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FULL PAPER

A new assembly of diiodine molecules at the triphenylphosphine sulfide template†

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The new I_2 adduct TPPS·3I_2 (TPPS = triphenylphosphine sulfide) has been synthesized and characterised by X-ray diffraction on a single crystal. It consists of a TPPS·I_2 1:1 molecular adduct interacting with two further diiodine molecules in a "head to tail" sequence to give an overall TPPS·$I_2 \cdots I_2 \cdots I_2$ arrangement in the asymmetric unit. Considering the I···I interactions below 3.6 Å, five of the six iodine atoms of the asymmetric unit are arranged in infinite polycyclic ribbons. The iodine atoms, to which the TPPS molecules are connected, are almost perpendicular appendages on opposite sides of each ribbon. Weaker interactions between the ribbons give rise to unprecedented continuous stepped layers of diiodine molecules anchored to TPPS donor units. The structural features of TPPS·3I_2 are discussed in comparison with those of the previously reported 2TPPS·3I_2, TPPS·I_2, TPPS·IBr and TPPS·ICl, and its FT-Raman spectrum compared with those of 2TPPS·3I_2 and TPPS·I_2. A re-examination of the equilibrium reaction between TPPS and I_2 by ^{31}P NMR confirms the formation of the 1:1 adduct in CH_2Cl_2 solution and gives a formation constant value of 137 ± 11 dm^3 mol^{-1}.

Introduction

Dihalogen charge-transfer complexes of tertiary phosphine chalcogenides R_3PE (R = alkyl or aryl; E = S or Se) were first reported by Zingaro and co-workers[1–5] who mainly used UV-visible and infrared spectroscopies to obtain information on the nature of $R_3PE·X_2$ 1:1 adducts ($X_2 = I_2$, IBr or ICl) both in solution (CCl_4) and in the solid state. The first reported crystallographic study concerned the compound of formula $2Ph_3PS·3I_2$ that was unexpectedly obtained from the stoichiometric reaction of triphenylphosphine sulfide (TPPS) with diiodine in CCl_4.[6] In this compound one diiodine molecule bridges two TPPS·I_2 1:1 adduct units *via* soft–soft I···I interactions of 3.570(1) Å to give a "Z"-shaped D·$I_2 \cdots I_2 \cdots I_2$·D arrangement (D = TPPS). Initially, it seemed that the power of TPPS as donor was not enough to stabilise a discrete 1:1 adduct. However, very recently Bricklebank and co-workers[7] reported the crystal structure of the 1:1 adduct TPPS·I_2, obtained by treating TPPS and I_2 in a 1:1 molar ratio in CH_2Cl_2.[8] At the same time, the 1:1 adducts TPPS·IBr and TPPS·ICl were structurally characterised by us,[9] clearly illustrating that triphenylphosphine sulfide can form 1:1 charge-transfer complexes with both I_2 and stronger acceptors such as ICl and IBr.

Diiodine is the halogen with the highest catenating ability, and the polyiodide anions which stem from the donor/acceptor interaction of I_3^- and/or I^- anions with I_2 molecules can assume a wide range of structural motifs.[10] Polyiodide cations such as I_4^{2+}, I_5^+ and I_{15}^{3+} have also been reported;[11] nevertheless, neutral extended poly(I_2) arrangements held up by soft–soft $I_2 \cdots I_2$ interactions are extremely rare, and the best example so far reported is the structure of solid I_2 itself.[12] This consists of an orthorhombic layer lattice: the I–I bond distance [2.715(6) Å] is longer than that in the gas phase [2.667(2) Å];[13] the inter-atomic I···I distances between two I_2 molecules are 3.497(6) and 3.972(7) Å within a layer (still less than the sum of the van der Waals radii for I_2 [4.2 Å][14]) and 4.269(6), 4.332(7) and 4.412(7) Å between layers; the angles between I_2 molecules within each layer have values very close to 90 and 180°. The $(I_2)_7$ chain observed in the compound bis(1,5-diphenylthiocarbazone) heptakis(diiodine) was described[15] on the basis of structural data, as a $D–I]^+ \cdots [I_5]^- \cdots I_2 \cdots [I_5]^- \cdots {}^+[I–D$ system, and not properly as a chain of neutral diiodine molecules. Several neutral I_2 adducts with a diiodine content higher than the 1:1 stoichiometry have been reported; normally, their crystal structures do not feature extended poly(I_2) networks, but only discrete D·$I_2 \cdots I_2$ or D·$I_2 \cdots I_2 \cdots I_2$·D arrangements (see for example the 1:2 adduct between *N*-methylbenzoxazole-2(*3H*)-selone[16] and I_2 or the above described 2TPPS·3I_2); rarely, as in *N*-methylbenzothiazole-2(3*H*)-selone–diiodine(1/2),[17] extended neutral networks of diiodine molecules can be observed.

Considering the ability of TPPS to give I_2 adducts with different stoichiometry on changing the reaction solvent, we argued that the same ligand could be used as a donor to stabilise extended neutral poly(I_2) networks when using a TPPS:I_2 molar ratio higher than 1:1. We report herein the first example of a genuine infinite three dimensional poly(I_2) assembly obtained by treating TPPS with an excess of I_2 in CH_2Cl_2 solution. The new adduct corresponding to the formulation TPPS·3I_2 has been characterised by single crystal X-ray diffraction, FT-IR and FT-Raman spectroscopic techniques.

Results and discussion

The reaction of triphenylphosphine sulfide with an excess of I_2 (1:3 molar ratio) in CH_2Cl_2 solution affords dark red crystals

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† *Supplementary data available*: FT-IR and FT Raman spectra. Available from BLDSC (No. SUP 57603, 3 pp.). See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

after slow evaporation of the solvent. An X-ray diffraction study shows that the crystals consist of a TPPS·I_2 1 : 1 molecular adduct interacting with two further diiodine molecules in a "head to tail" sequence (Fig. 1) to give an overall TPPS·$3I_2$ stoichiometry. The S-donor atom of the ligand binds the I(1)–I(2) diiodine molecule almost linearly [S–I(1) 2.591(1), I(1)–I(2) 2.982(1) Å, S–I(1)–I(2) 178.11(3)°] (Table 1), with a co-ordination geometry that is very similar to that of the related compounds, TPPS·I_2,[7] 2TPPS·$3I_2$,[6] TPPS·IBr[9] and TPPS·ICl.[9] Comparison of the structural features of the P–S–I–X (X = I, Br or Cl) moiety for all the structurally characterised charge-transfer adducts of TPPS with halogens and interhalogens (Table 2) shows that in all cases the P–S bond is lengthened with respect to the value found in pure TPPS [1.950(3)Å],[18] and that the new adduct TPPS·$3I_2$ has the shortest S–I bond. Even shorter S–I bonds have been observed only for some adducts of ethylenethiourea and 1,5-diphenylthiocarbazone with I_2.[15a] However, the S–I and I–I bond distances found in TPPS·$3I_2$ fall in the *d*(S–I) *versus* *d*(I–I) correlation reported for the adducts of sulfur containing donors and diiodine.[19]

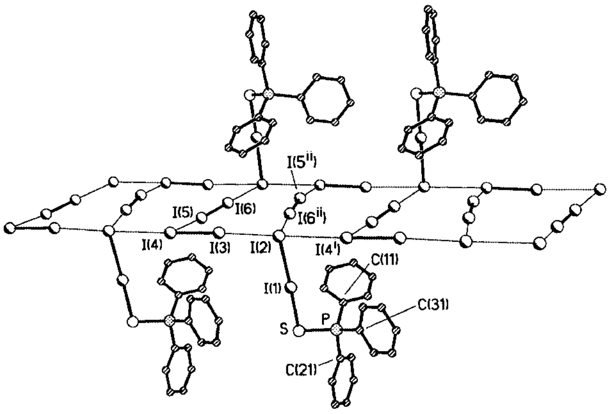

Fig. 1 Partial view of the ribbon of iodine atoms with the TPPS appendages.

Table 1 Selected interatomic distances (Å) and angles (°) in TPPS·$3I_2$

I(1)–I(2)	2.982(1)	I(3)–I(4)	2.744(1)
I(2)–I(3)	3.373(1)	I(4)–I(5)	3.582(1)
I(2)–I(4^{i})	3.561(1)	I(5)–I(6)	2.710(1)
I(2)–I(6^{ii})	3.503(1)	I(2) · · · I(2^{iii})	4.104(1)
I(3) · · · I(4^{iv})	4.169(1)	I(4) · · · I(4^{iv})	4.158(1)
I(1)–S	2.591(1)	S–P	2.030(2)
P–C(11)	1.797(5)	P–C(21)	1.805(5)
P–C(31)	1.795(4)		
I(2)–I(1)–S	178.11(3)	I(1)–S–P	105.47(6)
S–P–C(11)	112.9(2)	S–P–C(21)	104.0(2)
S–P–C(31)	113.1(2)	C(11)–P–C(21)	110.6(2)
C(11)–P–C(31)	107.4(2)	C(21)–P–C(31)	108.7(2)
I(1)–I(2)–I(3)	93.02(2)	I(2)–I(3)–I(4)	175.35(2)
I(3)–I(4)–I(5)	86.06(2)	I(4)–I(5)–I(6)	171.24(3)
I(1)–I(2)–I(6^{ii})	82.75(2)	I(3)–I(2)–I(4^{i})	175.78(2)
I(2)–I(6^{ii})–I(5^{ii})	177.27(3)		

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

It is interesting to point out the decrease and increase of the S–I and I–I bond distances respectively on passing from TPPS·I_2 to 2TPPS·$3I_2$ and TPPS·$3I_2$. Since the donor molecule is the same in the three compounds, the changes in such lengths in 2TPPS·$3I_2$ and TPPS·$3I_2$ should originate from the additional short contacts of the terminal iodine atom of the TPPS co-ordinated diiodine molecule with further iodine atoms. While in TPPS·I_2 the adduct units are discrete and are held together by normal van der Waals contacts, in 2TPPS·$3I_2$ two TPPS·I_2 units act as donors towards a bridging diiodine molecule that acts as an acceptor to give a TPPS·$I_2 \cdots I_2 \cdots I_2$·TPPS "Z"-shaped system [$I_2 \cdots I_2$ 3.57(2) Å]. In a different way, in TPPS·$3I_2$, the TPPS·I_2 unit interacts with a second diiodine molecule [I(3)–I(4), $I_2 \cdots I_2$ 3.373(1) Å], which in turn behaves as a donor towards a third diiodine molecule through the I(4) iodine atom [I(5)–I(6), $I_2 \cdots I_2$ 3.582(1) Å] to give an overall TPPS·$I_2 \cdots I_2 \cdots I_2$ system (Fig. 1). Therefore, a similar $(I_2)_3$ chain is present in 2TPPS·$3I_2$ and TPPS·$3I_2$; however, in 2TPPS·$3I_2$ both terminal diiodine molecules of the $I_2 \cdots I_2 \cdots I_2$ arrangement act as donors towards the central I_2, whereas in TPPS·$3I_2$ the terminal diiodine molecule I(5)–I(6) behaves as an acceptor. In other words, we can schematically represent the $(I_2)_3$ chain in 2TPPS·$3I_2$ and TPPS·$3I_2$ as TPPS·$I_2 \cdots I_2 \cdots D'$ and TPPS·$I_2 \cdots I_2 \cdots A$ respectively (D′ = TPPS·I_2 as donor, A = I_2 as acceptor). Clearly, in TPPS·$3I_2$ the partial negative charge induced on I(2) upon interaction of the I(1)–I(2) molecule with TPPS will be more effectively delocalised by the additional rather strong I(2) · · · I_2 bonding interactions, with consequent lengthening and shortening of the I(1)–I(2) and S–I(1) bonds respectively. These interactions are at the basis of the crystal packing in TPPS·$3I_2$.

In this new compound, if I · · · I interactions below 3.6 Å are considered, the iodine atoms I(2), I(3), I(4), I(5) and I(6) and their equivalents are arranged to form infinite polycyclic ribbons running along [010] and made up of 9-membered rings sharing eight iodine atoms. Iodine atoms I(1) are almost perpendicular appendages on opposite sides of each ribbon, to which the TPPS molecules are connected (Fig. 1). Weaker interactions between the ribbons (still below the value of the sum of the van der Waals radii for I_2), in the 4.104(1)–4.169(1) Å range (Table 1), give rise to unprecedented continuous stepped layers of diiodine molecules anchored to TPPS donor units (Fig. 2). Each of the I_2 molecules in the asymmetric unit displays a different environment. The I(1)–I(2) molecule, which interacts strongly with the TPPS ligand, is the most perturbed, and accordingly displays the largest I–I distance. Three other I_2 molecules within the ribbon interact at almost 90° with the I(1)–I(2) molecule *via* the I(2) iodine atom [I(2)–I(3) 3.373(1),

Table 2 Structural features of the P–S–I–X (X = I, Br or Cl) framework in all the structurally characterised adducts of triphenylphosphine sulfide with I–X

	X = I			X = Br	X = Cl
	TPPS·I_2[7]	2TPPS·$3I_2$[6]	TPPS·$3I_2$	TPPS·IBr[9]	TPPS·ICl[9]
P–S[a]	1.998(2)	2.007(3)	2.030(2)	2.014(1)	2.014(1)
S–I(1)	2.753(2)	2.729(2)	2.591(1)	2.665(1)	2.641(1)
I(1)–X	2.823(1)	2.838(1)	2.9818(5)	2.668(1)	2.586(1)
S–I(1)–X	175.51(3)	175.23(5)	178.11(3)	175.08(2)	174.86(3)
P–S–I(1)	108.78(7)	107.0(1)	105.47(6)	107.98(3)	108.29(5)

[a] The P=S bond distance found in pure TPPS is 1.950(3) Å.[18]

I(2)–I(4^{i}) 3.561(1), I(2)–I(6^{ii}) 3.503(1) Å, i x, $1 + y$, z; ii $-x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$]. This further contributes to the lengthening of the I(1)–I(2) bond. The I(2)–I(3) molecule is also engaged in a weaker inter-ribbon interaction with its symmetry equivalent [I(2)···I(2^{iii}) 4.104(1) Å, iii $-x$, $-y$, $2 - z$]. The I(3)–I(4) molecule has six interactions with the surrounding iodine atoms in the 3.373(1)–4.169(1) Å range (Table 1) and lengthens to 2.744(1) Å. Finally the I(5)–I(6) molecule, which only has two short interactions [3.503(1) and 3.582(1) Å (Table 1)], is almost unperturbed and displays an I–I bond length [2.710(1) Å] very close to that observed in the pure solid I_2 [2.715 Å].[12] The TPPS molecules, located between the poly(I_2) layers, are arranged as centrosymmetric pairs (Fig. 3); each has a phenyl ring parallel to the corresponding one of the symmetry-related molecule with a distance between the phenyl planes of about 3.83 Å, typical of a “graphite-like” stacking.

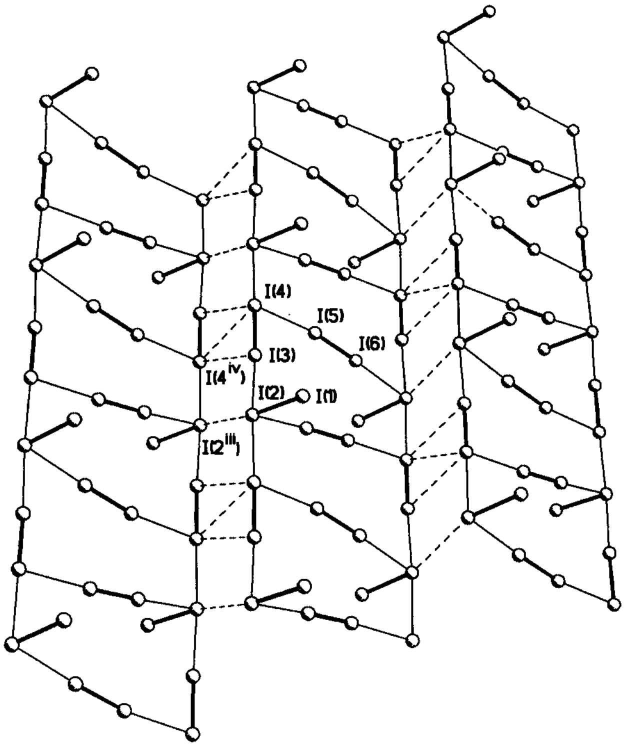

Fig. 2 Perspective view of a stepped layer of iodine atoms. Darker I–I bonds correspond to distances shorter than 3.0 Å. Thin lines correspond to I–I bonds within the 3.0–3.6 Å range. The remaining I···I interactions, shown as dashed lines, are shorter than 4.2 Å.

In the past, we classified 1 : 1 I_2 adducts in three classes[19] according to the value of the I–I bond order (n)[20] defined by the equation $d(\text{I–I}) = d_0 - c \log n$ [d_0 (2.67 Å) is the I–I bond distance for I_2 in the gas phase, c an empirical constant with a value of 0.85]: (1) weak or medium-weak [I–I bond order $n > 0.6$]; (2) strong [I–I bond order $0.4 > n > 0.6$]; (3) very strong [I–I bond order $n < 0.4$]. Weak or medium-weak I_2 adducts are characterised by the presence of only one Raman peak in the ν(I–I) stretching region, whose frequency depends on the I–I bond elongation; this is clearly pointed out by the linear correlation observed between the measured ν(I–I) Raman frequencies and d(I–I) bond distances, with ν(I–I) moving towards lower values compared to the stretching frequency reported for pure I_2 (180 cm^{-1}).[19] For strong adducts, two symmetric (ν_1) and antisymmetric (ν_3) stretching vibrations should be expected in the FT-Raman spectra for the E–I–I (E = donor atom) three-body system, whereas the spectra of very strong adducts should be characterised by the stretching vibration of the $[(\text{D})\text{E–I}]^+$ system.

For TPPS·3I_2 only two peaks at 173 and 140 cm^{-1} have been observed in the FT-Raman spectrum (SUP 57603) at exactly the same frequencies as the peaks found for 2TPPS·3I_2 [172.5 and 140 cm^{-1}],[9] despite their different structural features. For 2TPPS·3I_2 the two peaks were respectively assigned to the bridging I_2 molecule [I–I 2.757(2) Å; $n = 0.79$] and to the S-bonded diiodine molecules [I–I 2.838(1) Å; $n = 0.63$].[9]

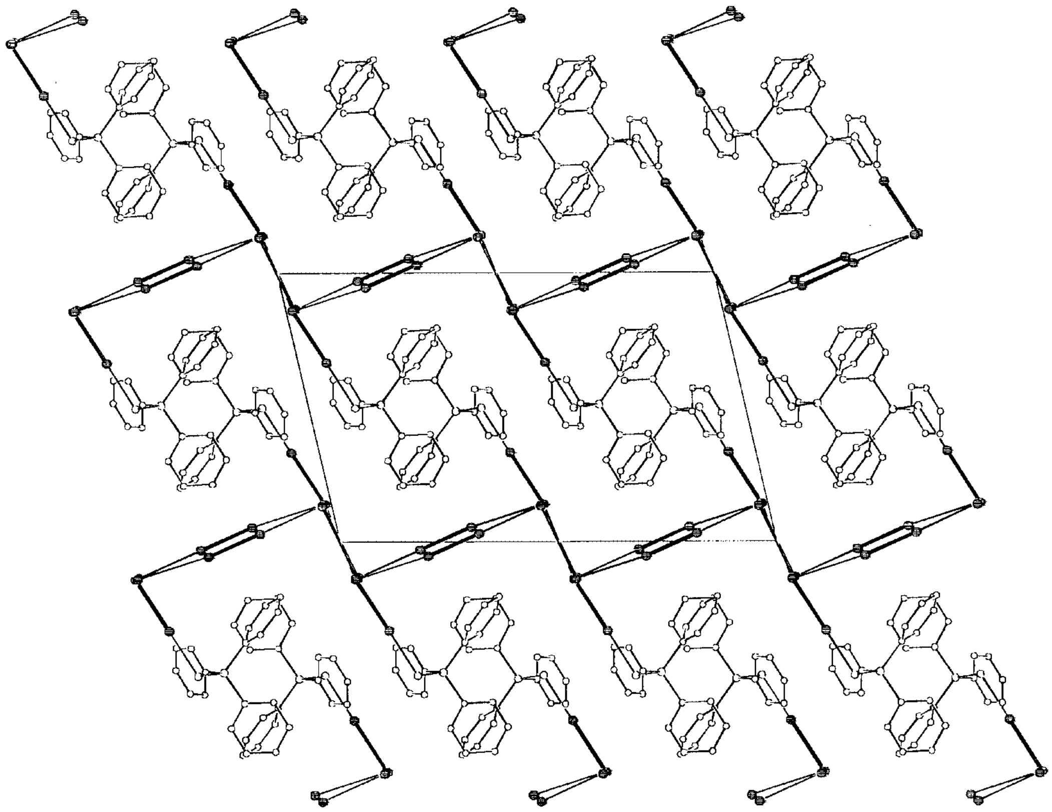

Fig. 3 Crystal packing of TPPS·3I_2 seen along [010].

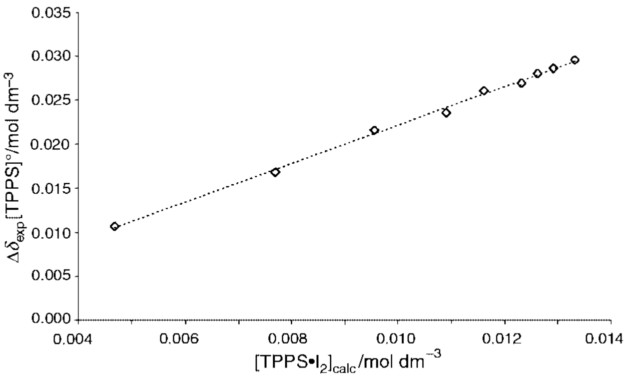

Fig. 4 Linear correlation between $\Delta\delta_{exp}$[TPPS]° *vs.* [TPPS·I$_2$]$_{calc}$. Correlation coefficient = 0.997; [TPPS]° = analytical concentration of TPPS. The ^{31}P NMR chemical shift of the adduct $\delta_{TPPS\cdot I_2}$ calculated from the slope is 40.68.

In TPPS·3I$_2$ the structural features show that the S-bonded diiodine molecule is very elongated [I–I 2.982(1) Å; $n = 0.43$]; consequently, the TPPS·I$_2$ moiety can be considered as an adduct falling on the borderline between the two classes of strong and very strong adducts. The band at 173 cm^{-1} falls fairly well in the above mentioned correlation of *d*(I–I) *versus* *ν*(I–I) considering both the bond distances found in I(3)–I(4) and I(5)–I(6) molecules. The other peak at 140 cm^{-1} should be tentatively assigned to the P–S–I system. The FT-IR spectrum confirms these assignments, since no bands are present around 173 cm^{-1}, while the most intense absorption falls at 141 cm^{-1}. We have synthesized the 1 : 1 adduct TPPS·I$_2$, recently characterised by X-ray diffraction by Bricklebank and co-workers;[7] its Raman spectrum shows a very strong peak, which dominates the whole spectrum, whose frequency at 145 cm^{-1} correlates very well with the elongation of the co-ordinated diiodine [I–I 2.823(1) Å].

Since contradictory results[3,21,22] have been reported on the TPPS·I$_2$ 1 : 1 adduct formation constant in solution, we re-examined the equilibrium reaction using the ^{31}P NMR chemical shifts of several CH$_2$Cl$_2$ solutions containing the same concentration of TPPS and increasing amounts of diiodine (see Experimental section). The linearity of the plot of $\Delta\delta$[TPPS]° *vs.* [TPPS·I$_2$]$_{calc}$ (see Fig. 4) confirms formation of only the 1 : 1 molecular adduct in solution.[23,24] The formation constant has been calculated by the non-linear least-squares program KEPS 11, as previously described.[23,24] The calculated *K* value of 137 ± 11 dm^3 mol^{-1} (21 °C, CH$_2$Cl$_2$) is very different from that reported in ref. 22 but it is close to the values reported by Tefteller and Zingaro[3] (106 dm^3 mol^{-1}; 25 °C, CHCl$_3$) and Sobczyk and co-workers[21] (160 dm^3 mol^{-1}; 25 °C, CCl$_4$).

Conclusion

An iodine-rich novel compound TPPS·3I$_2$, obtained by treating triphenylphosphine sulfide with diiodine, has been synthesized and characterised by X-ray single crystal diffraction. In TPPS·3I$_2$ the donor molecule is able to template a unique three-dimensional arrangement of diiodine molecules. This structure represents a very good example of the high catenating ability of diiodine in a very wide range of structural motifs.

Another very important point is related to FT-Raman spectroscopy. The compounds 2TPPS·3I$_2$ and TPPS·3I$_2$ represent a case in which characterisation by FT-Raman spectroscopy alone could lead to erroneous conclusions on their structures, since both compounds have identical spectra but different structural features. This shows that crystal stucture determination is indispensable to elucidate the nature of this kind of compound.

Experimental

Triphenylphosphine sulfide and CH$_2$Cl$_2$ were used as purchased from Aldrich; TPPS·I$_2$ was synthesized according to the literature.[7]

Synthesis of TTPS·3I$_2$

A solution of triphenylphosphine sulfide (100 mg, 0.34 mmol) and diiodine (258.8 mg, 1.02 mmol) in CH$_2$Cl$_2$ (50 cm^3) was stirred at room temperature for 2 h. Subsequently *n*-hexane (50 cm^3) was added and the resulting mixture was stored at 5 °C. Brown-red crystals were formed in a few days. Found (Calc. for C$_{18}$H$_{15}$I$_6$PS): C, 20.48 (20.33); H, 1.43(1.50); S, 3.04(2.98)%. FT-IR spectrum (300–50 cm^{-1}): 270m, 257m, 249m, 201ms, 193ms, 141s(br), 91w. FT-Raman spectrum (300–50 cm^{-1}; intensity of peaks related to the strongest taken equal to 10, in parentheses): 173 (10) and 140 (2.6).

Spectroscopic measurements

The FT-IR spectra (300–50 cm^{-1}, resolution 2 cm^{-1}) as polyethylene pellets were recorded on a Bruker IFS 66 spectrometer, FT-Raman spectra on pure powders (300–50 cm^{-1}, resolution 2 cm^{-1}; excitation frequency 1064 nm; Nd : YAG laser; power 100 mW) on a Bruker RFS 100 FTR spectrometer and ^{31}P NMR spectra in solution on a Varian VXR 300 FT-NMR spectrometer, operating at 120 MHz and using 85% H$_3$PO$_4$ (aq) as an external reference.

Solution studies

The redetermination of the formation constant of the 1 : 1 adduct between TTPS and diiodine was carried out in CH$_2$Cl$_2$ by measuring the ^{31}P NMR signals for ten different solutions of TTPS (0.015 mol dm^{-3}) with increasing amounts of diiodine ([I$_2$]/[TTPS] ranging between 0 and 5). The procedures for testing the presence of the 1 : 1 adduct in solution and for determining its formation constant have been described previously.[23]

Crystal structure determination

Crystal data for TTPS·3I$_2$. C$_{18}$H$_{15}$I$_6$PS, $M = 1055.78$, monoclinic, space group $P2_1/c$ (no. 14), $a = 13.335(6)$, $b = 9.672(3)$, $c = 21.022(5)$ Å, $\beta = 102.87(3)$°, $U = 2643(2)$ Å^3, $T = 293$ K, $Z = 4$, μ(Mo-Kα) = 71.2 cm^{-1}, 4745 reflections measured, 4632 unique ($R_{int} = 0.013$).

Intensity data were collected at room temperature with an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo-Kα radiation. Lorentz-polarisation and an empirical absorption[25] correction were applied to the data. The structure was solved by direct methods[26] and refined by full-matrix least squares with anisotropic parameters for all non-hydrogen atoms. The final *R* and *R′* indices were 0.036 and 0.049. All H atoms were seen in Fourier difference maps but placed at calculated positions and not refined. Sources of neutral atomic scattering factors for all atoms are given in ref. 27; the values of δf and $\delta f'$ were those of ref. 28. All calculations were performed using the Personal SDP software.[29]

CCDC reference number 186/1552.

See http://www.rsc.org/suppdata/dt/1999/3069/ for crystallographic files in .cif format.

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References

1 R. A. Zingaro and E. A. Meyers, *Inorg. Chem.*, 1962, **1**, 771.

2 R. A. Zingaro, R. E. McGlothlin and E. A. Meyers, *J. Phys. Chem.*, 1962, **66**, 2579.

3 W. Tefteller, Jr. and R. A. Zingaro, *Inorg. Chem.*, 1966, **5**, 2151.

4 R. A. Zingaro and R. M. Hedges, *J. Phys. Chem.*, 1961, **65**, 1132.

5 R. A. Zingaro, *Inorg. Chem.*, 1963, **2**, 192.

6 W. W. Schweikert and E. A. Meyers, *J. Phys. Chem.*, 1968, **72**, 1561; J. W. Bransford and E. A. Meyers, *Cryst. Struct. Commun.*, 1978, **7**, 697.

7 D. C. Apperley, N. Bricklebank, S. L. Burns and D. E. Hibbs, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 1289.

8 The results obtained by Bricklebank and co-workers[7] are a clear example of how important the solvent can be in determining the nature of the final products in this type of reaction. Some other examples have been reported by us: F. Demartin, F. A. Devillanova, F. Isaia, V. Lippolis and G. Verani, *Inorg. Chim. Acta*, 1997, **255**, 203 and refs. therein; F. Bigoli, P. Deplano, M. L. Mercuri, M. A. Pellinghelli and E. F. Trogu, *J. Chem. Res.*, 1993, (*S*) 90.

9 M. Arca, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis and G. Verani, *Z. Anorg. Allg. Chem.*, 1998, **624**, 745.

10 A. J. Blake, F. A. Devillanova, R. O. Gould, W.-S. Li, V. Lippolis, S. Parsons, C. Radek and M. Schröder, *Chem. Soc. Rev.*, 1998, **27**, 195.

11 R. Faggiani, R. J. Gillespie, R. Kapoor, C. J. L. Lock and J. E. Vekris, *Inorg. Chem.*, 1988, **27**, 4350.

12 F. van Bolhuis, P. B. Koster and T. Migehelsen, *Acta Crystallogr.*, 1967, **23**, 90.

13 I. L. Karle, *J. Chem. Phys.*, 1955, **23**, 1739.

14 S. C. Nyburg and C. H. Faerman, *Acta Crystallogr.*, *Sect. B*, 1985, **41**, 274.

15 F. H. Herbstein and W. Schwotzer, (*a*) *J. Am. Chem. Soc.*, 1984, **106**, 2367; (*b*) *Angew. Chem.*, *Int. Ed. Engl.*, 1982, **21**, 219.

16 F. Cristiani, F. A. Devillanova, F. Isaia, V. Lippolis, G. Verani and F. Demartin, *Polyhedron*, 1995, **14**, 2937.

17 F. Cristiani, F. Demartin, F. A. Devillanova, F. Isaia, V. Lippolis and G. Verani, *Inorg. Chem.*, 1994, **33**, 6315.

18 P. W. Codding and K. A. Kerr, *Acta Crystallogr.*, *Sect. B*, 1978, **34**, 3785.

19 M. C. Aragoni, M. Arca, F. Demartin, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis and G. Verani, *Research Trends*, 1999, in the press and refs. therein.

20 L. Pauling, *The Nature of the Chemical Bond*, 3rd edn., Cornell University Press, Ithaca, NY, 1960.

21 F. Lux, R. Paetzold, J. Danel and L. Sobczyk, *J. Chem. Soc.*, *Faraday Trans. 2*, 1975, 1610.

22 S. Kaur and T. S. Lobana, *J. Indian Chem. Soc.*, 1983, **60**, 126.

23 M. Arca, F. Cristiani, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis, G. Verani and F. Demartin, *Polyhedron*, 1997, **16**, 1983.

24 G. Carta, G. Crisponi and A. Lai, *J. Magn. Reson.*, 1982, **48**, 341.

25 A. C. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr.*, *Sect. A*, 1968, **24**, 351.

26 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. N. Wolfson, MULTAN 80, Universities of York and Louvain, 1980.

27 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. IV, Table 2.2B.

28 D. T. Cromer, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. IV, Table 2.3.1.

29 B. Frenz, *Comput. Phys.*, 1988, **2**, No. 3 (May/June), 42–8; B. Frenz, *Crystallographic Computing 5*, Oxford University Press, 1991, ch. 11, pp. 126–135.

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