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Supramolecular Soft−Soft Interactions of Diiodo(*tert*-butyl)(isopropyl)phosphonium Cations with μ_2- to μ_5-Bridging Iodide Anions. Formation of Chains, Helices, and Columnar Structures[†]

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tert-Butyl(isopropyl)iodophosphane (**1**) reacts with 1 equiv of iodine in dichloromethane furnishing yellow *tert*-butyl(isopropyl)diiodophosphonium iodide *t*-Bu(*i*-Pr)PI$_3$ (**2**). A byproduct is red crystalline *t*-Bu(*i*-Pr)PI$_{3.25}$ (**3**). Stepwise addition of iodine to **1** provides **2** and the *tert*-butyl(isopropyl)diiodophosphonium iodide/triiodides *t*-Bu(*i*-Pr)PI$_4$ (**4**) and *t*-Bu(*i*-Pr)PI$_{4.33}$ (**5**). NMR spectra from solutions prepared by adding various amounts of iodine to **1** always show only one ^{31}P-NMR signal and one set of ^{1}H-NMR resonances; chemical shifts and coupling constants, which depend on the amount of iodine added to **1,** indicate rapid exchange equilibria in solution and decreasing cation−anion interactions with increasing iodine content. The solid state structures of **2**−**5** were determined by X-ray crystallography. **2** (orthorhombic, space group *Pbcn*, $Z = 8$, $a = 13.413(3)$ Å, $b = 14.693(3)$ Å, $c = 14.240(3)$ Å) consists of helical chains of *tert*-butyl(isopropyl)diiodophosphonium ions bridged by μ_2-iodide anions through iodine−iodine interactions. *t*-Bu(*i*-Pr)PI$_{3.25}$ (**3**) (tetragonal, space group *P*4/*ncc*, $Z = 16$, $a = 19.730(3)$ Å, $c = 14.485(4)$ Å) is [*t*-Bu(*i*-Pr)PI$_2$]$_4$(μ_2-I)$_2$(μ_4-I)[I(I$_2$)$_x$] (mixed-valence columnar structure, $x \approx 0.5$): 16-membered rings from four *t*-Bu(*i*-Pr)PI$_2$−I moieties are connected in a spiro fashion by μ_4-iodide anions; each channel between four of these cationic stacks is occupied by iodine ([I(I$_2$)$_x$]$^-$, disordered). The backbone of the chain structure of crystalline **4** (orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 9.462(2)$ Å, $b = 11.130(3)$ Å, $c = 30.228(6)$ Å) is formed by [−P−I−I−I−] units from *tert*-butyl(isopropyl)diiodophosphonium ions and μ_3-donor iodide ions, each of which is connected with one iodine atom of a further side chain *tert*-butyl(isopropyl)diiodophosphonium ion. The other iodine atom of this side chain cation is coordinated by a terminal triiodide ion. **5** (monoclinic, space group $P2_1/c$, $Z = 4$, $a = 23.874(9)$ Å, $b = 21.858(7)$ Å, $c = 9.477(3)$ Å, $\beta = 94.30(3)°$) contains a double chain backbone of μ_2-acceptor phosphonium ions and μ_5-bridging donor iodide ions. Four I···I contacts of these μ_5-bridging donor iodide ions are within the double chain, and the fifth is to a side chain *tert*-butyl(isopropyl)diiodophosphonium ion, which is also connected to a terminal triiodide anion by an I···I interaction. A further triiodide anion within the unit cell has no soft−soft interaction with the cationic network.

Introduction

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, triorganyliodophosphonium iodides R$_3$PI$_2$ exist as monomeric ion pairs with one linear P−I−I moiety.[1,2] In diorganyldiiodophosphonium iodides R$_2$PI$_3$, iodide anions have to act as μ_2-bridging soft nucleophiles toward two of the diorganyldiiodophosphonium cations; thus, cation−anion *soft−soft interactions* between linear two-coordinated acceptor iodine atoms, bonded to tetracoordinated phosphorus, and two-coordinate iodide anions (with angular geometry) lead to ring or chain structures with [−I−P−I−I−]$_x$ backbones (x = 2 or ∞).[3,4] In alkyltriiodophosphonium iodides RPI$_4$, each cation contains three acceptor-iodine atoms bonded to phosphorus; thus, iodide counterions have to bridge three RPI$_3^+$ cations (Scheme 1).[5]

Compared with iodide anions, triiodide anions are much weaker nucleophiles toward iodophosphonium ions. When addition of 0.5 equiv of iodine to diorganyldiiodophosphonium iodides R$_2$PI$_3$ leads to consumption of half of the iodide ions by triiodide formation, the remaining iodide ions have to bridge more than two R$_2$PI$_2^+$ cations. Thus, in *i*-Pr$_2$PI$_4$, which is [(*i*-Pr$_2$PI$_2^+$)$_2$(I$^-$)(I$_3^-$)]$_x$, donor-iodide anions become μ_3-bridging whereas the triiodide anions act as terminal donors toward side chain R$_2$PI$_2^+$ cations.[3] Due to attachment of these side chains, all iodide anions of the helical chains become μ_3-bridging between three *i*-Pr$_2$PI$_2^+$ cations. The coordination geometry of these μ_3-bridging iodide ions is rather distorted, i.e., between pyramidal and a T-type structure [angles I−I−I are 76.5° (within the helical chain), 109°, and 171.6°]. The related 8-membered ring structure [Ph$_2$PI$_3$]$_2$ of dimeric Ph$_2$PI$_3$[4] would correspond to a helix of pitch 0. Crystalline *i*-Pr$_2$PI$_4$, containing helices with [−I−P−I−I−]$_x$ backbones, is *not* chiral.[3] However, attachment of a chiral marker in the side chain of the chiral [−I−P−I−I−]$_x$ backbone, leading to the formation of diastereomers, might allow diastereoselective crystallization, providing an optically active solid. To elucidate a possible access to such intensely colored solids, optically active due to the presence of chiral helices based on soft−soft interactions, we decided to use an iodophosphane with two slightly different alkyl substit-

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[†] Dedicated to Professor M. Baudler on the occasion of her 75th birthday.

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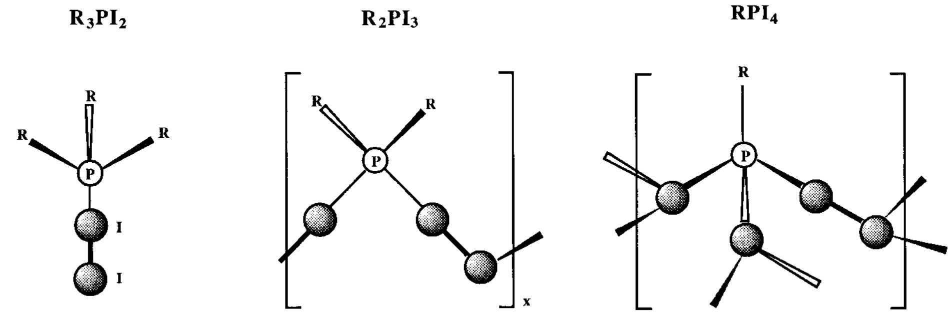
Scheme 1



- terminal iodide donor towards the I atom of $R_3PI^{\oplus}$
- μ_2 bridging iodide donor towards two I atoms of two $R_2PI_2^{\oplus}$ cations
- μ_3 bridging $I^{\ominus}$ donor towards three I atoms of three different $RPI_3^{\oplus}$ cations

Table 1. Crystallographic Data for **2**, **3**, **4**, and **5**

	t-Bu(*i*-Pr)PI$_3$ (**2**)	*t*-Bu(*i*-Pr)PI$_{3.25}$ (**3**)	*t*-Bu(*i*-Pr)PI$_4$ (**4**)	*t*-Bu(*i*-Pr)PI$_{4.33}$ (**5**)
formula	$C_7H_{16}I_3P$	$C_7H_{16}I_{3.25}P$	$C_{14}H_{32}I_8P_2$	$C_{21}H_{48}I_{13}P_3$
fw	511.87	543.59	1277.54	2043.20
space group	*Pbcn*	*P*4/*ncc*	*P*2$_1$2$_1$2$_1$	*P*2$_1$/*c*
a, Å	13.413(3)	19.730(3)	9.462(2)	23.874(9)
b, Å	14.693(3)		11.130(3)	21.858(7)
c, Å	14.240(3)	14.485(4)	30.228(6)	9.477(3)
β, deg				94.30(3)
V, Å^3	2806.4(10)	5638.6(20)	3183.4(13)	4931.5(29)
Z	8	16	4	4
T, °C	−130	−130	−100	−130
μ, mm^{-1}	6.433	7.271	7.896	8.273
d_{calcd}, Mg/m^3	2.423	2.561	2.666	2.752
R^a	0.0653	0.0356	0.0418	0.0465
R_w^{b}	0.2019	0.0800	0.1090	0.1381

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

uents for the formation of a novel compound RR′PI$_4$. Such compound would be likely to contain a chiral side chain moiety I−P*(R)(R′)−I−I$_3$ at a possibly chiral $[-I-P-I-I-]_x$ backbone. Here we present the results of this approach with R = *i*-Pr, R′ = *t*-Bu.

Experimental Section

The experiments were carried out under dry nitrogen as inert gas and in dry and deoxygenated solvents. All ^{1}H- and ^{31}P-NMR spectra were obtained on Bruker AC 200 spectrometers operating at 200.1 MHz (^{1}H) and 81 MHz (^{31}P) and an AM 400 spectrometer operating at 400.2 MHz (^{1}H). Chemical shifts are given with respect to TMS (^{1}H) and H_3PO_4. The Raman spectrum was obtained on a Bruker FT IR and Raman spectrometer at the Institut für Anorganische und Analytische Chemie, Technische Universität Clausthal. Mass spectra were obtained with Finnigan MAT 8430 and Finnigan MAT 4515 instruments (EI, 70 eV).

Elemental analyses were carried out on a Carlo Erba analytical gas chromatograph. For the determination of melting points, samples were heated in sealed glass capillaries in a Büchi 535 instrument. The P−I compounds were destroyed by oxidative hydrolysis with aqueous alkaline potassium permanganate solution and subsequent reduction with sodium sulfite.

***tert*-Butyl(isopropyl)iodophosphane (1).** A suspension of sodium iodide (40 g, 266 mmol) in 100 mL of toluene with 13 g (78 mmol) of *tert*-butyl(isopropyl)chlorophosphane[6] (40 g, 266 mmol) was stirred for 1 day at room temperature. After separation of the solution from the solid, the solvent was removed under vacuum. Distillation of the residue furnished 12.3 g (60.9%) of **1** at 60 °C (1.8 mbar) as a yellow oil. ^{1}H-NMR (CH_2Cl_2/C_6D_6): δ 1.18 (d), $^3J(^{31}P,^1H) = 12.3$ Hz, 9H [*tert*-butyl]; 1.14−1.26, 6H [isopropyl] not resolved; 1.87 (multiplet, 8 lines resolved, line distances 6.8 ± 0.1 Hz), 1H [CH of isopropyl]. ^{31}P-NMR (CH_2Cl_2/C_6D_6): δ 126.1. MS (70 eV): *m/z* (%) 258 (42) [M$^+$], 216 (2) [HM$^+$ − C_3H_4], 202 (32) [HM$^+$ − C_4H_9], 75 (5) [HM$^+$ − C_4H_9 − I], 58 (100) [$C_4H_{10}^+$].

***tert*-Butyl(isopropyl)diiodophosphonium Iodide (2).** To a solution of 6.53 g (25.3 mmol) of **1** in 100 mL of dichloromethane was added dropwise a solution of 6.43 g (25.3 mmol) of iodine in 150 mL of dichloromethane. After several hours, the yellow precipitate was separated from the solution and dried for 15 min in vacuo. Thus, 6.4 g (49.9%) of **2** was isolated as a yellow solid (decomposes above 138 °C). Single crystals suitable for an X-ray structure analysis were obtained by diffusion of *n*-pentane into a saturated solution of **2** in dichloromethane. Anal. Calcd for $C_7H_{16}I_3P$ (511.9 g/mol): C, 16.42; H, 3.15. Found: C, 16.33; H, 3.05. ^{31}P-NMR (CH_2Cl_2/C_6D_6): δ 43.8. ^{1}H-NMR (CH_2Cl_2/C_6D_6): δ 2.54 (d, sept), $^2J(PH) < 1$ Hz, $^3J(HH) = 6.7$ Hz, 1H [C*H*(CH$_3$)$_2$]; 1.35 (d, d, $^3J(PH) = 21.4$ Hz, $^3J(HH) = 6.7$ Hz, 6H [CH(C*H*$_3$)$_2$]; 1.45 (d), $^3J(PH) = 20.2$ Hz, 9H [C(C*H*$_3$)$_3$].

***tert*-Butyl(isopropyl)diiodophosphonium Iodide 0.1I$_2$ (3).** In the course of the diffusion of *n*-pentane into a saturated solution of **2** in dichloromethane, about 20% of the deposited crystalline material was dark red crystals of **3** that were also suitable for an X-ray crystal structure determination. **3** decomposes at 90 °C. Anal. Calcd for $C_7H_{16}I_{3.2}P$ (537.27 g/mol): C, 15.65; H, 3.00. Found: C, 15.60; H, 3.00.

Bis[*tert*-butyl(isopropyl)diiodophosphonium] Iodide Triiodide (4) and Tris[*tert*-butyl(isopropyl)diiodophosphonium] Iodide Bis(triiodide) (5). To a solution of 6.49 g (25.2 mmol) of **1** in 100 mL of dichloromethane was added dropwise a solution of 9.58 g (37.7 mmol) of iodine in 200 mL of dichloromethane. The solution turned dark brown, and a precipitate was formed. The precipitate was separated from the solvent and dried in vacuo. The crude solid product was composed of a small amount of red plates of **4** (among them were single crystals suitable for the structure determination); over 90% was brown needles of **5**. Pure **5** (13.9 g, 86.6%) was isolated by recrystallization of the crude product from dichloromethane (mp 114 °C). Single crystals of **5** were grown by diffusion of *n*-pentane into a saturated solution of **5** in dichloromethane. Anal. Calcd for $C_{21}H_{48}I_{13}P_3$ (2043.3 g/mol): C, 12.34; H, 2.36. Found: C, 12.40; H, 2.29. ^{31}P-NMR (CH_2Cl_2/C_6D_6): δ 54.7. ^{1}H-NMR (CD_2Cl_2): δ 2.77 (d, sept), $|^2J(PH)| = 2.0$ Hz, $^3J(HH) = 6.7$ Hz, 3H [C*H*(CH$_3$)$_2$]; 1.44 (d, d, $^3J(PH) = 23.35$ Hz, $^3J(HH) = 6.7$ Hz, 18H [CH(C*H*$_3$)$_2$], 1.55 (d), $^3J(PH) = 22.3$ Hz, 27H C(C*H*$_3$)$_3$]. Raman (between 20 and 600 cm^{-1}): 70 (vw), 97 (s), 105 (s), 113 (vs), 127 (m), 147 (s), 273 (vw, broad), 358 (m), 372 (w, broad), 407 (vw), 450 (vw), 488 (w), 590 (vw, broad).

Crystal Data. (See also Table 1). **2.** A yellow plate (0.90 × 0.35 × 0.08 mm) was mounted in inert oil. Using Mo Kα radiation on a Stoe STADI4 diffractometer, 2807 intensities were measured to $2\theta_{max} = 50°$, of which, after absorption corrections, 2349 were unique ($R_{int} = 0.0268$) and 2339 used for all calculations (39 restraints, 107 parameters).

3. A dark red prism (0.50 × 0.35 × 0.35 mm) was mounted as above. Using Mo/Kα radiation, 4788 intensities were measured to $2\theta_{max} = 50°$, of which, after absorption corrections, 2494 were unique (R_{int}

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Table 2. Atomic Coordinates [×10^4] and Equivalent Isotropic Displacement Parameters [$Å^2 \times 10^3$] for **2**, **3**, **4**, and **5**

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
				2: *t*-Bu(*i*-Pr)PI_3					
I(1)	1604.1(7)	1445.0(7)	1085.9(6)	34.6(3)	C(2)	2671(20)	3707(19)	1222(16)	102(7)
I(2)	1568.5(7)	3126.9(7)	−1077.9(7)	40.7(4)	C(3)	4012(18)	3697(19)	81(15)	95(7)
I(3)	0	4292.3(12)	−2500	51.8(5)	C(4)	3322(11)	1384(12)	−781(10)	42(3)
I(4)	0	356.9(10)	2500	42.2(4)	C(5)	2549(12)	793(10)	−1244(10)	38(3)
P	2641(3)	2267(2)	−36(2)	29.7(8)	C(6)	3950(12)	1932(11)	−1525(11)	46(3)
C(1)	3421(18)	3060(15)	678(15)	81(6)	C(7)	3980(12)	849(13)	−146(11)	51(4)
				3: *t*-Bu(*i*-Pr)$PI_{3.25}$					
I(2)	5254.1(3)	3356.0(3)	3808.5(4)	25.3(2)	C(1)	5044(4)	1619(4)	4210(5)	21(2)
I(3)	5265.6(3)	4734.4(3)	2500	26.7(2)	C(2)	4339(4)	1664(5)	3755(6)	35(2)
I(4)	7500	2500	7500	28.5(3)	C(3)	5601(5)	1581(5)	3458(7)	40(2)
I(5)	2500	2500	7467(3)	54.1(8)	C(4)	5088(5)	998(4)	4823(6)	37(2)
I(6)	2500	2500	3323(3)	62.3(9)	C(5)	4452(4)	2617(4)	5649(5)	28(2)
I(7)	2500	2500	5141(9)	98(3)	C(6)	4581(5)	3308(5)	6107(6)	41(2)
I(8)	2500	2500	10322(17)	253(11)	C(7)	4317(6)	2079(6)	6366(7)	55(3)
P	5167.3(10)	2412.6(10)	4883.5(14)	20.5(4)					
				4: *t*-Bu(*i*-Pr)PI_4					
I(1)	1472.2(6)	5138.7(6)	407.6(2)	29.4(2)	C(3)	3673(14)	5883(12)	1365(5)	52(3)
I(2)	−1410.5(7)	6355.6(6)	−110.9(3)	34.9(2)	C(4)	3550(11)	2608(8)	519(4)	30(2)
I(3)	5663.9(6)	5148.6(6)	348.8(3)	31.9(2)	C(5)	2223(11)	2014(12)	701(5)	49(3)
I(4)	−1267.8(8)	6165.1(6)	1460.0(3)	39.8(2)	C(6)	3579(13)	2533(11)	23(4)	41(3)
I(5)	−3813.9(8)	1847.0(7)	1992.9(3)	42.6(2)	C(7)	4875(12)	1988(11)	725(5)	42(3)
I(6)	−1671.6(9)	3085.5(8)	1411.1(4)	59.9(3)	C(8)	−2368(11)	9129(12)	1270(4)	41(3)
I(7)	−5795.1(9)	523.8(13)	2501.1(4)	72.9(3)	C(9)	−3700(12)	8595(14)	1468(6)	63(4)
I(8)	1123.2(7)	8557.5(6)	915.2(3)	34.1(2)	C(10)	−2451(17)	9219(22)	771(6)	89(7)
P(1)	3611(3)	4217(2)	684.3(9)	25.9(5)	C(11)	−115(11)	8771(11)	1999(4)	35(2)
P(2)	−756(3)	8288(2)	1451.7(10)	29.7(6)	C(12)	1165(14)	8018(13)	2126(5)	54(3)
C(1)	3808(11)	4530(10)	1279(4)	37(2)	C(13)	301(13)	10083(11)	1969(5)	49(3)
C(2)	2805(12)	3822(15)	1579(5)	52(4)	C(14)	−1291(17)	8580(15)	2340(5)	66(4)
				5: *t*-Bu(*i*-Pr)$PI_{4.33}$					
I(1)	1685.2(3)	6488.5(4)	278.5(8)	31.0(2)	C(4)	524(5)	6806(6)	2186(13)	32(3)
I(2)	1707.5(3)	6518.2(4)	4422.5(8)	31.1(2)	C(5)	182(6)	6661(7)	3433(15)	54(4)
I(3)	3366.5(3)	6536.5(3)	614.3(8)	29.0(2)	C(6)	169(6)	6734(7)	764(15)	51(4)
I(4)	3377.4(3)	6534.5(3)	4754.6(8)	29.0(2)	C(7)	753(6)	7464(6)	2283(15)	45(3)
I(5)	2531.0(4)	5163.4(3)	−2451.1(9)	37.6(2)	C(8)	4042(5)	5457(4)	2835(12)	27(3)
I(6)	3104.7(4)	3688.2(4)	−402.7(10)	43.3(2)	C(9)	3511(5)	5108(5)	2356(15)	43(3)
I(7)	2532.4(3)	6801.0(3)	−2478.7(8)	27.0(2)	C(10)	4274(6)	5244(6)	4260(14)	48(4)
I(8)	3908.1(4)	3062.9(4)	2400.9(10)	42.8(2)	C(11)	4566(4)	6777(5)	2851(12)	28(3)
I(9)	4811.3(4)	3984.5(3)	1949.7(8)	33.5(2)	C(12)	4887(5)	6614(6)	1568(14)	42(3)
I(10)	5678.7(4)	4836.6(4)	1520.6(10)	44.6(2)	C(13)	4385(5)	7439(5)	2781(15)	40(3)
I(11)	−542.4(5)	4558.6(6)	3326.7(11)	66.4(3)	C(14)	4919(5)	6658(7)	4237(15)	51(4)
I(12)	411.3(4)	3757.1(4)	3017.4(9)	43.8(2)	C(15)	1826(5)	3784(6)	−2205(14)	40(3)
I(13)	1346.5(6)	2933.1(5)	2563.2(13)	72.3(4)	C(16)	1594(6)	4057(8)	−904(17)	64(5)
P(1)	1144.2(13)	6287.6(14)	2274(3)	25.9(6)	C(17)	1416(5)	3896(7)	−3549(17)	58(4)
P(2)	3915.8(12)	6294.1(13)	2781(3)	22.4(6)	C(18)	2847(6)	3762(5)	−4061(14)	41(3)
P(3)	2532.9(13)	4057.8(13)	−2442(3)	30.2(7)	C(19)	2588(6)	4103(6)	−5360(13)	44(3)
C(1)	994(6)	5464(5)	2276(13)	35(3)	C(20)	2710(6)	3072(5)	−4142(14)	39(3)
C(2)	1528(5)	5100(5)	2558(15)	45(3)	C(21)	3480(6)	3872(7)	−3915(16)	55(4)
C(3)	661(7)	5260(6)	921(15)	52(4)					

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. NMR Parameters of Systems **1**/I_2 (in CH_2Cl_2/C_6D_6)

	1	**1** + $0.5I_2$[a]	**1** + I_2[b]	**1** + $1.6I_2$[c]	**1** + exc I_2[a]
δ ^{31}P	126.1	98.6[d]	43.8	54.7	73.4
δ ^1H (CH_3)[*t*-Bu]	1.18 (d)	1.29 (d)	1.45 (d)	1.55 (d)	1.59 (d)
$^3J(^{31}P,^1H)$, Hz	12.3	14.9	20.2	22.3	25.1
δ ^1H (CH_3)[*i*-Pr]	*e*	1.23 (d, d)	1.35 (d, d)	1.44 (d, d)	1.47 (d, d)
$^3J(^{31}P,^1H)$, Hz		16.2	21.4	23.4	25.9
$^3J(^1H,^1H)$, Hz		6.8	6.7	6.7	6.7
δ ^1H (CH)[*i*-Pr]	1.87[f]	2.12 (d, sept)	2.54 (d, sept)	2.77 (d, sept)	*g*
$I^2 J(^{31}P,^1H)I$, Hz		3.7	<1	2.03	

[a] Solution above a precipitate. [b] Compound 2 and solvent. [c] Pure sample and solvent. [d] Line width 190 Hz. [e] Multiplet (not resolved) 1.14−1.26 ppm, overlapped by the doublet of the *t*-Bu group. [f] Multiplet (8 equidistant lines resolved, line distance 6.8 ± 0.1 Hz). [g] No signal resolved (low concentration).

= 0.0305) and 2493 used for all calculations (116 parameters). Iodine atoms I5, I6, I7, I8 are disordered along the *z*-axis and were refined arbitrarily at half-occupation leading to the given formula in Table 1.

4. A red plate (0.30 × 0.30 × 0.05 mm) was mounted as above on a SIEMENS R3 diffractometer. Using Mo Kα radiation, 7475 intensities were measured to $2\theta_{max} = 55°$, of which, after absorption corrections, 7007 were unique ($R_{int} = 0.0226$) and used for all calculations (227 parameters). The absolute structure parameter *x* was refined to −0.01(6).

5. A brown cut needle (0.40 × 0.20 × 0.08 mm) was mounted as above (**4**). Using Mo Kα radiation, 12 182 intensities were measured to $2\theta_{max} = 55°$, of which, after absorption corrections, 11 382 were unique ($R_{int} = 0.0273$) and used for all calculations (349 parameters).

The structures were solved by direct methods (SHELXS-86) and refined anisotropically on F^2 (SHELXL-93). Methyl groups were treated as rigid, and the methine hydrogens were treated with a riding model. Atomic coordinates are given in Table 2.

Results

Products of the Reactions of *tert*-Butyl(isopropyl)iodophosphane (1) with Iodine. The Cl/I exchange reaction of *tert*-butyl(isopropyl)chlorophosphane in toluene with solid sodium iodide furnishes *tert*-butyl(isopropyl)iodophosphane (**1**) as a

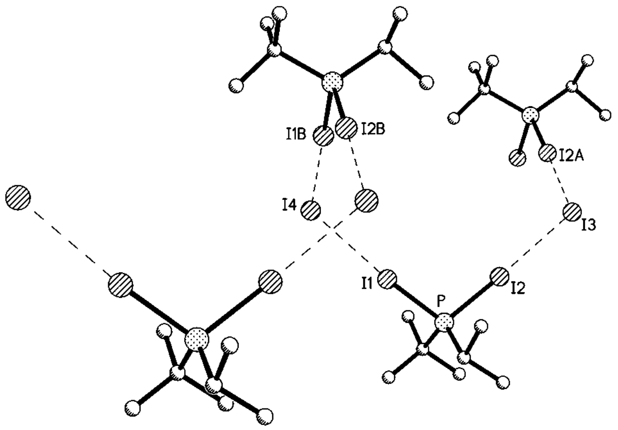

Figure 1. Helical structure of **2**: hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): P−C1 1.87; P−C4 1.91; I1−P 2.438; I2−P 2.423; I1−I4 3.353; I2−I3 3.385; P−I1−I4 174.75; P−I2−I3 177.99; I2A−I3−I2 119.23; I1−I4−I1B 123.045. Symmetry transformation of A: $-x, y, -0.5 - z$. B: $-x, y, 0.5 - z$.

distillable yellow oil. Addition of a small amount of iodine to a dichloromethane solution of **1** leads to broadening of the ^{31}P-NMR signal which appears slightly shifted to a lower field. With 1 equiv of iodine, *tert*-butyl(isopropyl)diiodophosphonium iodide (**2**) is obtained as a yellow solid moderately soluble in dichloromethane. In this respect, **1** and **2** behave similarly to the related "symmetric" dialkylphosphorus compounds R_2PI and R_2PI_3 (R = *i*-Pr or *t*-Bu).[3] However, on growing crystals of **2** by diffusion of pentane into a saturated solution of **2** in dichloromethane, about 20% of a dark red crystalline product **3** is obtained. Analytical data reveal that **3** has a slightly higher iodine content [(*i*-Pr)(*t*-Bu)$PI_{3.2}$] than **2** [(*i*-Pr)(*t*-Bu)PI_3]. Pure **3** is fairly soluble in dichloromethane. Dropwise addition of a larger amount of iodine solution (1.5 equiv) to **1** in dichloromethane leads initially to a yellow solution which turns into a dark brown suspension. The solid as separated by filtration consists of brown crystals (main product, over 90%) and a few red plates. The minor product (red plates) is the originally desired compound [(*i*-Pr)(*t*-Bu)PI_4] (**4**). The major product has a higher iodine content than **4**; its analytical composition is [(*i*-Pr)(*t*-Bu)$PI_{4.33}$] (**5**). Recrystallization of the crude product from dichloromethane provides a brown solid that consists only of brown needle-like crystals [(*i*-Pr)(*t*-Bu)$PI_{4.33}$] (**5**). **5** is moderately soluble in dichloromethane and practically insoluble in pentane.

In solution, NMR spectra from **1**−**5** or mixtures thereof always show only one set of ^{1}H- and ^{31}P-NMR signals, i.e., all exchange reactions in solution are fast compared with the NMR time scales. As in the cases of *i*-Pr_2PI_x and *t*-Bu_2PI_x (x = **1**−**5**),[3] the ^{31}P resonance of **2** (x = 3) appears far upfield from the P^{III} compound **1**, and with further increasing iodine content in solution the one ^{31}P-NMR signal shifts slightly (and steadily) back in the downfield direction (Table 3).

The ^{1}H-NMR resonances of all three types of protons within **2**−**5** are steadily shifted downfield with increasing iodine content of the solutions. The NMR-coupling $^3J(^{31}P,^1H)$ of the *tert*-butyl groups increases steadily from **1** (^3J = 12.3 Hz) to **5** (^3J = 23.4 Hz) and to **5** plus excess iodine (^3J = 25.1 Hz), indicating increasing the presence of "free" (*i*-Pr)(*t*-Bu)PI_2^+ cations. The NMR-coupling $^3J(^{31}P,^1H)$ of the isopropyl groups behaves in a similar fashion. Retrosynthetically, increasing cation−anion soft−soft interaction between iodophosphonium cations and "soft" anions in solution or in the solid state leads to slight decreases of $^3J(^{31}P, ^1H)$ and to slight ^{31}P upfield shifts.[1,3,5,7] The magnitude of the coupling $^2J(^{31}P,^1H)$, which is about 7 Hz in **1**, goes through a minimum in **2** (<1 Hz) and is 2 Hz in the case of solutions of **5**. However, beyond these general features of the NMR spectra reflecting steady changes in average cation−anion interactions, solution NMR data do not allow a prediction of any of the solid state structures of **2**−**5**. The Raman spectrum of solid **5** showed resolved signals, one very strong and three strong, in the typical range of triiodide valence vibrations (97 s, 105 s, 113 vs, and 147 s (cm^{-1})), indicating the presence of different types of triiodide ions. The very strong Raman emission at 113 cm^{-1} could arise from a symmetric or only slightly asymmetric triiodide ion as in Et_4NI_3 (ν_s = 113 cm^{-1}).[8] The splitting between the lines at 97/105 and 147 cm^{-1} indicates strongly distorted triodide anions as in CsI_3 (ν_s = 96 and 105, ν_{as} = 132 and 150 cm^{-1}).[8]

Structures of Solids 2−**5.** Solid **2** is a helical chain polymer from (*i*-Pr)(*t*-Bu)PI_2^+ cations bridged by two-coordinated iodide anions (Figure 1). Both iodine atoms adjacent to phosphorus are nearly linearly coordinated (174.7 and 180°), whereas the angles at the bridging iodide anions are 119.2 and 123°. This geometry allows the I···I contacts (3.3525(12) and 3.3850(13)

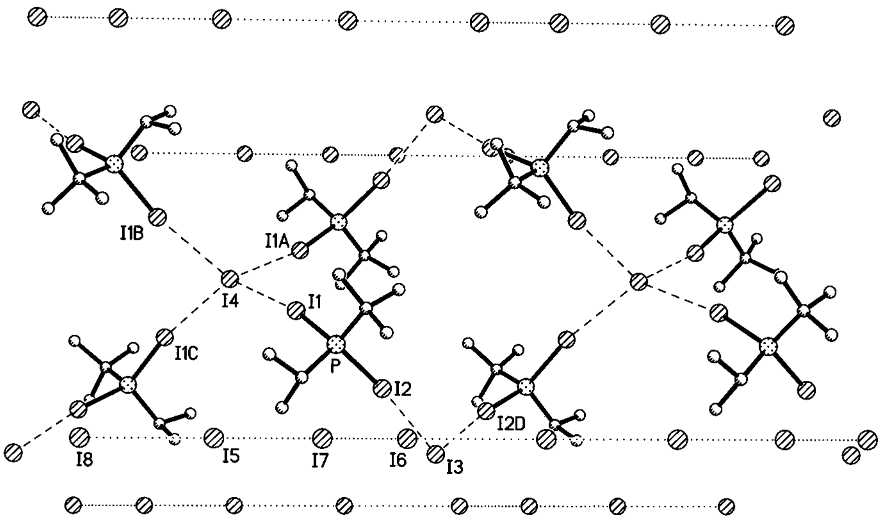

Figure 2. Columnar structure of **3**: view along the *a*-axis; hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): I1−P 2.415; I2−P 2.433; I1−I4 3.575; I2−I3 3.315; P−I1−I4 169.3; P−I2−I3 173.79; I2D−I3−I2 109.773; I1C−I4−I1 125.07; I1−I4−I1A 95.32; I1−I4−I1B 109.43; symmetry transformation of A: $1.5 - x, 0.5 - y, z$. B: $0.5 + y, -0.5 + x, 1.5 - z$. C: $1 - y, 1 - x, 1.5 - z$. D: $1 - y, 1 - x, 0.5 - z$.

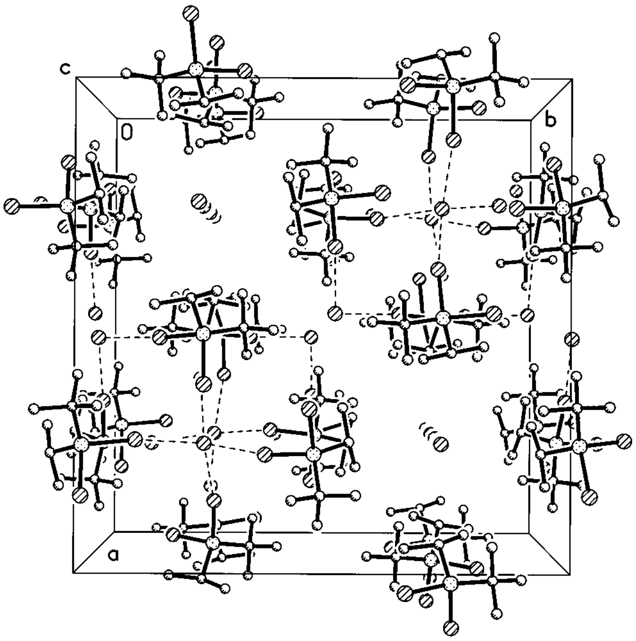

Figure 3. Columnar structure of **3**: view along the c-axis; hydrogen atoms omitted.

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. Due to the overlap of iodide (I3 and I4) lone pairs with σ^* orbitals of the P–I1 and P–I2 bonds, these cation–anion I···I interactions are associated with slight elongations of the P–I bonds (2.423(3) and 2.438(3) Å), compared with rather undisturbed iodophosphonium ions (2.40 ±0.01 Å).[9–12] The main difference between helical **2**, the zigzag chain of *t*-Bu_2PI_3 [3], and the dimeric structure of Ph_2PI_3 [4] is the interplanar angles of adjacent I–P–I units (**2**, 90°, the others, 0° or 180°).

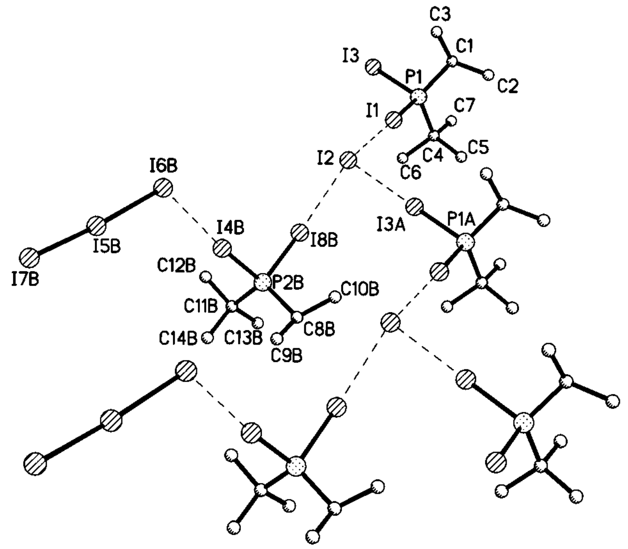

Figure 4. Chain structure of **4**: hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): I1–P1 2.416; I3–P1 2.424; I8–P2 2.425; I4–P2 2.412; I1–I2 3.427; I3A–I2 3.376; I8B–I2 3.371; I4–I6 3.452; I5–I7 2.836; I6–I5 3.017; P1–I1–I2 173.02; P2–I4–I6 173.94; I3A–I2–I1 107.91; I3A–I2–I8B 74.97; I1–I2–I8B 153.20; I7–I5–I6 175.67. Symmetry transformation of A: −1 + *x*, *y*, *z*. B: −0.5 + *x*, 1.5 − *y*, −*z*.

Table 4. Correlation of P–I and I–I Distances Concerning P–I···I⁻ Cation–Anion Interactions in **2**–**5**

		d(P–I), pm	CN of I⁻	*d*(I–I), pm
t-Bu(*i*-Pr)PI_3	**2**	243.8	2	335.3
		242.3	2	338.5
t-Bu(*i*-Pr)$PI_{3.2}$	**3**	241.5	4	357.5
		243.3	2	331.5
t-Bu(*i*-Pr)PI_4	**4**	241.6	3	342.7
		242.4	3	337.6
		242.5	3	337.1
		241.2	(I_3^- terminal)	345.2
t-Bu(*i*-Pr)$PI_{4.33}$	**5**	240.9	5	349.0 (basal)
		241.1	5	346.6 (basal)
		240.8	5	346.7 (basal)
		240.6	5	347.5 (basal)
		241.7	5	358.0 (apical)
		242.0	(I_3^- terminal)	344.1

Compound **3**, the byproduct of **2** upon crystallization from dichloromethane/pentane, has a completely different crystal structure. Unique among iodophosphonium salts, solid **3** exists in a tetragonal columnar structure which can be related to unidimensional mixed valence solids built up from staples of partially oxidized chelated d^8 metal cations and of staples containing disordered polyiodide counterions $I(I_2)_x^-$ (*x* generally between 1 and 2) (Figures 2 and 3).[13–15] Elemental analyses of solid **3** indicated a composition close to *t*-Bu(*i*-Pr)$PI_{3.2}$; for the refinement of its crystal structure the composition *t*-Bu(*i*-Pr)$PI_{3.25}$ was arbitrarily chosen. **3** can be described as [*t*-Bu(*i*-Pr)$PI_2]_4(\mu_2\text{-}I)_2(\mu_4\text{-}I)[I(I_2)_x]$ (*x* close to 0.5). Tetragonal cationic staples of the composition [*t*-Bu(*i*-Pr)$PI_2]_4(\mu_2\text{-}I)_2(\mu_4\text{-}I)^+$ are packed in such a way that isopropyl groups from *t*-Bu(*i*-Pr)-PI_2^+ cations of four different cationic staples surround linear channels filled with iodine anions of the overall composition I_2^- (I_4^{2-} corresponds to I^- and I_3^- in about a 1:1 ratio). The oxidation state of iodine within the staples appears to be determined by the necessary negative charge (1− per asymmetric unit of 7.2 Å), the space available, and the intrinsic tendency of triiodide formation from I^- and I_2. Like in known columnar structures with linear iodine chains (for instance Ni(dpg)$_2$I or amylose–polyiodide inclusion compounds containing iodine largely if not exclusively as I_5^-),[13,14] the polyiodide in the staples of **3** is highly disordered. The matrix formed from isopropyl groups surrounding the polyiodide channel of **3** is less rigid than the one given by tetramethylstibonium ions of $[Me_4Sb]_3[I_8]$, where the oxidation state ($I^{-0.375}$) and the unique equidistance of the iodine atoms within the chains are enforced by packing preferences (Me_4Sb···I interactions with exactly 50% of the iodine atoms) of solid $[Me_4Sb]_3[I_8]$.[15]

The cationic staples of **3** are built up from 16-membered rings that consist of four *t*-Bu(*i*-Pr)PI_2-I moieties with I3 as a bidentate-bridging donor and I1 and I2 as linear acceptors. This moiety of **3** appears like a kind of hypothetic tetrameric (*i*-Pr)(*t*-Bu)PI_3. These 16-membered rings [*t*-Bu(*i*-Pr)$PI_2]_4I_4$ are connected in a spiro fashion by sharing μ_4-iodide anions (I4); this sharing of μ_4-iodide anions leaves at the staple one positive

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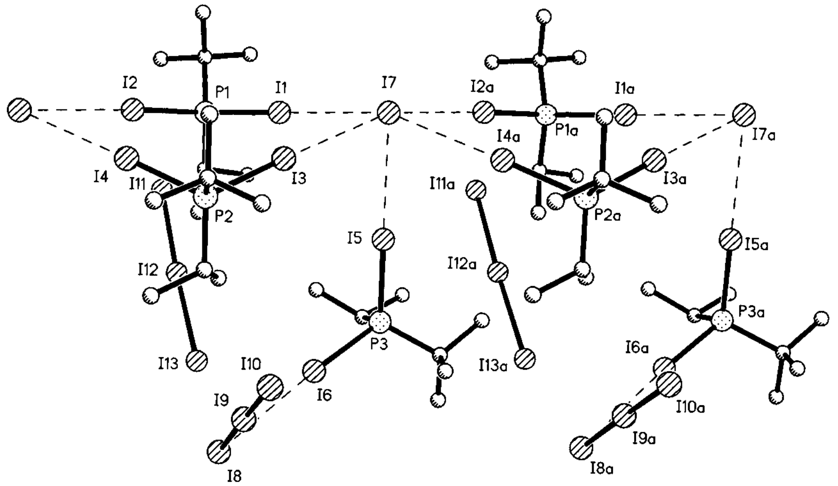

Figure 5. Cation−anion interactions in solid **5**: hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): I1−P1 2.409; I1−I7 3.490; I2−P1 2.408; I2a−I7 3.467; I5−P3 2.417; I5−I7 3.580; I6−P3 2.420; I6−I8 3.441; I8−I9 3.005; I9−I10 2.837; I11−I12 2.905; I12−I13 2.925; I1−I7−I5 78.34; I2a−I7−I5 80.05; I3−I7−I5 80.09; I3−I7−I1 70.28; I3−I7−I2a 160.13; I6−I8−I9 89.33; P1−I1−I7 176.79; P3−I5−I7 179.71. Symmetry transformation of A: *x*, *y*, −1 + *z*.

charge per [*t*-Bu(*i*-Pr)PI_2]$_4I_3$ moiety. I2···I3 contacts involving the μ_2-iodide anion within the 16-membered ring (3.315 Å) are significantly shorter than I1···I4 contacts of the μ_4-bridging iodide anion (3.571 Å). The shorter I2···I3 contacts coincide with the longer P−I2 bonds (2.433 Å) adjacent to μ_2-I; the quadruply bridging iodide anion has to distribute its donor ability to four P−I bonds which are “less disturbed” (P−I1 = 2.415 Å) (Table 4).

The backbone of the chain structure of crystalline **4** consists of −P−I−I−I− units from *tert*-butyl(isopropyl)diiodophosphonium ions and μ_3-donor iodide ions (P1A−I3A−I2−I1 in Figure 4), each of which is connected with one iodine atom of a further *side chain tert*-butyl(isopropyl)diiodophosphonium ion (involving phosphorus P2B in Figure 4). The other iodine atom of this side chain cation is coordinated by a terminal triiodide ion. Although **4** crystallizes in a chiral space group ($P2_12_12_1$), no chiral helices are formed. Thus, **4** consists of a zigzag main chain and chiral side chain phosphonium groups, whereas the related compound *i*-Pr_2PI_4 has achiral side chain phosphonium groups attached to a helical main chain. In each case, the close-range order (coordination geometry of I and P according to VSEPR expectations) is governed by overlap effects, whereas the long-range order (manifested as torsion angles, helical *vs* zigzag chain or cyclic structure) is determined by packing effects of the organic substituents.

5 contains three cations with altogether six acceptor iodine atoms per formula unit, but only one iodide anion. Surprisingly, in the solid, this iodide anion satisfies the acceptor needs of five of the six acceptor iodine atoms; only one of the six acceptor iodine atoms has an acceptor−donor contact to a donating triiodide anion! The structure of **5** consists of a double-chain backbone of μ_2-acceptor phosphonium ions (at P1, P2) and μ_5-bridging donor iodide ions (I7). Four I···I contacts of these μ_5-bridging donor iodide ions are within the double chain (I1−I7 3.490(2), I2a−I7 3.467(2), I3-I7 3.466(2), I4a-I7 3.475(2) Å), and the fifth is to a side chain *tert*-butyl(isopropyl)-diiodophosphonium ion (involving P3 in Figure 5, I5−I7 3.580(2) Å), which is also connected to a terminal triiodide anion (I8−I9−I10) by I···I interaction (I6-I8 3.441(2) Å). A further triiodide anion (I11−I12−I13) has no soft−soft interaction with the cationic network. This triiodide ion may be identified as the source of the strong Raman emission at 113 cm^{-1}.

In summary, secondary soft−soft interactions within the supramolecular chain helical and columnar structures of **2**−**5** based on the iodination of the “mixed” dialkyliodophosphane **1** follow essentially the geometrical preferences from covalent 3-center-4-electron bonding ($n \rightarrow \sigma^*$ overlap). However, the specific structures of **2**−**5**, depending largely on the specific substituents attached to phosphorus (like the isopropyl groups surrounding the linear iodine chains within the unique columnar structure of **3**), emphasize that future supramolecular archtitecture with soft−soft interactions will have to rely on both geometrical needs of heavy atom interactions and the packing preferences of neighboring organic substituents.

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Supporting Information Available: Four X-ray crystallographic files in CIF format. Access information is given on any current masthead page.

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