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## Dimethyldiphenylphosphonium Iodide, [PPh<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>.I<sup>-</sup>, and Dimethyldiphenylphosphonium Bromide, [PPh<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>.Br<sup>-</sup>

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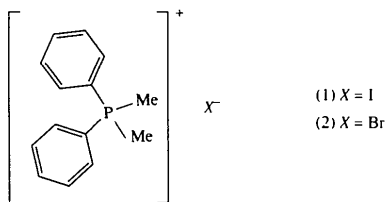
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### Abstract

Each of the title compounds, C<sub>14</sub>H<sub>16</sub>P<sup>+</sup>.I<sup>-</sup> (1) and C<sub>14</sub>H<sub>16</sub>P<sup>+</sup>.Br<sup>-</sup> (2), crystallized with the typical tetrahedral phosphorus center [the CH<sub>3</sub>—P—CH<sub>3</sub> angle is 109.0 for (1) and 110.3° for (2)] having no interactions with the associated anion. As expected, the two compounds are isostructural and essentially identical.

### Comment

No crystal structure containing the dimethyldiphenylphosphonium cation has been reported previously. Our use of this cation as a precursor to ylide ligands has prompted its crystal structure determination (Raptis, Murray, Staples, Porter & Fackler, 1993). We report here the structures of its iodide and bromide compounds, [PPh<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>.I<sup>-</sup>, (1), and [PPh<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>.Br<sup>-</sup>, (2).



Several studies have employed the tetraalkylphosphonium cation in an attempt to structurally characterize the associated anion. The greatest number of these use the tetraphenylphosphonium cation (see, *e.g.*, Sheldrick, Roesky, Schmieder, Isenberg & Sheldrick, 1982; Secheresse, Lavigne, Jeannin & Lefebvre, 1981; Coucouvanis, Stremple & Baenziger, 1981; Bates & Waters, 1985). The use of the methyltriphenylphosphonium cation has also been reported (see, *e.g.*, Holmes, Day, Holmes & Sau, 1982; Lewis, Braga, Henrick, Johnson, McPartlin, Nelson & Vargas, 1982; Cramer, Ho, Doorne, Ibers, Norton & Kashivagi, 1981). These reports reveal no unusual features of the cation and our structures are comparable with them. Fig. 1 shows the iodide complex with the atomic labeling scheme and Fig. 2 shows a stereopacking diagram.

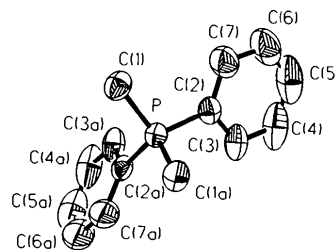


Fig. 1. A drawing of [PPh<sub>2</sub>Me<sub>2</sub>]<sup>+</sup>.I<sup>-</sup> with 50% displacement ellipsoids showing the atomic labeling scheme.

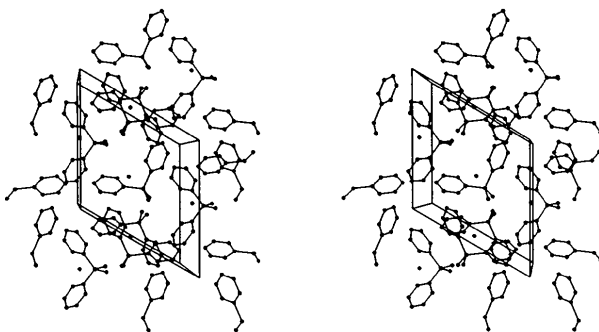


Fig. 2. Stereopacking diagram of [PPh<sub>2</sub>Me<sub>2</sub>]<sup>+</sup>.I<sup>-</sup> viewed along the *c* axis.

### Experimental

Compounds (1) and (2) were prepared by the reaction of CH<sub>3</sub>I and CH<sub>3</sub>Br, respectively, with methylphenylphosphine, as reported previously (Basil, 1983). The compounds were crystallized from a dry CH<sub>2</sub>Cl<sub>2</sub> solution into which dry diethyl ether was allowed to diffuse. This resulted in colorless crystals of the title compounds.

#### Compound (1)

##### Crystal data

C<sub>14</sub>H<sub>16</sub>P<sup>+</sup>.I<sup>-</sup>

*M<sub>r</sub>* = 342.159

Hexagonal

*P*6<sub>5</sub>22

*a* = 11.790 (6) Å

*c* = 18.373 (4) Å

*V* = 2212 (2) Å<sup>3</sup>

*Z* = 6

*D<sub>x</sub>* = 1.54 Mg m<sup>-3</sup>

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 12.5–15°

μ = 2.229 mm<sup>-1</sup>

*T* = 296 K

Thin plate needle

0.3 × 0.2 × 0.08 mm

Colorless

##### Data collection

R3m/E diffractometer

Wyckoff scans

Absorption correction:

empirical

*T<sub>min</sub>* = 0.623, *T<sub>max</sub>* =

0.999

3175 measured reflections

973 independent reflections

904 observed reflections

[*F<sub>o</sub>*<sup>2</sup> > 2σ(*F<sub>o</sub>*<sup>2</sup>)]

*R<sub>int</sub>* = 0.0170

θ<sub>max</sub> = 22.5°

*h* = -12 → 11

*k* = 0 → 12

*l* = -19 → 0

3 standard reflections

monitored every 97

reflections

intensity decay: none

## Refinement

Refinement on  $F$   
 $R = 0.0210$   
 $wR = 0.0242$   
 $S = 1.13$   
 904 reflections  
 74 parameters  
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o) + 0.0002F_o^2]$   
 $(\Delta/\sigma)_{\max} = 0.019$   
 $\Delta\rho_{\max} = 0.32 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.38 \text{ e } \text{Å}^{-3}$   
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

## Compound (2)

## Crystal data

$\text{C}_{14}\text{H}_{16}\text{P}^+ \cdot \text{Br}^-$   
 $M_r = 295.158$   
 Hexagonal  
 $P6_522$   
 $a = 11.603 (2) \text{ Å}$   
 $c = 17.968 (5) \text{ Å}$   
 $V = 2094.9 (9) \text{ Å}^3$   
 $Z = 6$   
 $D_x = 1.40 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ Å}$   
 Cell parameters from 25  
 reflections  
 $\theta = 12.5\text{--}15^\circ$   
 $\mu = 3.00 \text{ mm}^{-1}$   
 $T = 296 \text{ K}$   
 Thin needle  
 $0.1 \times 0.08 \times 0.05 \text{ mm}$   
 Colorless

## Data collection

R3m/E diffractometer  
 Wyckoff scans  
 Absorption correction:  
 empirical  
 $T_{\min} = 0.781$ ,  $T_{\max} = 0.908$   
 2464 measured reflections  
 924 independent reflections  
 757 observed reflections  
 $[F_o^2 > 2\sigma(F_o^2)]$

$R_{\text{int}} = 0.0265$   
 $\theta_{\max} = 22.5^\circ$   
 $h = -10 \rightarrow 0$   
 $k = 0 \rightarrow 12$   
 $l = -19 \rightarrow 19$   
 3 standard reflections  
 monitored every 97  
 reflections  
 intensity decay:  $<5\%$

## Refinement

Refinement on  $F$   
 $R = 0.0390$   
 $wR = 0.0464$   
 $S = 1.02$   
 757 reflections  
 74 parameters  
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o) + 0.00100F_o^2]$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.51 \text{ e } \text{Å}^{-3}$   
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2$ ) for (1)

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

	x	y	z	$U_{\text{eq}}$
I	0.4704 (1)	0	0	0.065 (1)
P	0.4262 (1)	0.8525 (1)	1/4	0.038 (1)
C(1)	0.3901 (4)	0.7522 (3)	0.1723 (2)	0.056 (2)
C(2)	0.3560 (4)	0.9565 (3)	0.2434 (2)	0.046 (2)
C(3)	0.3947 (4)	1.0567 (4)	0.2937 (3)	0.064 (2)
C(4)	0.3419 (6)	1.1375 (5)	0.2920 (4)	0.095 (3)
C(5)	0.2506 (7)	1.1179 (7)	0.2410 (4)	0.113 (5)
C(6)	0.2103 (6)	1.0198 (7)	0.1916 (3)	0.108 (5)
C(7)	0.2633 (5)	0.9366 (5)	0.1926 (3)	0.078 (3)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2$ ) for (2)

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

	x	y	z	$U_{\text{eq}}$
Br	0.4703 (1)	0	0	0.064 (1)
P	0.4270 (1)	0.8540 (2)	1/4	0.032 (1)
C(1)	0.3837 (6)	0.7530 (6)	0.1691 (3)	0.055 (3)
C(2)	0.3557 (6)	0.9597 (5)	0.2469 (3)	0.040 (3)
C(3)	0.4009 (7)	1.0639 (6)	0.2969 (4)	0.059 (3)
C(4)	0.3491 (10)	1.1475 (7)	0.2960 (6)	0.102 (6)
C(5)	0.2516 (12)	1.1224 (11)	0.2448 (6)	0.127 (10)
C(6)	0.2067 (11)	1.0240 (12)	0.1958 (5)	0.128 (10)
C(7)	0.2587 (8)	0.9395 (9)	0.1968 (4)	0.083 (5)

Table 3. Bond lengths ( $\text{Å}$ ) and angles ( $^\circ$ ) for (1) and (2)

	(1)	(2)
P—C(1)	1.764 (4)	1.774 (6)
P—C(2)	1.794 (5)	1.791 (8)
C(2)—C(3)	1.385 (6)	1.382 (9)
C(2)—C(7)	1.366 (7)	1.37 (1)
C(3)—C(4)	1.374 (9)	1.37 (1)
C(4)—C(5)	1.36 (1)	1.37 (2)
C(5)—C(6)	1.36 (1)	1.33 (1)
C(6)—C(7)	1.40 (1)	1.39 (2)
C(1)—P—C(2)	111.4 (2)	110.6 (3)
C(1)—P—C(1')	109.0 (2)	110.2 (4)
C(2)—P—C(1')	108.8 (2)	109.1 (3)
C(1)—P—C(2')	108.9 (2)	109.1 (3)
C(2)—P—C(2')	107.4 (2)	107.2 (4)
C(1')—P—C(2')	111.4 (2)	110.6 (3)
P—C(2)—C(3)	118.1 (4)	118.4 (6)
P—C(2)—C(7)	122.1 (4)	121.7 (6)
C(3)—C(2)—C(7)	119.8 (5)	119.9 (8)
C(2)—C(3)—C(4)	120.4 (5)	120.1 (7)
C(3)—C(4)—C(5)	119.6 (6)	117.7 (9)
C(4)—C(5)—C(6)	121.2 (9)	124 (1)
C(5)—C(6)—C(7)	120.0 (7)	119 (1)
C(2)—C(7)—C(6)	119.1 (5)	120.0 (8)

Symmetry code: (i)  $y - x, y, \frac{1}{2} - z$ .

The *SHELXTL* (Sheldrick, 1985) program package was used for crystallographic computations.

These studies have been supported by the National Science Foundation and the Welch Foundation.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles for compounds (1) and (2), and a displacement ellipsoid drawing of (2) have been deposited with the IUCr (Reference: HR1009). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Methyl Austrocorticate†

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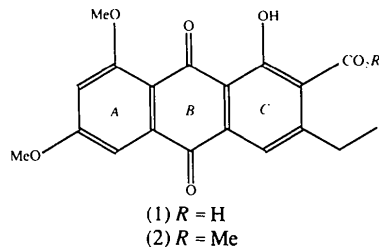
### Abstract

The crystal and molecular structure of methyl austrocorticate (methyl 3-ethyl-1-hydroxy-6,8-dimethoxy-9,10-dioxoanthracene-2-carboxylate, C<sub>20</sub>H<sub>18</sub>O<sub>7</sub>) has been determined. Crystals of the naturally derived material were found to be twinned, whereas the crystals of the totally synthetic material showed no evidence of twinning. The three six-membered rings and the two methoxy groups are almost coplanar, while the orientation of the methyl ester group is almost perpendicular to the ring plane.

### Comment

Austrocorticinic acid (3-ethyl-1-hydroxy-6,8-dimethoxy-9,10-dioxoanthracene-2-carboxylic acid) (1) is one of five unique anthraquinones isolated from the fruit bodies of an indigenous Australian toadstool that contain a C<sub>2</sub> side chain at C3 in the anthraquinone nucleus (Gill & Gimenez, 1988, 1990). The biogenetic origin of these quinones, which involves a propionate-initiated octaketide, has no precedent in nature (Gill & Gimenez, 1990). While the natural product (1) did not form crystals suitable for X-ray analysis, its methyl ester, methyl austrocorticate (methyl 3-ethyl-1-hydroxy-6,8-dimethoxy-9,10-dioxoanthracene-2-carboxylate), (2), gave orange-red needles, m.p. 483–485 K, from ethyl acetate–light petroleum. Methyl austrocorticate (2) has also been prepared by total synthesis (Cotterill & Gill, 1994) and gave yellow–orange needles, m.p. 462–463 K, from ethyl acetate–light petroleum. Although the spectroscopic data (NMR, IR, UV, mass spectra) of the ‘natural’ and the ‘synthetic’ ester (2) were identical, there were clear differences between the colours and the melting

points of the two samples. Therefore a crystal structure analysis was carried out on both samples of the ester (2) to confirm the assigned structure, and to see whether there were any differences between the two materials.



The intensity data collected from a crystal of the entirely synthetic material were found to have *2/m* symmetry, despite  $\beta$  being close to 90°, and showed the systematic absences  $h0l: l = 2n + 1$  and  $0k0: k = 2n + 1$ , defining the space group as *P2<sub>1</sub>/c*, for which a satisfactory solution was found. The crystals of the naturally derived material also showed the same systematic absences and gave similar cell parameters; however, intensity measurements indicated that many of the crystals were subject to varying degrees of twinning, including some where the intensity data showed almost *mmm* symmetry. Eventually, a crystal was found that showed only slight twinning, the intensity data giving an identical structure to that obtained from the totally synthetic material. Only the structure derived from the ‘synthetic’ crystal is reported.

The only difference between the two samples is that the crystals of the ‘natural’ material were found to be twinned, whereas the structural analysis, and intensity measurements on several other crystals of the ‘synthetic’ material, did not show any evidence of twinning. The bond lengths and angles found here compare well with those reported for similar structures, such as 7-methoxy-2-methyl-4,5-dihydroxy-9,10-anthracenedione (Ulický, Kožíšek & Ječný, 1991). In particular, O(9) is involved in a strong intramolecular hydrogen bond with O(1) [O(1)—H(O1) 0.96 (6), O(9)··H(O1) 1.72 (6) Å, O(1)—H(O1)··O(9) 138 (4)°] which results in the C(9)—O(9) distance being slightly longer than the C(10)—O(10) distance. Both methoxy groups lie almost in the plane of the aromatic ring A to which they are bonded, with C(6′)—O(6)—C(6)—C(7) and C(8′)—O(8)—C(8)—C(7) torsion angles of 10.5 (9) and 0.7 (9)°, respectively. In contrast, the plane of the methyl ester is almost perpendicular to the other aromatic ring C, with a torsion angle C(1)—C(2)—C(2′)—O(2′) of 103.8 (8)°. While the two six-membered aromatic rings show no significant deviation from planarity, the six atoms of the central ring B have a slightly less-planar relationship, with the greatest deviation from the plane being 0.030 (8) Å for C(10). Furthermore, the condensed-ring system is significantly

† Part 35 in the series *Pigments of Fungi*.