

A study of the pyramidity index in tris(2,4,6-triisopropylphenyl)phosphonium perchlorate

René T. Boéré* and Yuankui Zhang

Department of Chemistry and Biochemistry, University of Lethbridge, Lethbridge, AB, Canada T1K 3M4

Correspondence e-mail: boere@uleth.ca

Received 9 July 2013

Accepted 24 July 2013

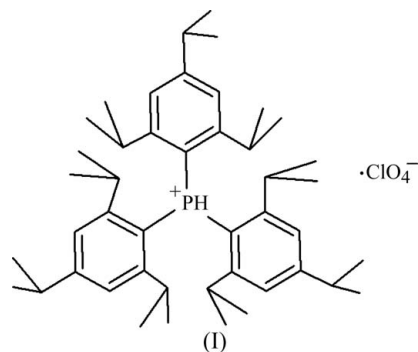
The title compound, $C_{45}H_{70}P^+ \cdot ClO_4^-$ or $[Tripp_3PH^+][ClO_4^-]$, was produced from the perchlorate salt of the corresponding radical cation $Tripp_3P^+$ through very slow H-atom abstraction reactions in a solution of 1,2-dimethoxyethane (Tripp is 2,4,6-triisopropylphenyl). The H atom on the P atom was located in a difference map and was freely refined with an isotropic displacement consistent with full occupancy [$P-H = 1.37(3) \text{ \AA}$]. It is the most sterically congested triarylphosphonium salt yet to be reported and has a 'propeller' arrangement of the three Tripp groups around the P atom, with the protonation site located along the molecular threefold axis. There are short contacts between the flanking isopropyl methine H atoms and the P atom [$P \cdots H = 1.99(2) - 2.17(2) \text{ \AA}$]. The sum of the angles around the P atom [$\Sigma(C-P-C) = 349.9(6)^\circ$] is a convenient index of pyramidity for tricoordinate centres. This value is significantly larger than in analogous Mes_3PH^+ salts (Mes is mesityl or 2,4,6-trimethylphenyl), for which the average of the three reported structures in the literature is $\Sigma(C-P-C) = 345.3(6)^\circ$. For comparison, in the ubiquitous Ph_3PH^+ salts, this parameter has a typical average value of only $333.3(9)^\circ$. The value of $\Sigma(C-P-C)$ in the title compound is midway between that of the neutral phosphane $Tripp_3P$ [$334.4(6)^\circ$] and the phosphoniumyl radical cation $Tripp_3P^+$ [$359.8(2)^\circ$]. This geometrical feature provides additional support for the assignment as a phosphonium salt.

Keywords: crystal structure; triarylphosphonium ions; pyramidity index; phosphoniumyl radical cations.

1. Introduction

There is intense current interest in the preparation and isolation of stable phosphoniumyl radical cations (Bullock *et al.*, 2013; Boéré *et al.*, 2008; Sasaki *et al.*, 2002, 2004, 2006; Sasaki & Yoshifuji, 2007; Chalier *et al.*, 1996). Exhaustive studies have shown that this can be achieved only when very bulky substituents are employed, and thus far all the successful

examples use bulky aryl groups. The widely used 2,4,6-trimethylphenyl (Mes) group has been shown to lead to persistent radical cations of the type $[Mes_3P^+]$, but these are still reactive species and salts have never been isolated. By increasing the steric bulk through the use of various aryl groups that have in common flanking 2,6-diisopropyl groups, designated ${}^{i-Pr}_2Ar$, a number of stable $[{}^{i-Pr}_2Ar_3P^+]$ radical cations have now been reported. Significantly, Pan *et al.* (2013) recently reported the first crystal structures in this class with a number of salts containing the 2,4,6-triisopropylphenyl (Tripp) group. Three structures of the type $[Tripp_3P^+]X^-$ were reported with $X^- = SbF_6^-$, $[Al\{OC(CF_3)_3\}_4^-]$ and $[Al\{OCMe(CF_3)_2\}_4^-]$, as well as $[MesTripp_2P^+][Al\{OC(CF_3)_3\}_4^-]$. Each of the $[Tripp_3P^+]X^-$ salts was found to have structures that are planar within experimental error, with an average of the sums of the angles around the P atom (for background on this parameter, see: Boéré & Zhang, 2005), denoted $\Sigma(C-P-C)$, of $359.8(2)^\circ$, whilst the $[MesTripp_2P^+]$ cation was found to be mildly pyramidal, with a $\Sigma(C-P-C)$ value of $349.15(6)^\circ$ (Pan *et al.*, 2013). These workers report that solutions of $[Tripp_3P^+]X^-$ salts retain their colour when reacted with the H-atom source nBu_3SnH . We have also prepared $[Tripp_3P^+]X^-$ salts with a variety of anions *via* the corresponding silver(I) salts with the identity of the radical cations confirmed by electron paramagnetic resonance (EPR) spectroscopy (see below). Although we obtained stable solid materials with $X^- = SbF_6^-$, AsF_6^- and ClO_4^- , we have been unable to obtain diffraction-quality crystals. However, solutions of $[Tripp_3P^+][ClO_4^-]$ slowly deposit large blocks over



long periods of storage in the dark that, while streaked with residual red colour (presumably from occluded radical cation), are predominantly colourless. The structure determination reported here demonstrates that these are the diamagnetic phosphonium salts which are probably obtained by very slow H-atom abstraction reactions. Thus, our results do not contradict the reports that a *rapid* reaction with reactive H-atom sources such as nBu_3SnH does not occur for the $[Tripp_3P^+]$ radical cation; over time, perhaps with lattice forces as a driving mechanism, the H-atom abstraction product does form even from relatively unreactive H-atom sources (other molecules of the radical cation or the 1,2-dimethoxyethane solvent). Radical attack on C-H bonds by phosphoniumyl ions has recently been reported and can be

made catalytic with the addition of suitable Lewis acids (Ménard *et al.*, 2013).

2. Experimental

2.1. Synthesis and crystallization

A small quantity of tris(2,4,6-triisopropylphenyl)phosphane (Tripp₃P), prepared according to the literature method of Sasaki *et al.* (2002), was placed in the wide limb [outer diameter (od) 8 mm] end of a Pyrex 'T' tube, and a grain of AgClO₄ was added to the solid. Dried degassed 1,2-dimethoxyethane (DME; distilled under N₂ from molten sodium) was added by syringe (1.0 ml) and the reaction mixture was immediately connected to a vacuum line and freeze–thaw degassed three times. While still under vacuum, the opening was sealed by melting the glass. After cooling the hot glass, the reaction mixture was carefully thawed and shaken to dissolve the reagents. An immediate intense deep-red colour developed. Small quantities of the red material were decanted into the other arm of the vessel, which consists of a 4 mm od EPR tube. Solvent was then carefully distilled into the narrow limb to ensure a dilute solution of the radical. The EPR spectrum (X-band, 9.7674 GHz) was determined (Fig. 1) at ambient temperature (*ca* 291 K). The spectrum displays the characteristic doublet from coupling to the single ³¹P nucleus with a hyperfine splitting of 23.62 mT and a third-order corrected *g* value of 2.0060. Unresolved coupling to H atoms of the 2,4,6-triisopropylphenyl ring is evident from the need to include about 15% Gaussian character to the simulated line shape. The spectrum displays unsymmetrical linewidths, which fit to a 'slow tumbling' equation: LW = (0.650 – 0.10*m*) mT (Murphy, 2009). This data may be compared to a reported *a*(³¹P) = 23.3 mT and (likely uncorrected) *g* = 2.008 for solutions made up from the corresponding SbF₆[–] salt in CH₂Cl₂ (Pan *et al.*,

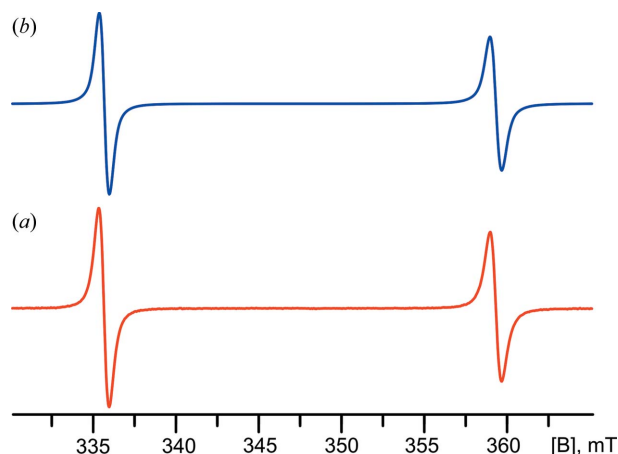


Figure 1
(a) The X-band (9.8 GHz) EPR spectrum of a solution of [Tripp₃P⁺][ClO₄[–]] in 1,2-dimethoxyethane at 291 K, showing the expected doublet with *a*(³¹P) = 23.62 mT. (b) The simulation obtained in which the linewidths fit to (0.650 – 0.10*m*) mT, consistent with incomplete averaging of the *g* and *a* tensors caused by slow tumbling in solution.

Table 1
Experimental details.

Crystal data	
Chemical formula	C ₄₅ H ₇₀ P ⁺ ·ClO ₄ [–]
<i>M_r</i>	741.43
Crystal system, space group	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 1
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.6822 (14), 17.0621 (18), 18.660 (2)
<i>V</i> (Å ³)	4356.1 (8)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ^{–1})	0.16
Crystal size (mm)	0.38 × 0.21 × 0.17
Data collection	
Diffractometer	Bruker APEXII CCD area-detector diffractometer
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2008)
<i>T_{min}</i> , <i>T_{max}</i>	0.941, 0.973
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	61837, 10021, 7663
<i>R_{int}</i>	0.054
(sin θ/λ) _{max} (Å ^{–1})	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.039, 0.097, 1.02
No. of reflections	10021
No. of parameters	483
No. of restraints	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ^{–3})	0.35, –0.31
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.49 (7)

Computer programs: *APEX2* (Bruker, 2008), *SAINT-Plus* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2013), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

2013). Repeated attempts to grow crystals of such salts with a variety of anions from many different solvents were unsuccessful, but over a very long time (4–5 years) during storage of the sealed T-tube in the dark at ambient temperature, large blocks developed containing red tinted streaks, but which are nevertheless predominantly colourless. Successful solution of the single-crystal structure shows that rather than the expected radical cation salt [Tripp₃P⁺][ClO₄[–]], which has a deep-red colour, the crystals are composed of the colourless diamagnetic phosphonium salt, [Tripp₃PH⁺][ClO₄[–]], (I). We believe that this product results from slow H-atom abstraction, either from the reaction medium (solvent or adventitious moisture) or from other cation molecules. The other possibility, that excess silver salt has hydrolysed to HClO₄ which then protonated unreacted phosphane, cannot be ruled out entirely, but does not seem to be consistent with the timescale of the reaction that was established from monitoring the EPR spectra.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms attached to C atoms were treated as riding, with C–H = 0.98 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C) for methyl, C–H = 1.00 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) for methine, and C–H = 0.95 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) for aromatic H atoms. The phosphonium H atom

Table 2
Pyramidity index in triarylphosphonium ion structures.

Aryl group	CSD refcode	$\Sigma(\text{C}-\text{P}-\text{C})$ ($^\circ$)	Reference
Ph_3PH^+	ABERAA	332.7 (5)	Junk & Atwood (1999)
Ph_3PH^+	BARVUL	334 (3)	Boorman <i>et al.</i> (1981)
Ph_3PH^+	KAXQUQ	333.0 (6)	Hagenbach & Abram (2005)
$[\text{2,4,6-(MeO)}_3\text{C}_6\text{H}_2]_3\text{PH}^+$	LAFGEE10	338.9 (5)	Dunbar & Quillevere (1993)
$[\text{2,4,6-(MeO)}_3\text{C}_6\text{H}_2]_3\text{PH}^+$	TAJGAM	342.3 (6)	Dunbar & Pence (1991)
$[\text{2,4,6-(MeO)}_3\text{C}_6\text{H}_2]_3\text{PH}^+$	WIBJEW	337.5 (9)	Dunbar & Quillevere (1993)
$[\text{2,4,6-(MeO)}_3\text{C}_6\text{H}_2]_3\text{PH}^+$	WIBJIA	343.0 (7)	Dunbar & Quillevere (1993)
Mes_3PH^+	LUWPOJ	345.3 (5)	Ménard & Stephan (2010)
Mes_3PH^+	QUHCAY	345.6 (6)	Jiang <i>et al.</i> (2009)
Mes_3PH^+	XALCUK	345.1 (6)	Schäfer <i>et al.</i> (2011)
$\text{Tripp}_3\text{PH}^+$		349.9 (6)	This work

was located in a difference Fourier map and refined freely with an isotropic U value. The 'CALC VOID' routine in *PLATON* (Spek, 2009) was used to identify solvent-accessible voids in the unit cell.

3. Results and discussion

We report here the structure determination of tris(2,4,6-triisopropylphenyl)phosphonium perchlorate, $[\text{Tripp}_3\text{PH}^+][\text{ClO}_4^-]$, (I) (Fig. 2). There are only a relatively small number of structures reported that contain Ar_3PH^+ cations. A search of the Cambridge Structural Database (CSD, Version 5.34, with updates to May 2013; Allen, 2002) resulted in 45 different structures; of these, 24 contain the Ph_3PH^+ ion and another eight are closely related [such as $(\text{XC}_6\text{H}_4)_2\text{PH}^+$ ions]. Taking three of the more accurately determined structures containing the Ph_3PH^+ ion [refcodes ABERAA (Junk & Atwood, 1999), BARVUL (Boorman *et al.*, 1981) and KAXQUW (Hagenbach & Abram, 2005)] yields an average $\Sigma(\text{C}-\text{P}-\text{C})$ value of 333.3 (9°) (see Table 2). Obviously more sterically bulky phosphonium salts identified from this

search include four exemplars of tris(2,4,6-trimethoxyphenyl)phosphonium salts [refcodes LAFGEE10, WIBJEW and WIBJIA (Dunbar & Quillevere, 1993), and TAJGAM (Dunbar & Pence, 1991)]. These structures show greater variation in pyramidity compared to Ph_3PH^+ apparently because the substituents take differing orientations around the P atom, resulting in an average $\Sigma(\text{C}-\text{P}-\text{C})$ value of 340 (3°), with a rather large s.u. value. The bulkiest structures reported to date contain Mes_3PH^+ ions, for which three structures are present in the CSD [refcodes LUWPOJ (Ménard & Stephan, 2010), QUHCAY (Jiang *et al.*, 2009) and XALCUK (Schäfer *et al.*, 2011)]. These display fairly consistent structural

features with 'propeller' orientations of the aryl rings, yielding an average $\Sigma(\text{C}-\text{P}-\text{C})$ value of 345.3 (6°). The increased steric bulk of the Tripp substituent is then clearly observable by the $\Sigma(\text{C}-\text{P}-\text{C})$ value of 349.9 (6°) in (I). The pyramidity index of (I) places it firmly between the planarity observed in Tripp_3P^+ salts, with an average $\Sigma(\text{C}-\text{P}-\text{C})$ value of 359.8 (2°) (Pan *et al.*, 2013), and the more pyramidal neutral Tripp_3P , for which the $\Sigma(\text{C}-\text{P}-\text{C})$ value is 334.4 (6°) (refcode XUNXEJ; Sasaki *et al.*, 2002). This distinctive structural feature provides strong support for our identification of the title cation as a phosphonium ion.

An unusual feature of the structure of (I), and one that is likely a direct consequence of steric crowding, is the presence of short intramolecular distances between atom H1 on P1 and the three flanking isopropyl group methine H atoms H7, H25 and H37, with $\text{H}\cdots\text{H}$ distances ranging from 1.99 (2) to 2.17 (2) Å, and thus shorter than or equal to the sums of the van der Waals radii of 2.18 Å. Perusal of space-filling mol-

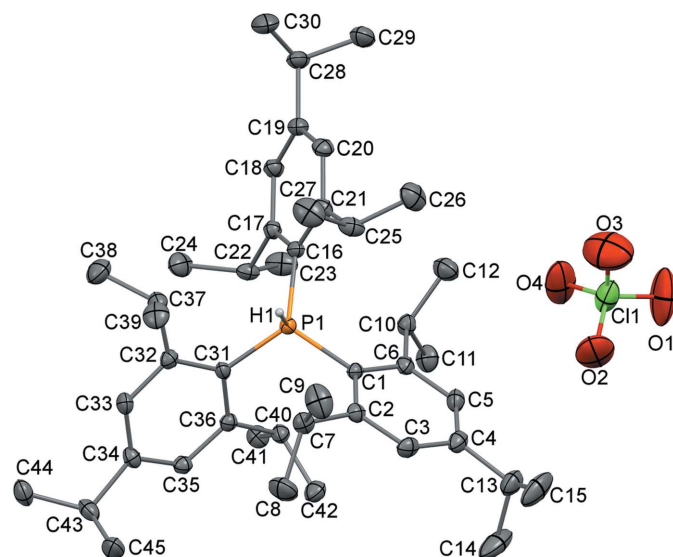


Figure 2

The structure of the cation-anion pair in (I), with displacement ellipsoids drawn at the 40% probability level and showing the atom-numbering scheme. H atoms on C atoms have been omitted to enhance visibility.

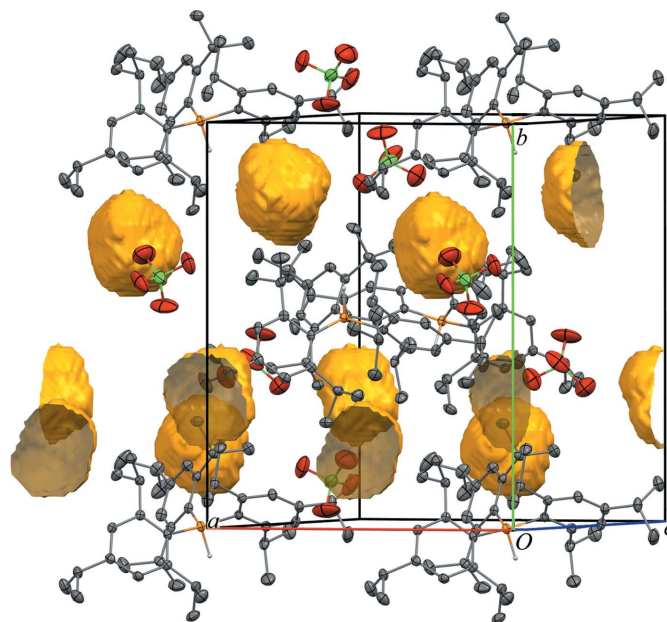


Figure 3

A packing view with the b axis vertical and the bisector of a and c perpendicular. The contact surfaces of the small void volumes in the lattice are shown (each cavity has a volume of 30 Å³). H atoms on C atoms have been omitted to enhance visibility.

ecular models shows that atom H1 is completely buried amongst these flanking isopropyl group atoms. Severe steric crowding is also indicated by distortions in the aryl ring. In particular, the C31-ring shows a distinct boat conformation; from the least-squares plane defined by atoms C32/C33/C35/C36 (r.m.s. deviation = 0.002 Å), the other atoms deviate by 0.058 (4) (C34) 0.064 (4) (C31) and 0.627 (5) Å (P1). In contrast, in neutral Tripp₃P, the most distorted ring has the *ipso*-C and P atoms 0.046 and 0.491 Å, respectively, out of plane (refcode XUNXEJ; Sasaki *et al.*, 2002). The final feature of note in this structure is the presence of four voids in the unit cell with a volume of 30 Å³ each (Fig. 3). These were identified with the help of the 'CALC VOID' routine in *PLATON* (Spek, 2009), as well as with *Mercury* (Macrae *et al.*, 2006). However, the voids seem to be empty of any nuclei. Most likely these cavities are merely consequences of packing such large cations with the relatively small perchlorate anions, but we cannot rule out the possibility that some contain free electrons left over from the H-atom abstraction reactions that lead to these phosphonium salts.

The Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged for Discovery Grants and an I2I award to RTB. We thank GEM Systems, Richmond Hill, Ontario, for their interest in our work on bulky phosphanes. The diffractometer was purchased with the help of NSERC and the University of Lethbridge, while the EPR spectrometer was funded by the Canada Foundation for Innovation, the Government of Alberta and Bruker Canada, Inc.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3145). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Boéré, R. T., Bond, A. M., Cronin, S., Duffy, N. W., Hazendonk, P., Masuda, J. D., Pollard, K., Roemmele, T. L., Tran, P. & Zhang, Y. (2008). *New J. Chem.* **32**, 214–231.
- Boéré, R. T. & Zhang, Y. (2005). *J. Organomet. Chem.* **690**, 2651–2657.
- Boorman, P. M., Moynihan, K. J. & Kerr, K. A. (1981). *Chem. Commun.* pp. 1286–1288.
- Bruker (2008). *APEX2, SAINT-Plus and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bullock, J. P., Bond, A. M., Boéré, R. T., Gietz, T. M., Roemmele, T. L., Seagrave, S. D., Masuda, J. D. & Parvez, M. (2013). *J. Am. Chem. Soc.* **135**, 11205–11215.
- Chalier, F., Berchadsky, Y., Finet, J., Gronchi, G., Marque, S. & Tordo, P. (1996). *J. Phys. Chem.* **100**, 4323–4330.
- Dunbar, K. R. & Pence, L. E. (1991). *Acta Cryst.* **C47**, 23–26.
- Dunbar, K. R. & Quillevere, A. (1993). *Polyhedron*, **12**, 807–819.
- Hagenbach, A. & Abram, U. (2005). *Z. Anorg. Allg. Chem.* **631**, 2303–2305.
- Jiang, C., Blacque, O. & Berke, H. (2009). *Organometallics*, **28**, 5233–5239.
- Junk, P. C. & Atwood, J. L. (1999). *J. Coord. Chem.* **46**, 505–518.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Ménard, G., Hatnean, J. A., Cowley, H. J., Lough, A. J., Rawson, J. M. & Stephan, D. W. (2013). *J. Am. Chem. Soc.* **135**, 6446–6449.
- Ménard, G. & Stephan, D. W. (2010). *J. Am. Chem. Soc.* **132**, 1796–1797.
- Murphy, D. M. (2009). *EPR (Electron Paramagnetic Resonance) Spectroscopy of Polycrystalline Oxide Systems*, in *Metal Oxide Catalysis*, pp. 1–50. Weinheim: Wiley-VCH Verlag GmbH & Co.
- Pan, X., Chen, X., Li, T., Li, Y. & Wang, X. (2013). *J. Am. Chem. Soc.* **135**, 3414–3417.
- Sasaki, S., Chowdhury, R. & Yoshifuji, M. (2004). *Tetrahedron Lett.* **45**, 9193–9196.
- Sasaki, S., Murakami, F. & Yoshifuji, M. (2006). *Organometallics*, **25**, 140–147.
- Sasaki, S., Sutoh, K., Murakami, F. & Yoshifuji, M. (2002). *J. Am. Chem. Soc.* **124**, 14830–14831.
- Sasaki, S. & Yoshifuji, M. (2007). *Curr. Org. Chem.* **38**, 17–31.
- Schäfer, A., Reissmann, M., Schäfer, A., Saak, W., Haase, D. & Müller, T. (2011). *Angew. Chem. Int. Ed.* **50**, 12636–12638.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2013). *SHELXL2013*. University of Göttingen, Germany.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supplementary materials

Acta Cryst. (2013). C69, 1051-1054 [doi:10.1107/S0108270113020647]

A study of the pyramidal index in tris(2,4,6-triisopropylphenyl)phosphonium perchlorate

René T. Boéré and Yuankui Zhang

Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE-Plus* (Bruker, 2008); data reduction: *SAINTE-Plus* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2013); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Tris(2,4,6-triisopropylphenyl)phosphonium perchlorate

Crystal data

$C_{45}H_{70}P^{+}ClO_4^{-}$	$D_x = 1.131 \text{ Mg m}^{-3}$
$M_r = 741.43$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Orthorhombic, $P2_12_12_1$	Cell parameters from 9973 reflections
$a = 13.6822 (14) \text{ \AA}$	$\theta = 2.2\text{--}27.4^\circ$
$b = 17.0621 (18) \text{ \AA}$	$\mu = 0.16 \text{ mm}^{-1}$
$c = 18.660 (2) \text{ \AA}$	$T = 173 \text{ K}$
$V = 4356.1 (8) \text{ \AA}^3$	Block, red
$Z = 4$	$0.38 \times 0.21 \times 0.17 \text{ mm}$
$F(000) = 1616$	

Data collection

Bruker APEXII CCD area-detector diffractometer	$T_{\min} = 0.941, T_{\max} = 0.973$
Radiation source: fine-focus sealed tube, Bruker D8	61837 measured reflections
Graphite monochromator	10021 independent reflections
Detector resolution: $66.06 \text{ pixels mm}^{-1}$	7663 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{\text{int}} = 0.054$
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2008)	$\theta_{\max} = 27.5^\circ, \theta_{\min} = 1.9^\circ$
	$h = -17 \rightarrow 17$
	$k = -22 \rightarrow 22$
	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.039$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.097$	$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
10021 reflections	$(\Delta/\sigma)_{\max} < 0.001$
483 parameters	$\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$
0 restraints	
Primary atom site location: structure-invariant direct methods	

$$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Refined as an inversion twin.

Absolute structure parameter: 0.49 (7)

Special details

Experimental. A crystal coated in Paratone (TM) oil was mounted on the end of a thin glass capillary and cooled in the gas stream of the diffractometer Kryoflex device.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
P1	0.71447 (5)	0.49036 (4)	0.96924 (3)	0.02084 (14)
H1	0.7281 (19)	0.4174 (15)	0.9396 (13)	0.029 (7)*
C1	0.63959 (17)	0.53394 (15)	0.90014 (12)	0.0195 (5)
C2	0.56611 (18)	0.48513 (15)	0.87098 (12)	0.0234 (5)
C3	0.50853 (19)	0.51520 (17)	0.81573 (13)	0.0288 (6)
H3	0.4585	0.4833	0.7958	0.035*
C4	0.5221 (2)	0.59044 (17)	0.78886 (13)	0.0300 (6)
C5	0.5947 (2)	0.63629 (16)	0.81843 (13)	0.0294 (6)
H5	0.6048	0.6873	0.7995	0.035*
C6	0.65371 (18)	0.61146 (15)	0.87468 (13)	0.0236 (5)
C7	0.54422 (19)	0.40214 (16)	0.89658 (14)	0.0283 (6)
H7	0.5865	0.3920	0.9393	0.034*
C8	0.4378 (2)	0.3928 (2)	0.92063 (19)	0.0512 (9)
H8A	0.4277	0.3398	0.9393	0.077*
H8B	0.3943	0.4017	0.8797	0.077*
H8C	0.4234	0.4311	0.9583	0.077*
C9	0.5711 (3)	0.34194 (19)	0.83992 (17)	0.0527 (9)
H9A	0.6397	0.3487	0.8262	0.079*
H9B	0.5294	0.3492	0.7977	0.079*
H9C	0.5615	0.2891	0.8593	0.079*
C10	0.7262 (2)	0.66905 (16)	0.90601 (14)	0.0275 (6)
H10	0.7506	0.6465	0.9521	0.033*
C11	0.6792 (2)	0.74829 (16)	0.92315 (16)	0.0374 (7)
H11A	0.6207	0.7401	0.9525	0.056*
H11B	0.6610	0.7746	0.8784	0.056*
H11C	0.7259	0.7809	0.9495	0.056*
C12	0.8143 (2)	0.68025 (19)	0.85671 (17)	0.0424 (8)
H12A	0.7923	0.7008	0.8104	0.064*
H12B	0.8470	0.6298	0.8495	0.064*
H12C	0.8601	0.7174	0.8787	0.064*
C13	0.4545 (2)	0.62553 (19)	0.73408 (15)	0.0405 (7)
H13	0.4855	0.6750	0.7166	0.049*
C14	0.3592 (3)	0.6481 (3)	0.77047 (19)	0.0691 (12)
H14A	0.3733	0.6806	0.8125	0.104*

H14B	0.3246	0.6006	0.7855	0.104*
H14C	0.3184	0.6777	0.7368	0.104*
C15	0.4353 (3)	0.5749 (2)	0.66933 (17)	0.0682 (13)
H15A	0.3998	0.5276	0.6840	0.102*
H15B	0.4976	0.5599	0.6474	0.102*
H15C	0.3960	0.6042	0.6346	0.102*
C16	0.84116 (17)	0.51992 (14)	0.97472 (13)	0.0207 (5)
C17	0.88062 (17)	0.56252 (14)	1.03215 (13)	0.0217 (5)
C18	0.98159 (18)	0.57168 (15)	1.03514 (14)	0.0258 (6)
H18	1.0092	0.5996	1.0742	0.031*
C19	1.04335 (18)	0.54141 (16)	0.98298 (14)	0.0265 (6)
C20	1.00227 (18)	0.50219 (16)	0.92537 (14)	0.0282 (6)
H20	1.0440	0.4824	0.8889	0.034*
C21	0.90236 (18)	0.49091 (16)	0.91918 (13)	0.0249 (5)
C22	0.81955 (18)	0.60123 (15)	1.08964 (13)	0.0256 (6)
H22	0.7495	0.5945	1.0758	0.031*
C23	0.8396 (2)	0.68941 (17)	1.09352 (18)	0.0423 (8)
H23A	0.8327	0.7124	1.0457	0.063*
H23B	0.9062	0.6982	1.1111	0.063*
H23C	0.7928	0.7140	1.1263	0.063*
C24	0.8328 (2)	0.5626 (2)	1.16243 (14)	0.0424 (8)
H24A	0.9015	0.5662	1.1769	0.064*
H24B	0.8135	0.5074	1.1594	0.064*
H24C	0.7919	0.5894	1.1979	0.064*
C25	0.8642 (2)	0.44669 (17)	0.85350 (15)	0.0314 (7)
H25	0.7921	0.4558	0.8503	0.038*
C26	0.9106 (2)	0.4753 (2)	0.78344 (15)	0.0468 (8)
H26A	0.9800	0.4612	0.7828	0.070*
H26B	0.9040	0.5324	0.7801	0.070*
H26C	0.8774	0.4508	0.7427	0.070*
C27	0.8810 (3)	0.35937 (19)	0.86237 (19)	0.0508 (9)
H27A	0.8545	0.3422	0.9086	0.076*
H27B	0.9512	0.3483	0.8607	0.076*
H27C	0.8480	0.3311	0.8236	0.076*
C28	1.15313 (19)	0.55200 (18)	0.98844 (15)	0.0329 (7)
H28	1.1677	0.5794	1.0346	0.039*
C29	1.1909 (2)	0.60306 (19)	0.92731 (16)	0.0414 (8)
H29A	1.1575	0.6538	0.9283	0.062*
H29B	1.1781	0.5770	0.8814	0.062*
H29C	1.2614	0.6111	0.9329	0.062*
C30	1.2057 (2)	0.4737 (2)	0.98903 (19)	0.0517 (9)
H30A	1.1978	0.4481	0.9424	0.078*
H30B	1.1779	0.4403	1.0266	0.078*
H30C	1.2754	0.4821	0.9985	0.078*
C31	0.64563 (17)	0.47203 (14)	1.05060 (12)	0.0201 (5)
C32	0.66011 (18)	0.39765 (15)	1.08289 (12)	0.0225 (5)
C33	0.58916 (19)	0.37086 (15)	1.13016 (13)	0.0256 (6)
H33	0.5978	0.3213	1.1524	0.031*
C34	0.50577 (19)	0.41436 (15)	1.14596 (13)	0.0246 (6)

C35	0.49834 (18)	0.48942 (15)	1.11824 (13)	0.0230 (5)
H35	0.4445	0.5211	1.1321	0.028*
C36	0.56674 (17)	0.52000 (15)	1.07095 (12)	0.0206 (5)
C37	0.74783 (19)	0.34504 (16)	1.06815 (14)	0.0292 (6)
H37	0.7949	0.3749	1.0375	0.035*
C38	0.8002 (2)	0.32274 (19)	1.13796 (16)	0.0445 (8)
H38A	0.7586	0.2873	1.1659	0.067*
H38B	0.8134	0.3702	1.1659	0.067*
H38C	0.8620	0.2965	1.1266	0.067*
C39	0.7175 (2)	0.27152 (16)	1.02758 (17)	0.0416 (7)
H39A	0.6848	0.2864	0.9829	0.062*
H39B	0.6726	0.2406	1.0572	0.062*
H39C	0.7756	0.2402	1.0165	0.062*
C40	0.55330 (18)	0.60468 (15)	1.04719 (12)	0.0240 (6)
H40	0.6086	0.6183	1.0144	0.029*
C41	0.5575 (2)	0.66073 (16)	1.11175 (14)	0.0298 (6)
H41A	0.5021	0.6502	1.1437	0.045*
H41B	0.5542	0.7150	1.0948	0.045*
H41C	0.6188	0.6526	1.1379	0.045*
C42	0.4580 (2)	0.61740 (17)	1.00626 (14)	0.0324 (6)
H42A	0.4025	0.6058	1.0377	0.049*
H42B	0.4561	0.5825	0.9646	0.049*
H42C	0.4542	0.6720	0.9902	0.049*
C43	0.4206 (2)	0.38079 (17)	1.18748 (15)	0.0332 (6)
H43	0.3853	0.4254	1.2106	0.040*
C44	0.4478 (2)	0.32272 (18)	1.24584 (16)	0.0399 (7)
H44A	0.4910	0.3482	1.2806	0.060*
H44B	0.4815	0.2778	1.2244	0.060*
H44C	0.3884	0.3047	1.2701	0.060*
C45	0.3518 (2)	0.3441 (2)	1.13227 (17)	0.0465 (8)
H45A	0.3874	0.3049	1.1042	0.070*
H45B	0.3269	0.3850	1.1002	0.070*
H45C	0.2970	0.3189	1.1570	0.070*
Cl1	0.78075 (7)	0.88844 (5)	0.75076 (5)	0.0552 (2)
O1	0.7831 (4)	0.96017 (17)	0.71385 (17)	0.1182 (14)
O2	0.6876 (2)	0.8538 (2)	0.74828 (17)	0.0901 (10)
O3	0.8475 (3)	0.8343 (2)	0.7175 (2)	0.1257 (14)
O4	0.8087 (2)	0.8991 (2)	0.82266 (15)	0.0973 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0185 (3)	0.0253 (3)	0.0188 (3)	-0.0014 (3)	0.0000 (3)	0.0019 (3)
C1	0.0177 (12)	0.0262 (14)	0.0145 (11)	0.0017 (10)	-0.0005 (9)	-0.0008 (10)
C2	0.0241 (13)	0.0294 (14)	0.0167 (11)	0.0011 (12)	0.0016 (10)	-0.0035 (11)
C3	0.0260 (14)	0.0398 (16)	0.0207 (12)	0.0001 (13)	-0.0050 (10)	-0.0070 (12)
C4	0.0323 (15)	0.0381 (17)	0.0196 (13)	0.0091 (13)	-0.0004 (11)	-0.0019 (12)
C5	0.0365 (16)	0.0298 (15)	0.0219 (13)	0.0042 (13)	0.0019 (12)	0.0049 (11)
C6	0.0245 (13)	0.0269 (14)	0.0194 (12)	0.0034 (11)	0.0037 (10)	0.0002 (11)
C7	0.0310 (15)	0.0282 (15)	0.0258 (13)	-0.0065 (12)	-0.0027 (11)	-0.0034 (11)

C8	0.0360 (18)	0.057 (2)	0.061 (2)	-0.0150 (17)	0.0068 (16)	0.0041 (18)
C9	0.080 (3)	0.0335 (18)	0.0446 (19)	-0.0040 (18)	0.0115 (18)	-0.0086 (15)
C10	0.0315 (15)	0.0241 (14)	0.0270 (13)	-0.0010 (12)	-0.0014 (12)	0.0046 (11)
C11	0.0480 (18)	0.0252 (15)	0.0389 (16)	-0.0005 (14)	0.0010 (14)	0.0004 (13)
C12	0.0354 (17)	0.0398 (18)	0.052 (2)	-0.0051 (14)	0.0081 (14)	0.0047 (15)
C13	0.0431 (18)	0.0502 (19)	0.0282 (15)	0.0111 (15)	-0.0090 (13)	0.0019 (14)
C14	0.063 (2)	0.098 (3)	0.047 (2)	0.051 (2)	-0.0156 (18)	-0.016 (2)
C15	0.080 (3)	0.090 (3)	0.0343 (18)	0.043 (2)	-0.0275 (18)	-0.0183 (19)
C16	0.0174 (11)	0.0218 (13)	0.0228 (12)	-0.0001 (10)	-0.0003 (10)	0.0019 (11)
C17	0.0227 (13)	0.0222 (13)	0.0201 (12)	0.0004 (10)	0.0004 (10)	0.0000 (11)
C18	0.0216 (13)	0.0325 (15)	0.0233 (12)	-0.0024 (11)	-0.0009 (11)	-0.0009 (12)
C19	0.0192 (13)	0.0321 (15)	0.0281 (14)	0.0016 (11)	0.0008 (10)	0.0022 (12)
C20	0.0233 (13)	0.0339 (16)	0.0273 (13)	0.0050 (12)	0.0048 (10)	-0.0025 (12)
C21	0.0254 (13)	0.0262 (14)	0.0230 (12)	-0.0018 (11)	0.0020 (10)	-0.0019 (11)
C22	0.0190 (12)	0.0325 (15)	0.0254 (13)	-0.0013 (11)	0.0016 (10)	-0.0082 (12)
C23	0.0353 (17)	0.0366 (18)	0.055 (2)	-0.0014 (14)	0.0025 (15)	-0.0204 (15)
C24	0.0401 (18)	0.063 (2)	0.0240 (15)	0.0047 (16)	0.0042 (13)	-0.0059 (14)
C25	0.0240 (14)	0.0371 (17)	0.0331 (15)	-0.0030 (12)	0.0032 (12)	-0.0133 (13)
C26	0.0512 (19)	0.061 (2)	0.0283 (15)	-0.0086 (17)	0.0038 (14)	-0.0092 (15)
C27	0.057 (2)	0.0396 (19)	0.056 (2)	-0.0027 (16)	0.0104 (17)	-0.0166 (17)
C28	0.0186 (13)	0.0521 (19)	0.0279 (15)	-0.0014 (13)	-0.0017 (11)	-0.0009 (13)
C29	0.0275 (16)	0.056 (2)	0.0406 (16)	-0.0087 (15)	0.0012 (13)	0.0034 (16)
C30	0.0270 (16)	0.065 (2)	0.063 (2)	0.0111 (16)	0.0034 (15)	0.0160 (18)
C31	0.0196 (12)	0.0250 (14)	0.0156 (11)	-0.0032 (11)	0.0008 (9)	0.0026 (10)
C32	0.0243 (13)	0.0240 (13)	0.0193 (12)	0.0012 (11)	-0.0014 (10)	-0.0018 (11)
C33	0.0298 (14)	0.0240 (14)	0.0231 (13)	-0.0004 (11)	0.0011 (11)	0.0056 (11)
C34	0.0290 (14)	0.0255 (14)	0.0194 (12)	-0.0034 (12)	0.0036 (10)	-0.0012 (11)
C35	0.0214 (13)	0.0251 (14)	0.0226 (12)	0.0019 (11)	0.0006 (10)	-0.0016 (11)
C36	0.0203 (12)	0.0244 (14)	0.0173 (11)	-0.0002 (11)	-0.0018 (9)	-0.0016 (10)
C37	0.0298 (15)	0.0280 (15)	0.0298 (14)	0.0059 (12)	0.0059 (11)	0.0046 (12)
C38	0.0427 (19)	0.0468 (19)	0.0439 (18)	0.0132 (16)	-0.0075 (15)	0.0040 (15)
C39	0.0512 (18)	0.0303 (16)	0.0432 (16)	0.0136 (15)	0.0068 (17)	-0.0055 (14)
C40	0.0250 (13)	0.0247 (14)	0.0221 (13)	0.0026 (11)	0.0029 (10)	0.0024 (11)
C41	0.0328 (16)	0.0253 (15)	0.0313 (14)	-0.0007 (12)	0.0029 (12)	-0.0027 (12)
C42	0.0311 (15)	0.0336 (16)	0.0325 (14)	0.0075 (13)	-0.0027 (12)	0.0017 (12)
C43	0.0329 (16)	0.0317 (16)	0.0349 (15)	-0.0021 (13)	0.0144 (12)	0.0037 (13)
C44	0.0462 (18)	0.0438 (18)	0.0296 (15)	-0.0114 (14)	0.0043 (14)	0.0090 (14)
C45	0.0308 (16)	0.061 (2)	0.0475 (19)	-0.0125 (16)	-0.0042 (14)	0.0205 (17)
Cl1	0.0641 (6)	0.0443 (5)	0.0572 (5)	-0.0157 (5)	-0.0263 (5)	0.0151 (4)
O1	0.219 (4)	0.0507 (17)	0.085 (2)	-0.015 (2)	-0.022 (3)	0.0322 (16)
O2	0.0644 (19)	0.120 (3)	0.086 (2)	-0.0278 (17)	-0.0308 (16)	-0.002 (2)
O3	0.106 (3)	0.090 (2)	0.182 (4)	0.021 (2)	0.026 (3)	-0.016 (3)
O4	0.112 (3)	0.114 (3)	0.0653 (18)	-0.060 (2)	-0.0460 (18)	0.0211 (17)

Geometric parameters (Å, °)

P1—C1	1.807 (2)	C24—H24C	0.9800
P1—C16	1.808 (2)	C25—C27	1.517 (4)
P1—C31	1.814 (2)	C25—C26	1.533 (4)
P1—H1	1.37 (3)	C25—H25	1.0000

C1—C2	1.414 (3)	C26—H26A	0.9800
C1—C6	1.419 (4)	C26—H26B	0.9800
C2—C3	1.395 (3)	C26—H26C	0.9800
C2—C7	1.524 (4)	C27—H27A	0.9800
C3—C4	1.391 (4)	C27—H27B	0.9800
C3—H3	0.9500	C27—H27C	0.9800
C4—C5	1.379 (4)	C28—C30	1.517 (4)
C4—C13	1.503 (4)	C28—C29	1.525 (4)
C5—C6	1.390 (3)	C28—H28	1.0000
C5—H5	0.9500	C29—H29A	0.9800
C6—C10	1.513 (4)	C29—H29B	0.9800
C7—C9	1.519 (4)	C29—H29C	0.9800
C7—C8	1.532 (4)	C30—H30A	0.9800
C7—H7	1.0000	C30—H30B	0.9800
C8—H8A	0.9800	C30—H30C	0.9800
C8—H8B	0.9800	C31—C36	1.407 (3)
C8—H8C	0.9800	C31—C32	1.419 (3)
C9—H9A	0.9800	C32—C33	1.389 (3)
C9—H9B	0.9800	C32—C37	1.524 (3)
C9—H9C	0.9800	C33—C34	1.393 (4)
C10—C12	1.529 (4)	C33—H33	0.9500
C10—C11	1.530 (4)	C34—C35	1.385 (4)
C10—H10	1.0000	C34—C43	1.512 (4)
C11—H11A	0.9800	C35—C36	1.388 (3)
C11—H11B	0.9800	C35—H35	0.9500
C11—H11C	0.9800	C36—C40	1.522 (4)
C12—H12A	0.9800	C37—C39	1.523 (4)
C12—H12B	0.9800	C37—C38	1.534 (4)
C12—H12C	0.9800	C37—H37	1.0000
C13—C15	1.508 (4)	C38—H38A	0.9800
C13—C14	1.519 (5)	C38—H38B	0.9800
C13—H13	1.0000	C38—H38C	0.9800
C14—H14A	0.9800	C39—H39A	0.9800
C14—H14B	0.9800	C39—H39B	0.9800
C14—H14C	0.9800	C39—H39C	0.9800
C15—H15A	0.9800	C40—C42	1.527 (4)
C15—H15B	0.9800	C40—C41	1.539 (4)
C15—H15C	0.9800	C40—H40	1.0000
C16—C17	1.403 (3)	C41—H41A	0.9800
C16—C21	1.421 (3)	C41—H41B	0.9800
C17—C18	1.391 (3)	C41—H41C	0.9800
C17—C22	1.512 (3)	C42—H42A	0.9800
C18—C19	1.389 (4)	C42—H42B	0.9800
C18—H18	0.9500	C42—H42C	0.9800
C19—C20	1.385 (4)	C43—C44	1.518 (4)
C19—C28	1.516 (4)	C43—C45	1.530 (4)
C20—C21	1.385 (4)	C43—H43	1.0000
C20—H20	0.9500	C44—H44A	0.9800
C21—C25	1.531 (3)	C44—H44B	0.9800

C22—C24	1.520 (4)	C44—H44C	0.9800
C22—C23	1.531 (4)	C45—H45A	0.9800
C22—H22	1.0000	C45—H45B	0.9800
C23—H23A	0.9800	C45—H45C	0.9800
C23—H23B	0.9800	C11—O1	1.405 (3)
C23—H23C	0.9800	C11—O2	1.406 (3)
C24—H24A	0.9800	C11—O4	1.407 (3)
C24—H24B	0.9800	C11—O3	1.439 (4)
C1—P1—C16	117.98 (11)	C27—C25—C21	110.2 (3)
C1—P1—C31	111.95 (11)	C27—C25—C26	110.1 (3)
C16—P1—C31	119.91 (11)	C21—C25—C26	112.6 (2)
C1—P1—H1	99.3 (11)	C27—C25—H25	107.9
C16—P1—H1	98.4 (11)	C21—C25—H25	107.9
C31—P1—H1	104.5 (10)	C26—C25—H25	107.9
C2—C1—C6	121.1 (2)	C25—C26—H26A	109.5
C2—C1—P1	115.81 (19)	C25—C26—H26B	109.5
C6—C1—P1	123.06 (18)	H26A—C26—H26B	109.5
C3—C2—C1	118.0 (2)	C25—C26—H26C	109.5
C3—C2—C7	117.5 (2)	H26A—C26—H26C	109.5
C1—C2—C7	124.5 (2)	H26B—C26—H26C	109.5
C4—C3—C2	122.0 (3)	C25—C27—H27A	109.5
C4—C3—H3	119.0	C25—C27—H27B	109.5
C2—C3—H3	119.0	H27A—C27—H27B	109.5
C5—C4—C3	118.4 (2)	C25—C27—H27C	109.5
C5—C4—C13	119.3 (3)	H27A—C27—H27C	109.5
C3—C4—C13	122.0 (3)	H27B—C27—H27C	109.5
C4—C5—C6	123.2 (3)	C19—C28—C30	111.4 (2)
C4—C5—H5	118.4	C19—C28—C29	110.7 (2)
C6—C5—H5	118.4	C30—C28—C29	110.4 (2)
C5—C6—C1	117.2 (2)	C19—C28—H28	108.1
C5—C6—C10	118.3 (2)	C30—C28—H28	108.1
C1—C6—C10	124.4 (2)	C29—C28—H28	108.1
C9—C7—C2	111.3 (2)	C28—C29—H29A	109.5
C9—C7—C8	111.3 (3)	C28—C29—H29B	109.5
C2—C7—C8	112.0 (2)	H29A—C29—H29B	109.5
C9—C7—H7	107.3	C28—C29—H29C	109.5
C2—C7—H7	107.3	H29A—C29—H29C	109.5
C8—C7—H7	107.3	H29B—C29—H29C	109.5
C7—C8—H8A	109.5	C28—C30—H30A	109.5
C7—C8—H8B	109.5	C28—C30—H30B	109.5
H8A—C8—H8B	109.5	H30A—C30—H30B	109.5
C7—C8—H8C	109.5	C28—C30—H30C	109.5
H8A—C8—H8C	109.5	H30A—C30—H30C	109.5
H8B—C8—H8C	109.5	H30B—C30—H30C	109.5
C7—C9—H9A	109.5	C36—C31—C32	120.9 (2)
C7—C9—H9B	109.5	C36—C31—P1	121.60 (18)
H9A—C9—H9B	109.5	C32—C31—P1	115.93 (18)
C7—C9—H9C	109.5	C33—C32—C31	117.8 (2)

H9A—C9—H9C	109.5	C33—C32—C37	118.1 (2)
H9B—C9—H9C	109.5	C31—C32—C37	124.1 (2)
C6—C10—C12	111.4 (2)	C32—C33—C34	122.1 (2)
C6—C10—C11	112.3 (2)	C32—C33—H33	118.9
C12—C10—C11	110.3 (2)	C34—C33—H33	118.9
C6—C10—H10	107.5	C35—C34—C33	118.3 (2)
C12—C10—H10	107.5	C35—C34—C43	119.0 (2)
C11—C10—H10	107.5	C33—C34—C43	122.5 (2)
C10—C11—H11A	109.5	C34—C35—C36	122.4 (2)
C10—C11—H11B	109.5	C34—C35—H35	118.8
H11A—C11—H11B	109.5	C36—C35—H35	118.8
C10—C11—H11C	109.5	C35—C36—C31	118.0 (2)
H11A—C11—H11C	109.5	C35—C36—C40	117.4 (2)
H11B—C11—H11C	109.5	C31—C36—C40	124.5 (2)
C10—C12—H12A	109.5	C39—C37—C32	111.1 (2)
C10—C12—H12B	109.5	C39—C37—C38	110.2 (2)
H12A—C12—H12B	109.5	C32—C37—C38	111.1 (2)
C10—C12—H12C	109.5	C39—C37—H37	108.1
H12A—C12—H12C	109.5	C32—C37—H37	108.1
H12B—C12—H12C	109.5	C38—C37—H37	108.1
C4—C13—C15	115.1 (3)	C37—C38—H38A	109.5
C4—C13—C14	109.0 (2)	C37—C38—H38B	109.5
C15—C13—C14	110.8 (3)	H38A—C38—H38B	109.5
C4—C13—H13	107.2	C37—C38—H38C	109.5
C15—C13—H13	107.2	H38A—C38—H38C	109.5
C14—C13—H13	107.2	H38B—C38—H38C	109.5
C13—C14—H14A	109.5	C37—C39—H39A	109.5
C13—C14—H14B	109.5	C37—C39—H39B	109.5
H14A—C14—H14B	109.5	H39A—C39—H39B	109.5
C13—C14—H14C	109.5	C37—C39—H39C	109.5
H14A—C14—H14C	109.5	H39A—C39—H39C	109.5
H14B—C14—H14C	109.5	H39B—C39—H39C	109.5
C13—C15—H15A	109.5	C36—C40—C42	112.6 (2)
C13—C15—H15B	109.5	C36—C40—C41	110.9 (2)
H15A—C15—H15B	109.5	C42—C40—C41	109.6 (2)
C13—C15—H15C	109.5	C36—C40—H40	107.9
H15A—C15—H15C	109.5	C42—C40—H40	107.9
H15B—C15—H15C	109.5	C41—C40—H40	107.9
C17—C16—C21	120.7 (2)	C40—C41—H41A	109.5
C17—C16—P1	123.83 (18)	C40—C41—H41B	109.5
C21—C16—P1	115.24 (18)	H41A—C41—H41B	109.5
C18—C17—C16	118.1 (2)	C40—C41—H41C	109.5
C18—C17—C22	118.1 (2)	H41A—C41—H41C	109.5
C16—C17—C22	123.8 (2)	H41B—C41—H41C	109.5
C19—C18—C17	122.3 (2)	C40—C42—H42A	109.5
C19—C18—H18	118.9	C40—C42—H42B	109.5
C17—C18—H18	118.9	H42A—C42—H42B	109.5
C20—C19—C18	118.5 (2)	C40—C42—H42C	109.5
C20—C19—C28	120.8 (2)	H42A—C42—H42C	109.5

C18—C19—C28	120.8 (2)	H42B—C42—H42C	109.5
C21—C20—C19	122.2 (2)	C34—C43—C44	115.2 (2)
C21—C20—H20	118.9	C34—C43—C45	106.5 (2)
C19—C20—H20	118.9	C44—C43—C45	111.5 (2)
C20—C21—C16	118.2 (2)	C34—C43—H43	107.8
C20—C21—C25	118.1 (2)	C44—C43—H43	107.8
C16—C21—C25	123.7 (2)	C45—C43—H43	107.8
C17—C22—C24	112.3 (2)	C43—C44—H44A	109.5
C17—C22—C23	111.3 (2)	C43—C44—H44B	109.5
C24—C22—C23	111.2 (2)	H44A—C44—H44B	109.5
C17—C22—H22	107.2	C43—C44—H44C	109.5
C24—C22—H22	107.2	H44A—C44—H44C	109.5
C23—C22—H22	107.2	H44B—C44—H44C	109.5
C22—C23—H23A	109.5	C43—C45—H45A	109.5
C22—C23—H23B	109.5	C43—C45—H45B	109.5
H23A—C23—H23B	109.5	H45A—C45—H45B	109.5
C22—C23—H23C	109.5	C43—C45—H45C	109.5
H23A—C23—H23C	109.5	H45A—C45—H45C	109.5
H23B—C23—H23C	109.5	H45B—C45—H45C	109.5
C22—C24—H24A	109.5	O1—C11—O2	111.8 (2)
C22—C24—H24B	109.5	O1—C11—O4	110.4 (2)
H24A—C24—H24B	109.5	O2—C11—O4	109.4 (2)
C22—C24—H24C	109.5	O1—C11—O3	109.5 (3)
H24A—C24—H24C	109.5	O2—C11—O3	106.9 (2)
H24B—C24—H24C	109.5	O4—C11—O3	108.8 (3)
C16—P1—C1—C2	146.53 (17)	C17—C16—C21—C20	3.4 (4)
C31—P1—C1—C2	-68.1 (2)	P1—C16—C21—C20	-171.3 (2)
C16—P1—C1—C6	-32.0 (2)	C17—C16—C21—C25	-177.6 (2)
C31—P1—C1—C6	113.3 (2)	P1—C16—C21—C25	7.7 (3)
C6—C1—C2—C3	0.7 (3)	C18—C17—C22—C24	-69.6 (3)
P1—C1—C2—C3	-177.85 (18)	C16—C17—C22—C24	112.4 (3)
C6—C1—C2—C7	-178.2 (2)	C18—C17—C22—C23	55.8 (3)
P1—C1—C2—C7	3.2 (3)	C16—C17—C22—C23	-122.1 (3)
C1—C2—C3—C4	0.5 (4)	C20—C21—C25—C27	77.1 (3)
C7—C2—C3—C4	179.5 (2)	C16—C21—C25—C27	-101.8 (3)
C2—C3—C4—C5	-0.3 (4)	C20—C21—C25—C26	-46.2 (4)
C2—C3—C4—C13	-174.3 (2)	C16—C21—C25—C26	134.8 (3)
C3—C4—C5—C6	-1.2 (4)	C20—C19—C28—C30	-58.8 (3)
C13—C4—C5—C6	173.0 (3)	C18—C19—C28—C30	122.0 (3)
C4—C5—C6—C1	2.4 (4)	C20—C19—C28—C29	64.4 (3)
C4—C5—C6—C10	-175.8 (2)	C18—C19—C28—C29	-114.8 (3)
C2—C1—C6—C5	-2.1 (3)	C1—P1—C31—C36	-30.9 (2)
P1—C1—C6—C5	176.36 (19)	C16—P1—C31—C36	113.7 (2)
C2—C1—C6—C10	176.0 (2)	C1—P1—C31—C32	134.71 (18)
P1—C1—C6—C10	-5.5 (3)	C16—P1—C31—C32	-80.7 (2)
C3—C2—C7—C9	69.0 (3)	C36—C31—C32—C33	5.8 (3)
C1—C2—C7—C9	-112.1 (3)	P1—C31—C32—C33	-159.94 (19)
C3—C2—C7—C8	-56.4 (3)	C36—C31—C32—C37	-175.0 (2)

C1—C2—C7—C8	122.6 (3)	P1—C31—C32—C37	19.2 (3)
C5—C6—C10—C12	-75.3 (3)	C31—C32—C33—C34	0.3 (4)
C1—C6—C10—C12	106.6 (3)	C37—C32—C33—C34	-178.9 (2)
C5—C6—C10—C11	48.9 (3)	C32—C33—C34—C35	-5.7 (4)
C1—C6—C10—C11	-129.2 (3)	C32—C33—C34—C43	169.8 (2)
C5—C4—C13—C15	135.5 (3)	C33—C34—C35—C36	5.4 (4)
C3—C4—C13—C15	-50.6 (4)	C43—C34—C35—C36	-170.3 (2)
C5—C4—C13—C14	-99.5 (3)	C34—C35—C36—C31	0.5 (4)
C3—C4—C13—C14	74.5 (4)	C34—C35—C36—C40	-177.0 (2)
C1—P1—C16—C17	113.2 (2)	C32—C31—C36—C35	-6.2 (3)
C31—P1—C16—C17	-29.3 (3)	P1—C31—C36—C35	158.77 (18)
C1—P1—C16—C21	-72.3 (2)	C32—C31—C36—C40	171.1 (2)
C31—P1—C16—C21	145.16 (19)	P1—C31—C36—C40	-24.0 (3)
C21—C16—C17—C18	-3.5 (4)	C33—C32—C37—C39	67.4 (3)
P1—C16—C17—C18	170.7 (2)	C31—C32—C37—C39	-111.7 (3)
C21—C16—C17—C22	174.4 (2)	C33—C32—C37—C38	-55.6 (3)
P1—C16—C17—C22	-11.3 (4)	C31—C32—C37—C38	125.2 (3)
C16—C17—C18—C19	1.1 (4)	C35—C36—C40—C42	-62.3 (3)
C22—C17—C18—C19	-177.0 (2)	C31—C36—C40—C42	120.5 (3)
C17—C18—C19—C20	1.3 (4)	C35—C36—C40—C41	60.9 (3)
C17—C18—C19—C28	-179.5 (3)	C31—C36—C40—C41	-116.4 (3)
C18—C19—C20—C21	-1.4 (4)	C35—C34—C43—C44	-149.6 (3)
C28—C19—C20—C21	179.4 (3)	C33—C34—C43—C44	34.9 (4)
C19—C20—C21—C16	-0.9 (4)	C35—C34—C43—C45	86.2 (3)
C19—C20—C21—C25	-179.9 (3)	C33—C34—C43—C45	-89.3 (3)

Pyramidal index in triarylphosphonium ion structures

Aryl group	CSD refcode	$\Sigma(\text{C—P—C})$ (°)	Reference
Ph ₃ PPH ⁺	ABERAA	332.7 (5)	Junk & Atwood (1999)
Ph ₃ PPH ⁺	BARVUL	334 (3)	Boorman <i>et al.</i> (1981)
Ph ₃ PPH ⁺	KAXQUQ	333.0 (6)	Hagenbach & Abram (2005)
(2,4,6-MeOC ₆ H ₂) ₃ PPH ⁺	LAFGEE10	338.9 (5)	Dunbar & Quillevère (1993)
(2,4,6-MeOC ₆ H ₂) ₃ PPH ⁺	TAJGAM	342.3 (6)	Dunbar & Pence (1991)
(2,4,6-MeOC ₆ H ₂) ₃ PPH ⁺	WIBJEW	337.5 (9)	Dunbar & Quillevère (1993)
(2,4,6-MeOC ₆ H ₂) ₃ PPH ⁺	WIBJIA	343.0 (7)	Dunbar & Quillevère (1993)
Mes ₃ PPH ⁺	LUWPOJ	345.3 (5)	Ménard & Stephan (2010)
Mes ₃ PPH ⁺	QUHCAY	345.6 (6)	Jiang <i>et al.</i> (2009)
Mes ₃ PPH ⁺	XALCUK	345.1 (6)	Schäfer <i>et al.</i> (2011)
Tripp ₃ PPH ⁺		349.9 (6)	This work