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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraphenylphosphonium Triiodide

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Abstract

The crystals of the title compound, $C_{24}H_{20}P^+.I_3^-$, are composed of slightly bent I_3^- anions and Ph_4P^+ cations separated by normal van der Waals distances; both ions lie on twofold axes. The I—I distances in the anion are 2.9180 (4) Å, with an I—I—I angle of 175.27 (3)°. In the cation, the P—C distances are identical [1.790 (4) Å] and the C—P—C angles are in the range 105.5 (3)–111.6 (2)°.

Comment

The alkylation of tetrathio tungstate ions is known to lead to a variety of polynuclear thio tungstates (Dhar & Chandrasekaran, 1989; Boorman, Wang & Parvez,

1995). During a study of the reaction between ethyl iodide and $(PPh_4)_2[WS_4]$, a red crystalline product was obtained from MeCN solution which had different spectroscopic properties from any known thio tungstate. Believing it to contain a new $[W_xS_y]^{n-}$ ion, we undertook an X-ray structural study. This product is shown here to be $PPh_4^+.I_3^-$, (I), which was formed as an unexpected by-product of this alkylation reaction.

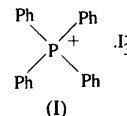


Fig. 1 shows the anion and the cation, together with the numbering scheme used. There are no short interactions of any significance between the anions and the cations. The I—I distances [2.9180 (4) Å] and I—I—I angle [175.27 (3)°] in the anion, which lies on a twofold axis, agree well with the corresponding distances and angles reported for $(C_2H_5)_4N^+.I_3^-$, form I [2.928 (3), 2.943 (3) Å and 180.0° in two anions in the asymmetric unit (Migchelsen & Vos, 1967)], and $(C_6H_5)_4As^+.I_3^-$ [2.920 (2) Å and 175.61 (5)° (Runsink, Swen-Walstra & Migchelsen, 1972)]. Several structures have been reported with unequal I—I distances in the anion, e.g. $(C_2H_5)_4N^+.I_3^-$, form II [2.981 (4), 2.892 (4) and 2.912 (4), 2.961 (4) Å in the two anions in the asymmetric unit (Migchelsen & Vos, 1967)], $(n-C_4H_9)_4N^+.I_3^-$ [2.887 (4), 2.951 (4) and 2.911 (4), 2.940 (4) Å (Herbstein, Kaftory, Kapon & Saenger, 1981)] and $(Ph_3P)_2N^+.I_3^-$ [2.896 (1) and 2.928 (1) Å (Tebbe & Krauss, 1990)]. The molecular dimensions in the cation, which also lies on a twofold axis, are as ex-

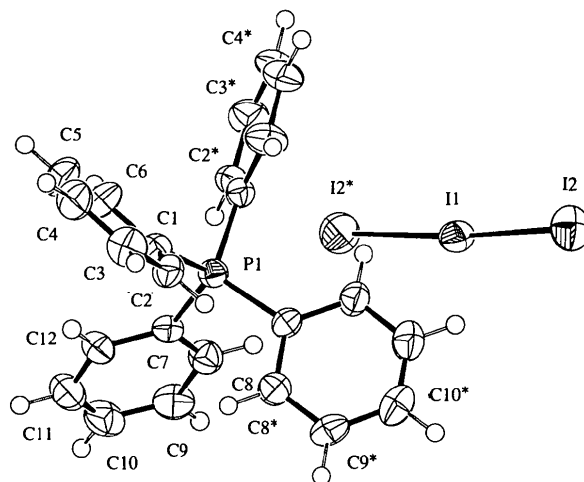


Fig. 1. An ORTEPII drawing (Johnson, 1976) of the title compound. The non-H atoms have been plotted as 50% probability displacement ellipsoids and H atoms have been assigned arbitrary radii. Starred atoms are symmetry generated.

pected, with identical P—C distances of 1.790 (4) Å, a mean C—C_{aromatic} distance of 1.381 (11) Å and C—P—C angles in the range 105.5 (3)–111.6 (2)°.

Experimental

Red prismatic crystals of the title compound were obtained from its solution in MeCN at room temperature.

Crystal data

C ₂₄ H ₂₀ P ⁺ .I ₃ ⁻	Mo Kα radiation
<i>M_r</i> = 720.11	λ = 0.71069 Å
Monoclinic	Cell parameters from 25 reflections
<i>P</i> 2/ <i>n</i>	θ = 15.0–24.0°
<i>a</i> = 10.332 (2) Å	μ = 3.909 mm ⁻¹
<i>b</i> = 7.690 (3) Å	<i>T</i> = 295 K
<i>c</i> = 15.406 (2) Å	Prismatic
β = 92.77 (1)°	0.30 × 0.25 × 0.20 mm
<i>V</i> = 1222.6 (4) Å ³	Red
<i>Z</i> = 2	
<i>D_x</i> = 1.956 Mg m ⁻³	

Data collection

Rigaku AFC-6S diffractometer	1329 observed reflections
ω/2θ scans	[<i>I</i> > 3σ(<i>I</i>)]
Absorption correction:	<i>R</i> _{int} = 0.0376
ψ scans of 3 reflections	θ _{max} = 25°
(North, Phillips & Mathews, 1968)	<i>h</i> = 0 → 12
<i>T</i> _{min} = 0.928, <i>T</i> _{max} = 0.999	<i>k</i> = -9 → 9
4968 measured reflections	<i>l</i> = -18 → 18
2354 independent reflections	3 standard reflections
	frequency: 120 min
	intensity decay: 0.20%

Refinement

Refinement on <i>F</i>	Δρ _{max} = 0.40 e Å ⁻³
<i>R</i> = 0.0230	Δρ _{min} = -0.42 e Å ⁻³
<i>wR</i> = 0.0220	Extinction correction:
<i>S</i> = 1.400	Zachariasen (1968)
1329 reflections	Gaussian isotropic
129 parameters	Extinction coefficient:
H atoms geometrically idealized (C—H 0.95 Å)	6.90735
<i>w</i> = 1/σ ² (<i>F</i> _o)	Atomic scattering factors
(Δ/σ) _{max} = 0.0180	from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
I1	1/4	0.15918 (6)	1/4	0.0476 (2)
I2	0.20103 (4)	0.17484 (6)	0.06203 (3)	0.0644 (1)
P1	1/4	0.0092 (2)	3/4	0.0321 (5)
C1	0.3844 (4)	0.1501 (6)	0.7334 (3)	0.034 (1)
C2	0.4590 (5)	0.1361 (6)	0.6613 (3)	0.040 (1)
C3	0.5554 (5)	0.2540 (7)	0.6476 (3)	0.053 (2)
C4	0.5792 (5)	0.3868 (7)	0.7056 (4)	0.059 (2)
C5	0.5069 (6)	0.4019 (7)	0.7786 (4)	0.061 (2)
C6	0.4097 (5)	0.2854 (6)	0.7931 (3)	0.052 (2)
C7	0.2823 (5)	-0.1309 (5)	0.8413 (3)	0.033 (1)

C8	0.1905 (5)	-0.2563 (6)	0.8596 (3)	0.045 (2)
C9	0.2125 (6)	-0.3717 (6)	0.9276 (3)	0.051 (2)
C10	0.3259 (6)	-0.3606 (7)	0.9782 (3)	0.056 (2)
C11	0.4172 (5)	-0.2386 (7)	0.9586 (4)	0.055 (2)
C12	0.3972 (5)	-0.1234 (6)	0.8917 (3)	0.042 (2)

Table 2. Selected geometric parameters (Å, °)

I1—I2	2.9180 (4)	P1—C7	1.790 (4)
P1—C1	1.790 (4)	I2—I1—I2 ⁱ	175.27 (3)
I2—I1—I2 ⁱ	175.27 (3)	P1—C1—C2	122.2 (4)
C1—P1—C1 ⁱⁱ	105.5 (3)	P1—C1—C6	118.4 (4)
C1—P1—C7	111.1 (2)	P1—C7—C8	118.2 (4)
C1—P1—C7 ⁱⁱ	111.6 (2)	P1—C7—C12	122.5 (4)
C7—P1—C7 ⁱⁱ	106.0 (3)		

Symmetry codes: (i) $\frac{1}{2} - x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, y, \frac{3}{2} - z$.

Based on the systematic absences (*h*0*l*: *h* + *l* = 2*n* + 1), packing considerations, a statistical analysis of intensity distribution and the successful solution and refinement of the structure, the space group was determined to be *P*2/*n*.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI91* (Fan, 1991) in *DIRDIF92* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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