

The reaction of tertiary aryl phosphites with diiodine at ambient temperatures; structural characterisation of the tertiary phosphite tetraiodides (PhO)₃PI₄, (4-MeC₆H₄O)₃PI₄ and (2,4-Bu^t₂C₆H₃O)₃PI₄

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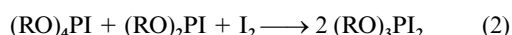
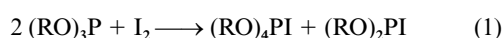
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The reaction of the tertiary phosphites (RO)₃P (R = Ph, 4-MeC₆H₄, 4-Bu^tC₆H₄, 2,4-Bu^t₂C₆H₃, 2,6-Me₂C₆H₃, 2,4,6-Me₃C₆H₂ or 2-PhC₆H₄) with one and two mole equivalents of diiodine has been investigated. In all cases the tetraiodide compounds (RO)₃PI₄ were isolated regardless of the stoichiometry employed. The three compounds (RO)₃PI₄ (R = Ph, 4-MeC₆H₄ or 2,4-Bu^t₂C₆H₃) have been crystallographically characterised for comparative purposes and represent the first examples of crystal structures for compounds of this formula. The structural characterisation of these compounds illustrates the structural dependence of (RO)₃PI₄ compounds on R. For (RO)₃PI₄ (R = Ph or 2,4-Bu^t₂C₆H₃) the compounds exist as discrete molecular species whereas, for R = 4-MeC₆H₄ the triiodide fragments of discrete molecules link *via* long-range I–I interactions to form a dimer. Additionally, *d*(I–I) for the (RO)₃PI and I₃ fragments is sensitive to R, being 3.227(1) Å for (2,4-Bu^t₂C₆H₃O)₃PI₄ and 3.3888(7) Å for (PhO)₃PI₄. In contrast to the analogous R₃PI₄ compounds, which show great variation in δ in their ³¹P-¹H NMR spectra depending on R, the (RO)₃PI₄ compounds described all exhibit quite similar δ values irrespective of R.

Introduction

The reaction of tertiary phosphites with diiodine has received only very limited attention; indeed, there have been no literature citations for the past forty years. In 1956 Rydon and Tonge¹ reported the formation of two triaryl phosphite diiodides, (ArO)₃PI₂, which were used as iodination compounds for alcohols. From conductimetric titrations the reaction of these triaryl phosphites with diiodine in light petroleum (bp 60–80 °C) at RT appeared to proceed *via* two steps, eqns. (1) and (2) (where



R = Ph or 2,6-Me₂C₆H₃). The same workers also investigated the reaction of triphenyl phosphite with diiodine at elevated temperatures (60 °C).¹ At this temperature, reaction (3) was



postulated to occur, *i.e.* ‘free’ triphenyl phosphite and the tetraiodide [(PhO)₃PI]₃ were produced; the latter was assigned an ionic structure. The existence of this tetraiodide had previously been reported by Forsman and Lipkin² in 1953 along with the enneaiodide, (PhO)₃PI₉. Both species were assumed to contain identical cations, [(PhO)₃PI]⁺, with the tetraiodide containing a triiodide anion and (PhO)₃PI₉ containing equal quantities of heptaoidide and enneaiodide anions, I₇[−] and I₉[−].

We have reported the reaction of tertiary phosphines with diiodine and have found that, in the case of the 1:1 reaction, the CT complexes R₃PI–I result.³ The *d*(I–I) for such complexes is dependent on R; for example, *d*(I–I) for Ph₃PI₂ is 3.142(2) Å whereas for PhMe₂PI₂ *d*(I–I) is 3.409(2) Å. The reaction of tertiary phosphines with two mole equivalents of diiodine has

also been investigated, being first reported by Gridunova *et al.*⁴ These workers described the structure of R₃PI₄ (R = ferrocenyl) and found a weak cation–anion interaction between the iodine atom of the cation and an iodine atom of the triiodide anion [3.736(1) Å]. In 1987, Cotton and Kibala⁵ described the products obtained from the reaction of two mole equivalents of diiodine with triphenylphosphine and crystallographically characterised two products. The first, [(Ph₃PI)₂I]₃, reveals parallel zigzag chains of [(Ph₃PI)₂I]⁺ cations sandwiched between layers of I₃[−] anions. The second, [Ph₃PI]₃, reveals a strong interaction between the [Ph₃PI]⁺ cation and the triiodide anion [*d*(I–I) = 3.551(1) Å]. The triiodide anions further link into a polymeric ribbon *via* weak I–I interactions [*d*(I–I) = 3.741(1) Å]. Very recently, we have reported⁶ two further crystallographically characterised compounds of formula R₃PI₄, Pr¹₃PI₄ and (PrⁿN)₃PI₄, and have found that these display subtly different structural arrangements compared to those of the R₃PI₄ compounds described previously: Pr¹₃PI₄ exists as a single [Pr¹₃PI]⁺ cation interacting with both the terminal iodine atoms of an I₃[−] anion to produce the cation [(Pr¹₃PI)₂I]⁺, the charge being balanced by a discrete I₃[−] anion; in contrast, (PrⁿN)₃PI₄ is essentially ionic, [(PrⁿN)₃PI]₃.

In view of the structural diversity exhibited by tertiary phosphine di- and tetra-iodide compounds and the fact that there is a paucity of data concerning the analogous tertiary phosphite di- and tetra-iodide compounds, we decided to undertake a comprehensive study of the reaction of a variety of tertiary phosphites with one and two mole equivalents of diiodine. The aim of the present study was therefore to synthesise and characterise structurally new and existing triaryl phosphite di- and tetra-iodide compounds and to investigate whether the compounds formed are R group dependent. Such a study will enable a comparison to be drawn between the products formed from the reaction of diiodine with triaryl phosphites and their tertiary phosphine analogues.

Table 1 Analytical and spectroscopic data for the compounds (RO)₃PI₄ (R = Ph, 4-MeC₆H₄, 4-Bu^tC₆H₄, 2,4-Bu^t₂C₆H₃, 2,6-Me₂C₆H₃, 2,4,6-Me₃C₆H₂ or 2-PhC₆H₄)

Compound	Colour	mp/°C	Found (% Calc.) ^a			³¹ P-{ ¹ H} NMR, δ ^b
			C	H	I	
(PhO) ₃ PI ₄	Red/brown	79(1)	26.4 (26.5)	1.8 (1.9)	62.1 (62.2)	−4.8
(4-MeC ₆ H ₄ O) ₃ PI ₄	Brown	86(1)	29.3 (29.2)	2.5 (2.5)	59.4 (59.0)	−4.4
(4-Bu ^t C ₆ H ₄ O) ₃ PI ₄	Dark red	89(1)	36.5 (34.8)	4.0 (3.6)	51.5 (52.7)	−4.0
(2,4-Bu ^t ₂ C ₆ H ₃ O) ₃ PI ₄	Brown	76(1)	43.6 (44.3)	5.5 (5.5)	43.9 (42.1)	−9.2
(2,6-Me ₂ C ₆ H ₃ O) ₃ PI ₄	Red/brown	93(1)	32.0 (33.5)	3.0 (3.0)	56.3 (55.4)	1.8
(2,4,6-Me ₃ C ₆ H ₂ O) ₃ PI ₄	Red/brown	117(1)	34.3 (33.0)	3.5 (3.2)	53.8 (54.9)	3.0
(2-PhC ₆ H ₄ O) ₃ PI ₄	Dark red	98(1)	41.3 (39.5)	2.6 (2.4)	48.5 (48.2)	−5.4

^a For some of the compounds the values are a little out with respect to the theoretical values due to the extreme moisture sensitivity, which meant that perfect analyses were difficult to obtain despite numerous attempts. ^b All shifts recorded in CDCl₃ solution relative to concentrated phosphoric acid as standard.

Results and discussion

All attempts to synthesize tertiary phosphite diiodine compounds, (RO)₃PI₂, in diethyl ether solution at RT were unsuccessful; equimolar quantities of the tetraiodide, (RO)₃PI₄, and free tertiary phosphite being observed in each case, eqn. (4)



(R = Ph, 4-MeC₆H₄, 4-Bu^tC₆H₄, 2,4-Bu^t₂C₆H₃, 2,6-Me₂C₆H₃, 2,4,6-Me₃C₆H₂ or 2-PhC₆H₄).

Analytical data of the dark red solids produced from each reaction indicated the formation of the tetraiodides, (RO)₃PI₄. The existence of free triaryl phosphite was confirmed using ³¹P-{¹H} NMR spectroscopy. These observations would appear to mirror the results of Rydon and Tonge at 60 °C.¹ However, in contrast to Rydon's observation at RT (*i.e.* the proposed formation of a diiodide (RO)₃PI₂), in our hands no evidence for the formation of a diiodide (RO)₃PI₂ was noted in any of the reactions performed during this study. The same reactions were also performed in a 2:1 diiodine : triaryl phosphite stoichiometric ratio. As expected, the same tertiary phosphite tetraiodide compounds, (RO)₃PI₄, were obtained in quantitative yield. All of the tertiary phosphite tetraiodide compounds described are acutely air and moisture sensitive (far more so than the analogous R₃PI₄), decomposing to black oils in a matter of minutes upon exposure to the atmosphere; consequently, strictly anaerobic and anhydrous conditions were adhered to. Only one of the compounds described in Table 1, (PhO)₃PI₄, has been reported previously.^{1,2}

No compound containing a tertiary phosphite and iodine has previously been crystallographically characterised. We were therefore interested in crystallographically characterising (PhO)₃PI₄, to compare to the two polymorphs of Ph₃PI₄ described by Cotton and Kibala⁵ and other (RO)₃PI₄ compounds to determine the effect of R on the solid state structure.

Crystals of (PhO)₃PI₄ were prepared by recrystallisation of the bulk solid in diethyl ether, appearing in the reaction vessel on standing in a refrigerator at *ca.* 2 °C after 5 d. They were plunged into an inert oil and a suitable one was chosen for single crystal X-ray diffraction after examination under the microscope. The crystal structure of (PhO)₃PI₄ **1** is illustrated in Fig. 1 and selected bond lengths and angles are displayed in Table 2. Compound **1** was previously assigned an ionic structure, [(PhO)₃PI]₃I₃; however, Fig. 1 shows that it is actually a molecular species in the solid state and is similar in structure to one polymorph of Ph₃PI₄ previously described.⁵ The *d*(I–I) **1**, 3.3888(7) Å, is significantly shorter than that exhibited by Ph₃PI₄, 3.55(1) Å. Unlike that molecule, which exhibits long range I–I interactions [*d*(I–I) = 3.741(1) Å] between individual I₃[−] anions linking the structure into a polymer, **1** is a discrete molecular entity with no long I–I contacts. The triiodide fragment of **1** has distinctly different I–I distances, 3.0485(7)

Table 2 Selected bond lengths (Å) and angles (°) for (RO)₃PI₄ (R = Ph for **1**, 4-MeC₆H₄ for **2** and 2,4-Bu^t₂C₆H₃ for **3**)

	1	2	3
P(1)–I(1)	2.366(2)	2.361(3)	2.390(5)
I(1)–I(2)	3.3888(7)	3.345(1)	3.227(1)
I(2)–I(3)	3.0485(7)	2.9863(12)	3.033(2)
I(3)–I(4)	2.7992(7)	2.8726(13)	2.819(3)
P(1)–O(1)	1.550(6)	1.536(7)	1.530(12)
P(1)–O(2)	1.566(6)	1.536(8)	1.552(14)
P(1)–O(3)	1.578(5)	1.551(8)	1.552(12)
I(1)–I(2)–I(3)	170.5(3)	170.79(3)	170.77(8)
P(1)–I(1)–I(2)	125.10(3)	86.59(4)	80.77(6)
I(2)–I(3)–I(4)	177.52(2)	177.58(4)	176.14(8)
I(1)–P(1)–O(1)	111.3(2)	111.7(3)	107.0(5)

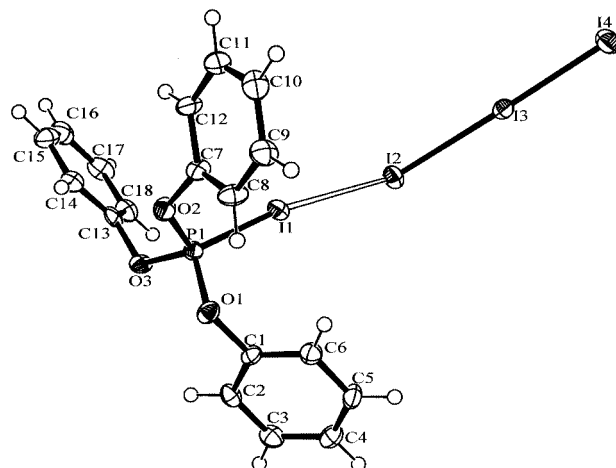


Fig. 1 The molecular structure of compound **1**.

and 2.7992(7) Å. The difference between these bond lengths, 0.2493(7) Å, is large but shorter than the largest known: 0.322(6) Å in NH₄I₃.⁷ The asymmetry in I–I bond lengths exhibited by **1** is easily explained by the close approach of the (PhO)₃PI fragment to one iodine atom in the triiodide fragment. This causes polarisation of the triiodide leading to one short and one long iodine–iodine bond. The triiodide fragment is virtually linear, 177.52(2)°, and is very similar to that exhibited by Ph₃PI₄, 177.23(4)°.⁵

In order to investigate the effect of R on (RO)₃PI₄ compounds, we decided crystallographically to characterise two further examples of compounds with this formula, where R = 4-MeC₆H₄ and 2,4-Bu^t₂C₆H₃. Crystals of both compounds were prepared in an identical manner to that described for (PhO)₃PI₄. The crystal structure of (4-MeC₆H₄O)₃PI₄ **2** is illustrated in Fig. 2. Selected bond lengths and angles are displayed in Table 2. As expected, **2** has a similar structure to that of **1**,

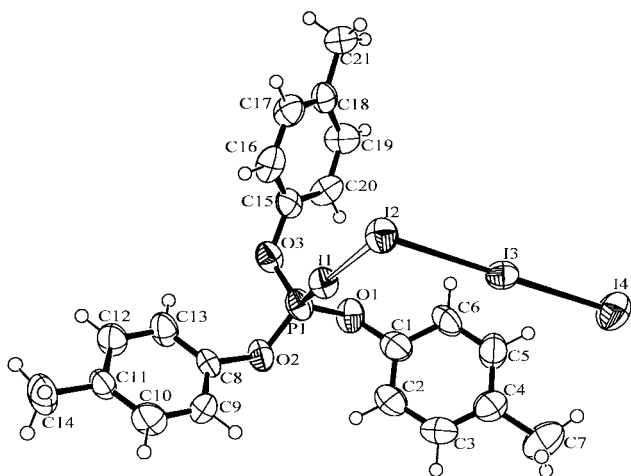


Fig. 2 The molecular structure of compound 2.

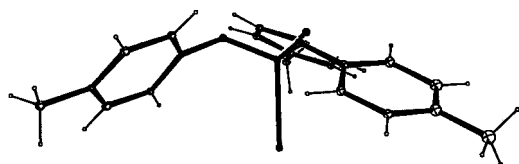


Fig. 3 The 'umbrella' configuration of the (4-MeC₆H₄O)₃PI fragment (atoms are represented by ellipsoids at 5% probability level).

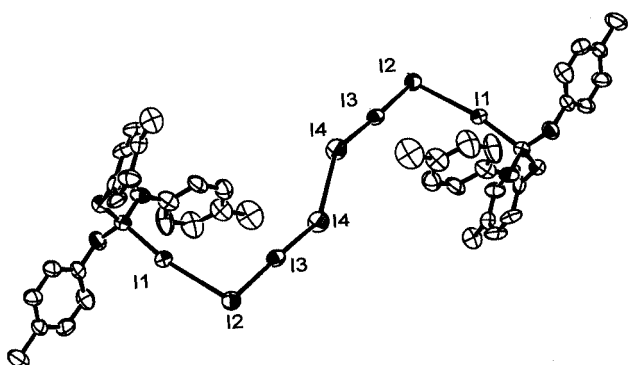


Fig. 4 The linking of two molecules of compound 2 through a weak I-I bond (3.521(2) Å) to form the dinuclear compound [(4-MeC₆H₄O)₃PI₄]₂ (non-iodine atoms are unlabelled and hydrogen atoms are omitted for clarity).

once again being a molecular species in the solid state. The I-I bond between the (4-MeC₆H₄O)₃PI fragment and the I₃ fragment is 3.345(1) Å, very similar to that exhibited by **1** (3.3888(7) Å). The phosphorus atom adopts a near-perfect tetrahedral geometry with the aryl rings orientating to point towards the iodine atom in an umbrella configuration, Fig. 3. The reason for this is probably due to an electrostatic interaction between P-I^{δ+} and the π electrons of the aromatic rings. A major difference between **1** and **2** is the P-I-I bond angle: 125.10(3)° for the former and 86.59(4)° for the latter. The asymmetry in $d(I-I)$ for the I₃ fragment of **2** is significantly smaller than that exhibited by **1**, the $d(I-I)$ distances for **2** being 2.9863(12) and 2.8276(13) Å. This phenomenon would appear to suggest that the I₃ fragment in this molecule is less polarised than in **1**. However, in contrast to **1** (and in common with Ph₃PI₄) there is significant interaction between the I₃ fragments of adjacent molecules of **2**, $d(I-I) = 3.521(2)$ Å, Fig. 4.

As previously mentioned, we also prepared crystals of (2,4-Bu₂C₆H₃O)₃PI₄ **3** for comparative purposes. The crystal structure of this compound is illustrated in Fig. 5. Selected bond lengths and angles are displayed in Table 2. The $d(I-I)$ for the iodine atom of (2,4-Bu₂C₆H₃O)₃PI and the I₃ moiety, 3.227(1) Å, is well within the range quoted for molecular CT complexes

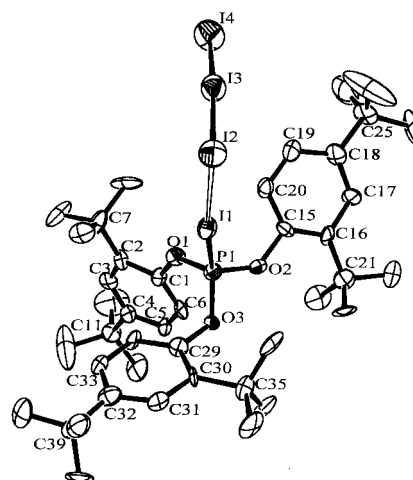


Fig. 5 The molecular structure of compound 3 (hydrogen atoms are omitted for clarity).

of formula R₃PI₄³ and this indicates that the compound is best described as molecular rather than ionic. In common with **1**, but in contrast to **2**, **3** is a discrete molecule with no long-range iodine-iodine interactions. This is reflected in $d(I-I)$ for the triiodide fragment, the bond lengths being distinctly asymmetric (3.033(2) and 2.819(3) Å).

³¹P-{¹H} NMR studies

In contrast to the analogous R₃PI₂ and R₃PI₄ compounds, which show a significant difference in δ depending on the R groups present on the tertiary phosphine (*e.g.* δ 9.1 for Bu₃PI₄, 87.9 for Prⁿ₃PI₄), little variation is seen in the ³¹P-{¹H} NMR spectra of (RO)₃PI₄ compounds. The δ values for compounds of that formula (described within) range from -9.2 to 3.0. This is as expected since the R groups are not bound directly to the phosphorus atom in (RO)₃PI₄ but are in R₃PI₄.

Conclusion

The first comprehensive study of the reaction of tertiary phosphites with diiodine is described. In contrast to earlier reports, in our hands no evidence was noted for the formation of the diiodide compound (RO)₃PI₂. In all cases the tetraiodides resulted, *i.e.* (RO)₃PI₄. In common with the analogous compounds R₃PI₄,³ the solid state structures of (RO)₃PI₄ are sensitive to R. For example, **1** and **3** are discrete molecular species whereas **2** is linked *via* long-range I-I contacts into a dimeric species, similar to one polymorph of Ph₃PI₄. Although all of the compounds described are molecular, $d(I-I)$ for the (RO)₃PI and I₃ fragments is sensitive to R, being 3.227(1) Å for **3** and 3.3888(7) Å for **1**. In other words, $d(I-I)$ increases with increasing basicity of the tertiary phosphite. A concurrent decrease in $d(P-I)$ is also noted. These observations mirror those seen for analogous R₃PI₄ compounds. Also observed with the increasing basicity of the tertiary phosphite is a decrease in the angle between the two linear sections of the molecule, *i.e.* the P-I bond of the (RO)₃PI fragment and the triiodide fragment at the apex, Table 2.

Experimental

All of the compounds reported are very moisture sensitive, consequently strictly anaerobic and anhydrous conditions were employed for their synthesis. Any subsequent manipulations were carried out inside a Vacuum Atmospheres HE-493 glove box. Diethyl ether (BDH) was dried by standing over sodium wire for *ca.* 1 d, subsequently refluxed over CaH₂ in an inert atmosphere and distilled directly into the reaction vessel. Tertiary phosphites were either obtained commercially

Table 3 Crystal data and details of refinement for compounds **1**, **2** and **3**

	1	2	3
Empirical formula	C ₁₈ H ₁₅ I ₄ O ₃ P	C ₄₂ H ₄₂ I ₈ O ₆ P ₂	C ₄₂ H ₆₃ I ₄ O ₃ P
Formula weight	817.87	1719.90	1154.49
<i>T</i> /K	146(2)	203(2)	203(2)
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	9.3386(10)	10.594(5)	11.763(10)
<i>b</i> /Å	10.000(2)	18.425(6)	19.565(2)
<i>c</i> /Å	24.168(2)	28.120(5)	21.003(2)
β /°		98.65(3)	
<i>V</i> /Å ³	2257.0(3)	5427(3)	4833.9(8)
<i>Z</i>	4	4	4
<i>D_c</i> /Mg m ⁻³	2.407	2.105	1.586
No. reflections	2244	5073	4704
No. observations	2244	5073	4704
Final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0214, 0.0848	0.0533, 0.0683	0.0646, 0.1379
(all data)	0.0224, 0.0874	0.1366, 0.0880	0.1247, 0.1681

[(PhO)₃P, (4-MeC₆H₄O)₃P, (2-PhC₆H₄O)₃P and (2,4-Bu^t₂-C₆H₃O)₃P (Lancaster)] or synthesized according to the method published elsewhere.⁸ Diiodine was obtained commercially (Aldrich) and used as received. All of the reactions performed resulted in the isolation of (RO)₃PI₄ regardless of the stoichiometry (either 1 : 1 or 1 : 2 (RO)₃P : I₂). The synthesis of (PhO)₃PI₄ **1** is typical. Triphenyl phosphite (2.00 g, 6.45 mmol) was dissolved in Et₂O (*ca.* 75 cm³) and subsequently diiodine (3.28 g, 12.9 mmol) added. After *ca.* 2 d the resultant red-brown solid was isolated using standard Schlenk techniques. The material was then transferred to pre-dried argon-filled ampoules, which were flame-sealed.

Elemental analyses were performed by the analytical laboratory of this department and the results are presented in Table 1. The ³¹P-{¹H} NMR spectra were recorded as CDCl₃ solutions on a Bruker AC200 high-resolution multiprobe spectrometer relative to concentrated phosphoric acid as standard.

Crystallography

Crystals of (RO)₃PI₄ (R = Ph in **1**, 4-MeC₆H₄ in **2** and 2,4-Bu^t₂C₆H₃ in **3**) were submerged in an inert oil under anaerobic conditions and suitable ones were chosen by examination under a microscope. Each crystal, with its protective coating of oil, was then mounted on a glass fibre, transferred to the diffractometer and cooled to *ca.* 203(2) K in the cold gas stream derived from liquid nitrogen. All measurements were performed on a Nonius MAC3 CAD4 diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) and ω -2 θ scans. All three structures were solved by direct methods. Unit cell dimensions were derived from the setting angles of 25 accurately centred reflections. Lorentz-polarisation corrections were applied. Details of the X-ray measurements and subsequent structure determinations are presented in Table 3. Hydrogen atoms were confined to chemically reasonable positions. Neutral atom scattering factors were taken from ref. 9,

anomalous dispersion effects from ref. 10. All calculations were performed using SHELXS 86¹¹ and SHELXL 93¹² crystallographic software packages.

CCDC reference number 186/1875.

See <http://www.rsc.org/suppdata/dt/a9/a909057f/> for crystallographic files in .cif format.

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