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Two Trimethylphenylphosphonium Iodides

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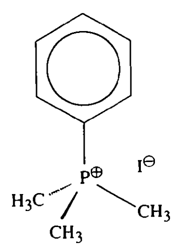
Abstract

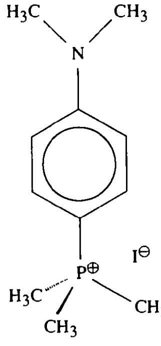
The structures of trimethylphenylphosphonium iodide, $C_9H_{14}P^+.I^-$, and (*p*-dimethylaminophenyl)trimethylphosphonium iodide, $C_{11}H_{19}NP^+.I^-$, have been determined at 100 K in order to study the substituent perturbation of the trimethylphosphonium group and the additional effect of a *p*-dimethylamino group. Trimethylphenylphosphonium iodide crystallizes in the orthorhombic space group $Pca2_1$ with two independent molecules in the asymmetric unit. The *p*-dimethylamino-substituted compound has a planar amino group with an N—C(phenyl) bond distance in the double-bond range. Both structures contain short C—H···I distances below the sum of the van der Waals radii.

Comment

Quaternary phosphonium salts and phosphabetaines are common reagents in the Wittig olefin synthesis. Phosphine oxides resulting from phosphonium salts can be removed as an insoluble complex with lithium halide in ether solution. For *p*-dimethylaminophenyl-substituted phosphonium salts, the separation of the resulting phosphine oxide is facilitated by utilization of their solubility in dilute acid (Trippett & Walker, 1961). Trimethylphenylphosphonium iodide, (I), was chosen in order to study its ring geometry and, consequently, the acceptor or donor effect of the trimethylphosphonium group, which is indicated by the deviation of the *ipso* angle from 120° (Domenicano, 1989). The structures of (I) and (*p*-dimethylaminophenyl)trimethylphosphonium iodide, (II), were determined. Only one trimethylphosphonium salt is reported in the Cambridge Structural Database (1992), the decachlorotantalate (Cotton & Najjar, 1981). However, the phenyl ring geometry was not determined exactly and, therefore, no conclusion is provided concerning substituent effects.



(I)



(II)

The phosphonium iodide (I) does not show any significant perturbation of the phenyl ring and, therefore, the trimethylphosphonium substituent exhibits neither a donor nor an acceptor effect. Insertion of the electron-donating *p*-dimethylamino group in (II) causes only a slight change in the ring geometry but a significant flattening of the N-atom environment. Both *ipso* angles are reduced [117.7 (2) and 117.6 (2)°] and the phenyl ring is elongated. The N—C(phenyl) bond length is 1.373 (3) Å and, therefore, within the double-bond range, whereas the P—C(phenyl) distance of 1.797 (6) Å represents a single bond. The sum of these structural changes suggests the existence of a substituent push–pull effect. Hence, our results are in satisfactory agreement with spectroscopic measurements (Schiemenz, 1964), which show only a small effect for compound (I) but a strong bathochromic effect after dimethylamino substitution. Views of (I) and (II) are shown in Figs. 1 and 2, respectively.

The packing of both crystal structures is dominated by short C—H···I contacts with a minimum distance of 2.99 (2) Å (Tables 3 and 6), about 0.35 Å lower than the sum of the van der Waals radii [r(I) + r(H) = 2.15 + 1.20 = 3.35 Å (Pauling, 1960)]. In both cases, the I^- ions are positioned almost symmetrically above the triangle formed by the trimethylphosphonium group, and one C—H bond of each methyl group is directed towards

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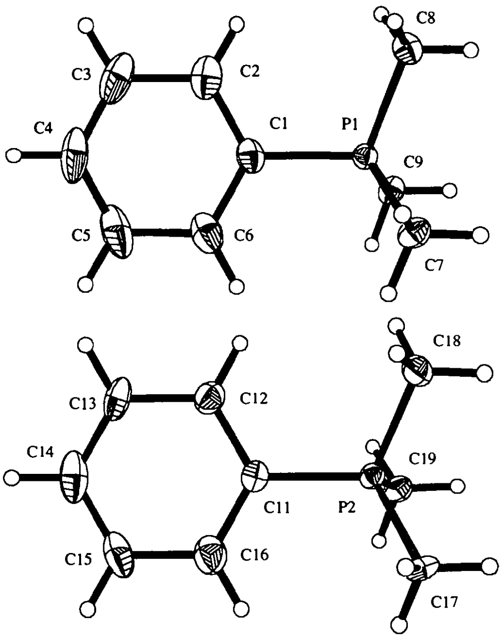

Fig. 1. View of the two independent molecules of (I) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels.

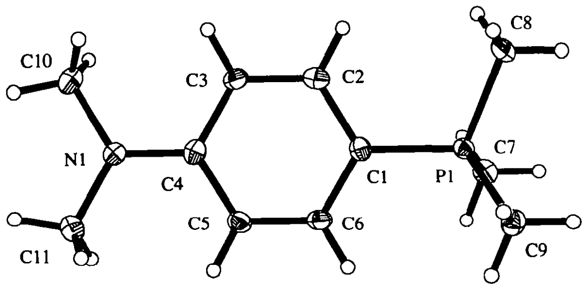

Fig. 2. View of (II) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels.

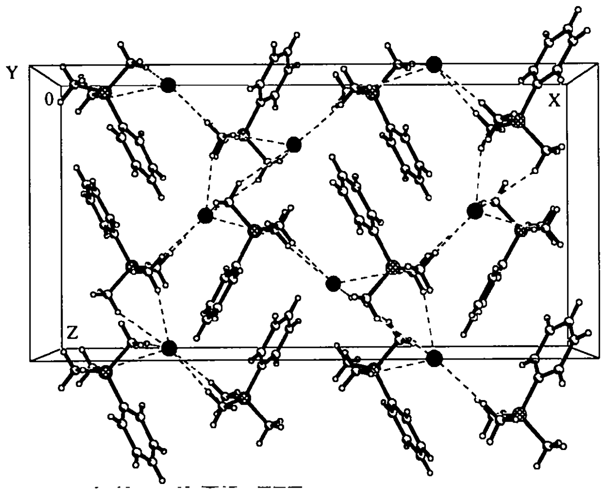

Fig. 3. Packing diagram of (I) along the *b* direction showing intermolecular C—H···I contacts as dotted lines. I atoms are represented by filled circles, C atoms by open circles and P atoms by latticed circles.

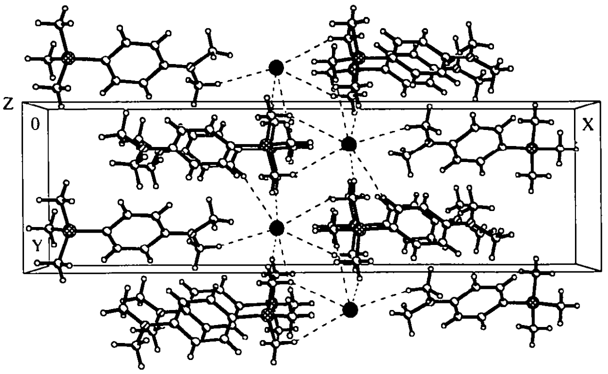

Fig. 4. Packing diagram of (II) along the *a* direction showing intermolecular C—H···I contacts as dotted lines. I atoms are represented by filled circles, C atoms by open circles, P atoms by latticed circles and N atoms by lined circles.

the I^- ion (Fig. 3). In the substituted compound (II), there is an additional contact between a C—H bond of the dimethylamino group and an I^- ion, thus forming a linear chain of alternating anions and cations (Fig. 4).

Experimental

The preparation of trimethylphenylphosphonium iodide was based on the method of Michaelis (1876) using dioxane as solvent. Single crystals were obtained from ethanol solution in an *n*-hexane atmosphere at room temperature. For the preparation of (*p*-dimethylaminophenyl)trimethylphosphonium iodide, methyl iodide in toluene solution was added dropwise to a stirred toluene solution of *p*-dimethylphosphino-*N*,*N*-dimethylaniline, which can be obtained readily by the method of Kaim & Bock (1978).

Compound (I)

Crystal data

$C_9H_{14}P^+.I^-$
$M_r = 280.07$
Orthorhombic
$Pca2_1$
$a = 24.699\,(2)$ Å
$b = 7.343\,(1)$ Å
$c = 12.748\,(2)$ Å
$V = 2312.0\,(5)$ Å^3
$Z = 8$
$D_x = 1.609$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 78 reflections
$\theta = 12.5–17°$
$\mu = 2.86$ mm^{-1}
$T = 100\,(2)$ K
Transparent block
0.3 × 0.1 × 0.1 mm
Colourless

Data collection

Siemens Stoe AED-2 four-circle diffractometer
ω–θ scans
Absorption correction: ψ-scan
$T_{\min} = 0.67$, $T_{\max} = 0.80$
3422 measured reflections
3360 independent reflections
2787 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0126$
$\theta_{\max} = 29.05°$
$h = 0 \rightarrow 33$
$k = -2 \rightarrow 8$
$l = -12 \rightarrow 17$
4 standard reflections frequency: 120 min intensity decay: negligible

Refinement

Refinement on F^2
$R(F) = 0.0201$
$wR(F^2) = 0.0507$
$S = 1.039$
3360 reflections
222 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 0.1730P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.511$ e Å^{-3}
$\Delta\rho_{\min} = -0.468$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00113 (7)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (I)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
I1	0.713940 (12)	−0.04821 (4)	1.00000 (2)	0.01939 (7)
P1	0.63926 (6)	−0.0203 (2)	0.69083 (11)	0.0173 (3)
C1	0.6049 (2)	−0.0274 (7)	0.5666 (5)	0.0239 (11)
C2	0.6038 (2)	−0.1887 (8)	0.5088 (5)	0.0320 (11)
C3	0.5764 (2)	−0.1922 (10)	0.4121 (5)	0.042 (2)
C4	0.5507 (3)	−0.0398 (10)	0.3775 (5)	0.044 (2)
C5	0.5507 (2)	0.1183 (11)	0.4334 (5)	0.045 (2)
C6	0.5781 (2)	0.1273 (9)	0.5308 (4)	0.0335 (14)
C7	0.6815 (2)	0.1766 (7)	0.6964 (4)	0.0222 (11)
C8	0.6786 (2)	−0.2219 (7)	0.7091 (4)	0.0219 (11)
C9	0.5913 (2)	−0.0030 (7)	0.7958 (4)	0.0208 (11)
I2	0.463856 (13)	0.49905 (4)	0.25334 (2)	0.02048 (7)
P2	0.38875 (5)	0.5460 (2)	0.56215 (10)	0.0161 (3)
C11	0.3546 (2)	0.5689 (7)	0.6861 (4)	0.0178 (10)
C12	0.3508 (2)	0.7391 (7)	0.7334 (4)	0.0255 (11)
C13	0.3237 (2)	0.7553 (9)	0.8306 (5)	0.0339 (15)
C14	0.3007 (2)	0.6047 (10)	0.8765 (5)	0.0351 (14)
C15	0.3039 (3)	0.4373 (9)	0.8293 (5)	0.0362 (15)
C16	0.3302 (2)	0.4188 (8)	0.7320 (4)	0.0322 (13)
C17	0.4240 (2)	0.3345 (6)	0.5568 (4)	0.0216 (11)
C18	0.4360 (2)	0.7294 (7)	0.5450 (4)	0.0224 (11)
C19	0.3405 (2)	0.5501 (7)	0.4584 (4)	0.0206 (11)

Table 2. *Selected geometric parameters* (Å, °) *for* (I)

P1—C7	1.785 (5)	P2—C19	1.780 (6)
P1—C8	1.786 (5)	P2—C17	1.782 (5)
P1—C9	1.792 (6)	P2—C18	1.796 (5)
P1—C1	1.797 (6)	P2—C11	1.799 (5)
C1—C6	1.392 (7)	C11—C16	1.385 (7)
C1—C2	1.395 (7)	C11—C12	1.390 (7)
C2—C3	1.407 (8)	C12—C13	1.415 (7)
C3—C4	1.360 (9)	C13—C14	1.374 (9)
C4—C5	1.362 (9)	C14—C15	1.371 (9)
C5—C6	1.415 (8)	C15—C16	1.406 (8)
C7—P1—C8	110.4 (3)	C19—P2—C17	108.3 (2)
C7—P1—C9	107.5 (2)	C19—P2—C18	109.4 (2)
C8—P1—C9	108.7 (2)	C17—P2—C18	109.3 (3)
C7—P1—C1	109.5 (2)	C19—P2—C11	109.7 (2)
C8—P1—C1	110.4 (3)	C17—P2—C11	110.1 (2)
C9—P1—C1	110.3 (3)	C18—P2—C11	110.0 (2)
C6—C1—C2	120.7 (6)	C16—C11—C12	120.2 (5)
C6—C1—P1	119.3 (4)	C16—C11—P2	120.0 (4)
C2—C1—P1	119.9 (4)	C12—C11—P2	119.7 (4)
C1—C2—C3	119.2 (6)	C11—C12—C13	119.2 (5)
C4—C3—C2	119.6 (6)	C14—C13—C12	120.1 (6)
C3—C4—C5	122.0 (7)	C15—C14—C13	120.7 (6)
C4—C5—C6	120.0 (6)	C14—C15—C16	120.1 (6)
C1—C6—C5	118.5 (6)	C11—C16—C15	119.7 (6)

Table 3. H· · ·I *distances* (Å) *in* (I)

I1· · ·H7B^{i}	3.07 (3)	I2· · ·H6$^{\text{iii}}$	3.204 (6)
I1· · ·H8C^{i}	3.09 (3)	I2· · ·H9A^{iv}	3.01 (3)
I1· · ·H8B	3.125 (6)	I2· · ·H9B^{iii}	3.03 (2)
I1· · ·H9C	3.115 (6)	I2· · ·H17A^{iii}	3.05 (4)
I1· · ·H17C^{ii}	3.19 (3)	I2· · ·H18A^{iii}	3.17 (3)
I1· · ·H19A^{v}	2.99 (2)	I2· · ·H19C	3.136 (6)
I1· · ·H19B^{ii}	3.04 (1)		

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

Compound (II)

Crystal data

$C_{11}H_{19}NP^+.I^-$
$M_r = 323.14$
Monoclinic
$P2_1/c$
$a = 6.033$ (1) Å
$b = 8.048$ (1) Å
$c = 27.348$ (5) Å
$\beta = 91.30$ (2)°
$V = 1327.5$ (4) Å^3
$Z = 4$
$D_x = 1.617$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 36 reflections
$\theta = 10.5$–18.5°
$\mu = 2.50$ mm^{-1}
$T = 100$ (2) K
Transparent block
0.54 × 0.36 × 0.27 mm
Colourless

Data collection

Siemens Stoe AED-2 four-circle diffractometer
ω–θ scans
Absorption correction: numerical
$T_{\min} = 0.41$, $T_{\max} = 0.53$
3919 measured reflections
2760 independent reflections
2112 observed reflections [$I > 2\sigma(I)$]

$R_{\text{int}} = 0.0144$
$\theta_{\max} = 26.52°$
$h = -5 \rightarrow 7$
$k = 0 \rightarrow 10$
$l = -34 \rightarrow 34$
3 standard reflections
frequency: 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R(F) = 0.0213$
$wR(F^2) = 0.0555$
$S = 1.024$
2760 reflections
137 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0290P)^2 + 0.3450P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.713$ e Å^{-3}
$\Delta\rho_{\min} = -0.707$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0011 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
I1	0.31305 (2)	0.74193 (2)	−0.066027 (5)	0.01593 (7)
P1	0.03771 (10)	0.75084 (6)	0.08052 (2)	0.01311 (13)
N1	−0.3177 (4)	0.7794 (3)	0.28335 (7)	0.0190 (4)
C1	−0.0665 (4)	0.7576 (2)	0.14100 (9)	0.0147 (5)
C2	0.0262 (4)	0.6613 (3)	0.17896 (9)	0.0182 (5)

C3	−0.0515 (4)	0.6706 (3)	0.22626 (9)	0.0172 (5)
C4	−0.2326 (4)	0.7744 (3)	0.23723 (9)	0.0154 (5)
C5	−0.3234 (4)	0.8731 (3)	0.19891 (9)	0.0171 (5)
C6	−0.2405 (4)	0.8648 (3)	0.15238 (9)	0.0171 (5)
C7	0.1977 (4)	0.9331 (3)	0.06816 (10)	0.0189 (5)
C8	0.2104 (4)	0.5727 (3)	0.07349 (10)	0.0195 (5)
C9	−0.1867 (4)	0.7432 (3)	0.03677 (9)	0.0183 (5)
C10	−0.2044 (4)	0.6942 (3)	0.32375 (9)	0.0225 (5)
C11	−0.5154 (4)	0.8768 (3)	0.29290 (10)	0.0226 (6)

Table 5. *Selected geometric parameters* (Å, °) *for* (II)

P1—C1	1.784 (2)	C1—C6	1.400 (3)
P1—C8	1.785 (2)	C1—C2	1.401 (3)
P1—C9	1.788 (2)	C2—C3	1.388 (3)
P1—C7	1.793 (2)	C3—C4	1.413 (3)
N1—C4	1.373 (3)	C4—C5	1.415 (3)
N1—C11	1.456 (3)	C5—C6	1.379 (3)
N1—C10	1.457 (3)		
C1—P1—C8	110.1 (1)	C6—C1—P1	120.5 (2)
C1—P1—C9	110.1 (1)	C2—C1—P1	121.8 (2)
C8—P1—C9	109.6 (1)	C3—C2—C1	121.6 (2)
C1—P1—C7	110.7 (1)	C2—C3—C4	120.6 (2)
C8—P1—C7	108.6 (1)	N1—C4—C3	121.3 (2)
C9—P1—C7	107.8 (1)	N1—C4—C5	121.1 (2)
C4—N1—C11	120.4 (2)	C3—C4—C5	117.6 (2)
C4—N1—C10	120.3 (2)	C6—C5—C4	120.9 (2)
C11—N1—C10	119.3 (2)	C5—C6—C1	121.6 (2)
C6—C1—C2	117.7 (2)		

Table 6. H· · ·I *distances* (Å) *in* (II)

I1· · ·H7*A*	3.163 (3)	I1· · ·H8*B*^{ii}	3.163 (3)
I1· · ·H8*A*	3.235 (3)	I1· · ·H9*C*^{ii}	3.178 (2)
I1· · ·H6^{i}	3.105 (2)	I1· · ·H11*A*^{iii}	3.164 (3)
I1· · ·H7*C*^{i}	3.107 (3)		

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

For both (I) and (II), all H atoms were located by a difference synthesis but positioned geometrically and refined with free isotropic displacement parameters using a riding model. The two independent molecules of (I) differ significantly in the torsion angle of their trimethylphosphonium group [C8—P1—C1—C2 10.9 (5) and C18—P2—C11—C12 23.7 (5)°, respectively; see Fig. 1]. The Flack (1983) absolute-structure parameter converged to χ = 0.18 (3) and, therefore, the absolute structure cannot be determined successfully. Origin constraints were generated automatically by the program of Flack & Schwarzenbach (1988).

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1988*a*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1988*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL*/*PC XP* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*93 *CIFTAB*.

This project is supported by the Deutsche Forschungsgemeinschaft, the State of Hesse, the Fonds der Chemischen Industrie and the A. Messer Foundation.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: JZ1022). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Acetamidocyclohexanone Semicarbazone Dihydrate

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Abstract

The cyclohexane ring of the title molecule, $C_9H_{16}N_4O_2.2H_2O$, adopts a slightly distorted chair conformation. The $NHCONH_2$ group has a conformation in which the C═O bond is *trans* with respect to the N—N bond. The molecules in the crystal are linked by hydrogen bonding involving the $NHCONH_2$ group, the acetamido group and the water molecules.

Comment

This investigation is part of systematic studies of 4-*R*-substituted cyclohexanone semicarbazone derivatives. The X-ray structures of derivatives with *R* = H and *R* = *tert*-butyl (Di Maio, Li, Portalone, Zhou, Marciante

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