z*; (B) 1 − *x*, 1 − *y*, −*z*; (C) 0.5 + *x*, 1.5 − *y*, −0.5 + *z*; (D) 1.5 − *x*, −0.5 + *y*, 0.5 − *z*; (E) *x*, −1 + *y*, *z*. (b) Backbone of the helical structure of **3b**.

increasing cation–anion *soft–soft* interaction leads to ^{31}P- and ^{1}H-NMR upfield shifts and decreasing magnitude of $^{3}J(^{31}P,^{1}H)$. Thus the question arises if the presence of weakly nucleophilic triiodide counterions has already an impact (upfield shift) on the ^{31}P nucleus of the *t*-Bu$_2$PI$_2^+$ cation. To obtain reference data for a nearly "free" *t*-Bu$_2$PI$_2^+$ cation, we prepared *t*-Bu$_2$PI$_2^+$ AlI$_4^-$ (**5a**) from **2a** with aluminum triiodide. As expected, the ^{31}P NMR singlet of **5a** appears even further downfield (+96.6 ppm) than that of solutions containing **3a**/**4a** (87.5 ppm). The ^{27}Al NMR signal of **5a** appearing in the range of "free" AlI$_4^-$ (−26 ppm)[14] confirms that in solution the symmetry of the counterion in **5a** is not disturbed by cation–anion interactions.

$$\underset{\mathbf{1}}{R_2PI} + I_2 \rightarrow \underset{\mathbf{2}}{R_2PI_3} \qquad (1)$$

$$\underset{\mathbf{2*}}{R_2P^{*}I_3} + \underset{\mathbf{1}}{R_2PI} \rightleftharpoons \underset{\mathbf{1}}{R_2PI_3} + \underset{\mathbf{2*}}{R_2P^{*}I} \qquad (2)$$

$$\underset{\mathbf{2}}{2R_2PI_3} + I_2 \rightarrow \underset{\mathbf{3}}{(R_3PI)_2(I)(I_3)} \qquad (3)$$

$$\underset{\mathbf{3}}{(R_3PI)_2(I)(I_3)} + I_2 \rightarrow \underset{\mathbf{4}}{2(R_2PI_2)_2(I_3)_3} \qquad (4)$$

$$\underset{\mathbf{2a}}{R_2PI_3} + AlI_3 \rightarrow \underset{\mathbf{5a}}{(R_2PI_2)(AlI_4)} \qquad (5)$$

R = *t*-Bu, **a**; *i*-Pr, **b**; Et, **c**

Reactions of Iodine with Iododiisopropylphosphane (1b). As in the previous case (**1a**), mixtures of **1b** with iodine in dichloromethane solution in any ratio furnish one-peak ^{31}P-NMR spectra: with minor amounts of iodine, line broadening and a slight downfield shift from 112.6 ppm (**1b**) to 105.6 ppm for **1b**/I$_2$ above a precipitate of *i*-Pr$_2$PI$_3$ (**2b**) were observed. With a 1:1 ration of **1b** and iodine, a weak and broad signal of **2b** appeared at 35 ppm; with excess iodine a sharp and much stronger signal of (**2b**/**3b**/excess I$_2$) was resolved at 47 ppm. With increasing iodine content, the magnitude of $^{3}J(^{31}P,^{1}H)$ increases, whereas the magnitude of $^{2}J(^{31}P,^{1}H)$ goes through a minimum (**1b**, $J = 9.8$ Hz [probably negative]; **2b**, **3b**, J = not resolved; with excess I$_2$, $J = 2$ Hz). **2b** was isolated as yellow crystals, sparingly soluble in dichloromethane (yellow solution); pure *i*-Pr$_2$PI$_4$ (**3b**) gave violet crystals that are moderately soluble in dichloromethane (brown solution).

The X-ray crystal structure determination of **3b** (Figures 2 and 3) reveals that the compound consists of diiododisopropylphosphonium cations and iodide *and* triiodide anions. The *i*-Pr$_2$PI$_2^+$ cations are present in two different environments: one (central atom P1) as part of helical chains from *i*-Pr$_2$PI$_2^+$ cations interacting with I$^-$ anions, and the other (central atom P2) as part of side chains attached to the helices by further I···I interactions. The side chain *i*-Pr$_2$PI$_2^+$ cations are also in I···I contact with *terminal* I$_3^-$ anions. Because of attachment of these side chains, all iodide anions I5 of the helical chains become μ_3-bridging between three *i*-Pr$_2$PI$_2^+$ cations. The coordination geometry of I5 is distorted between pyramidal and a T structure (∠I–I–I are 76.5 [within the helical chain], 109, and 171.6°); P–I–I angles are all between 173 and 179°, emphasising the acceptor character of the iodine atoms bonded to four-coordinated phosphorus. Compared with the chain structure of **2a**, all I···I contacts within **3b** are longer, and all P–I bonds within **3b** are shorter (2.410–2.419 Å). The iodide anion is a much better donor than the triiodide anion toward iodophosphonium cations: becoming three-coordinated in **3b**, the iodide

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[14] Kidd, R. G.; Truax, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 6867.

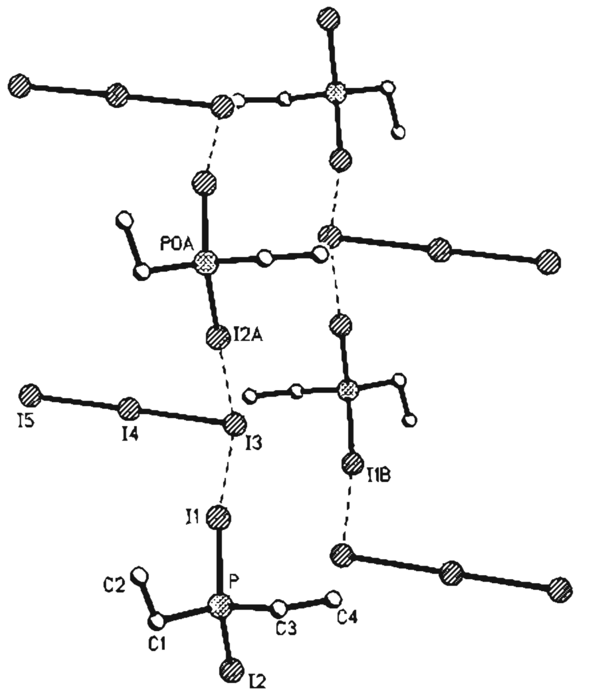

Figure 3. Two adjacent chains of solid **4c**. Selected distances (Å) and angles (deg): I1−P 2.391, I2−P 2.402, I1−I3 3.5685, I2−I3 3.4488; P0A−I2A−I3 172.83, I2A−I3−I4 90.20, I1−I3−I2A 79.69, I5−I4−I3 179.34. Shortest contacts between chains (Å): I3−I1B 4.212. Symmetry operations: (A) $-1 + x, y, z$; (B) $1 - x, 1 - y, 1 - z$.

competes successfully with the triiodide, which is only a monodentate ligand towards the side chain *i*-$Pr_2PI_2^+$ cations of **3b**.

Reactions of Iodine with Diethyliodophosphane (1c). The 1:1 reaction with iodine provides yellow Et_2PI_3 (**2c**).[15] The very low solubility of **2c** in dichloromethane and carbon disulfide and possibly also line broadening precluded the determination of its ^{31}P-NMR shift. In presence of a precipitate of **2c**, **1c** gives a broad signal at 84 ppm (Table 1). With one further equivalent of iodine, **2c** provides the violet triiodide Et_2PI_5 **4c** ($\delta(^{31}P)$ −11 ppm), moderately soluble in dichloromethane; adding excess iodine to solutions of **4c** does not lead to a significant change of its NMR parameters. Consistent with four-coordination at phosphorus and only weak cation−anion *soft−soft* interactions, the magnitude of $^3J(^{31}P,^1H)$ of **4c** is nearly double (29.2 Hz) that of the phosphane **1c** (14.9 Hz).

The X-ray crystal structure determination of **4c** (Figure 3) reveals that the compound consists of chains of diethyldiiodophosphonium ions bridged by I···I contacts with triiodide ions, leading to a pleated ribbon structure (Figure 3) when weak I···I contacts (4.2 Å) between chains are considered.

The average I···I distance in the diiodophosphonium triiodide **4c** is about 0.1 Å longer than in the mixed iodide triiodide **3b** and nearly 0.2 Å longer than in the iodide **2a**. The longer (weaker) I···I interaction within **4c** is reflected by comparatively strong ("undisturbed") P−I bonds [*d*(P−I): **2a** > **3b** > **4c**]. Obviously, the nucleophilicity of the triiodide anion is not sufficient to lead to a *significant* destabilization of the P−I bonds by population of σ^*(P−I) orbitals of two $Et_2PI_2^+$ cations. The bridging iodine atom (I3) of **4c** may, like the central iodide anion in the known cation $[(Ph_3PI)_2\,I{-}I_2]^{+8}$, be regarded as a trigonal-pyramidal iodide anion with strong coordination to an iodine molecule (I4, I5) and with weaker interaction with two acceptor iodine atoms of two different $Et_2PI_2^+$ cations. The bridging triiodide ion of **4c** (I−I 2.975 and 2.842 Å) is only a little more asymmetric than the terminal triiodide of **3b** (I−I 2.939 and 2.884 Å). In agreement with this X-ray structural evidence, the "splitting" ($\nu_{as} - \nu_s$) of the pair of I−I vibrations of triiodide ions in the Raman spectra is larger for the more asymmetric triiodide ion within solid **4c** ($\nu_{as} - \nu_s = 34$ cm^{-1}) than for the triiodide ion of solid **3b** ($\nu_{as} - \nu_s = 28$ cm^{-1}).

Summary

In iodophosphonium cations, each iodine atom attached to four-coordinated phosphorus behaves as a soft electrophile seeking contact with a soft nucleophile. To meet this requirement in dialkyldiiodophosphonium iodides, iodide anions have to act as μ_2-bridging soft nucleophiles toward two of the dialkyldiiodophosphonium cations. Cation−anion *soft−soft interactions* between linear two-coordinated acceptor iodine atoms—bonded to tetracoordianted phosphorus—and angular two-coordinated iodide anions lead to the chain structure of **2a**. Compared with iodide anions, triiodide anions are much weaker nucleophiles towards iodophosphonium ions. When addition of iodine to R_2PI_3 leads to consumption of a part of the iodide ions by triiodide formation, the remaining iodide ions have to bridge more than two $R_2PI_2^+$ cations. Thus, in **3b**, iodide anions become μ_3-bridging between three cations, whereas each triiodide anions acts as terminal donor towards a side chain $R_2PI_2^+$ cation. In **4c**, triiodide anions have to behave as μ_2-bridging soft donors towards two of the cations because no iodide anions are available. Average I···I contacts become slightly longer, when iodide anions have to coordinate more acceptor units. Compared with the chain structure of **2a**, helical **3b** contains an additional R_2PI_5 moiety as additional acceptor coordinated to the donor-iodide anion, whereas the chains of **4c** contain one I_2 molecule per unit as an additional acceptor coordinated to the donor-iodide anion.

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Supporting Information Available: Tables S1−S15 listing crystallographic data, anisotropic displacement parameters, positional parameters of hydrogen atoms, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

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[15] Kudryatseva, L. I.; Fesbenko, N. G.; Povolotskii, M. I. *Zh. Obshch. Khim.* **1978**, *48*, 222.