Data Article

Dataset on synthesis and crystallographic structure of phenyl(TMP)iodonium(III) acetate

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1. Data

Recently, utilization of the auxiliary and the dummy ligand in diaryliodonium (III) salts for a selective aryl-transfer has been actively investigated after the discovery of Mes-iodonium (III) reagents (Koseki et al., 2019). The organic salts consisting of phenyl (2,4,6-trimethoxyphenyl)iodonium (III) cation (Ph(TMP)IOAc), the single-crystal X-ray diffraction measurement together with NMR analysis, like also the method of synthesis and crystallization are presented. The X-ray structure analysis has revealed that the two types of geometries regarding the acetate anion attached to phenyl (TMP)iodonium (III) cation are found in the crystal states.

The data in this article are related to research article “Efficient N-arylation ofazole compounds utilizing selective aryl-transfer TMP-iodonium (III) reagents (Koseki et al., 2019). For the title compound, phenyl(2,4,6-trimethoxyphenyl)iodonium(III) acetate (Ph(TMP)IOAc), the single-crystal X-ray diffraction measurement together with NMR analysis, like also the method of synthesis and crystallization are presented. The X-ray structure analysis has revealed that the two types of geometries regarding the acetate anion attached to phenyl (TMP)iodonium (III) cation are found in the crystal states.

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work, the aryl (TMP)iodonium (III) salts were applied as the efficient arylating agents for the copper-catalyzed N-arylation of azole compounds, which turned out that these iodonium (III) salts have high reactivities even in the metal-catalyzed coupling together with the reported exclusive aryl-group transfer behavior [1]. Therefore, the synthesis and structural information for Ph(TMP)IOAc are very important. The first example of the X-ray structural analysis is worth to notice. Our original method for preparation of the diaryliodonium (III) salts [12] enables to obtain the studied compound of high purity suitable for single-crystal growth (see Tables 1–4).

Ph(TMP)IOAc was synthesized by direct condensation between phenyliodine (III) diacetate (PIDA) and 1,3,5-trimethoxybenzene (TMP) in fluoroalcohol medium under mild conditions (Scheme 1). The structure of Ph(TMP)IOAc was determined by two-dimensional NMR analyses (Figs. 3 and 4). The 1H NMR spectrum in Fig. 1 supports the high purity of Ph(TMP)IOAc obtained in this study. X-ray structural analysis have suggested that two geometrical states for Ph(TMP)IOAc appear in a crystal in the three-dimensional structure (Figs. 5 and 6).

2. Experimental design, materials, and methods

2.1. Materials

The solvents, starting materials, and reagents were purchased from Nacalai tesque and Tokyo Chemical Industry CO. Ltd.

2.2. Synthesis of Ph(TMP)IOAc

Ph(TMP)IOAc was prepared according to our reported procedure [12]. Thus, to a solution of 1,3,5-trimethoxybenzene (TMP, 168 mg, 1.0 mmol) in 2,2,2-trifluoroethanol (TFE, 2 mL) was added
Table 1
X-ray experimental details for Ph(TMP)IOAc.

| Crystal data | Crystal data |
|--------------|--------------|
| Chemical formula | C\textsubscript{17}H\textsubscript{19}IO\textsubscript{5} |
| \(M_w\) | 430.22 |
| Crystal system, space group | Orthorhombic, \(Pbc\\alpha\) |
| Temperature (K) | 120 |
| \(a, b, c\) (Å) | 15.7731 (1), 12.6253 (1), 17.1040 (2) |
| \(V\) (Å\textsuperscript{3}) | 3406.09 (5) |
| \(Z\) | 8 |
| Radiation type | Cu \(K\alpha\) |
| \(\mu\) (mm\textsuperscript{-1}) | 14.98 |
| Crystal size (mm) | 0.46 \(\times\) 0.26 \(\times\) 0.13 |

**Data collection**

Diffractometer

X-ray crystallographic analysis was performed on a HPC diffractometer (Rigaku XtaLAB P200).

Absorption correction

Multi-scan CrysAlis PRO 1.171.39.2a (Rigaku Oxford Diffraction, 2015)

Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

\(T_{\text{min}}\) - \(T_{\text{max}}\)

No. of measured, independent and observed \(|I > 2\sigma(I)|\) reflections

\(R_{\text{int}}\)

0.106

\(\sin \theta/\lambda_{\text{max}}\) (Å\textsuperscript{-1})

0.625

Refinement

\(R\) \(|F^2 > 2\sigma(F^2)\), \(wR\) \((F^2), S\)

0.056, 0.156, 1.09

No. of reflections

3456

No. of parameters

208

H-atom treatment

H-atom parameters constrained

\(\Delta p_{\text{max}}, \Delta p_{\text{min}}\) (e Å\textsuperscript{3})

2.50, −3.39

Computer programs: CrysAlis PRO 1.171.39.3a (Rigaku OD, 2015), SHELXT-2014/5 (Sheldrick, 2014), SHELXL2014/7. (Sheldrick, 2014).

Table 2
Selected bond lengths (Å) of Ph(TMP)IOAc.

| Bond | Length (Å) | Bond | Length (Å) |
|------|-----------|------|-----------|
| I1A–C1B | 2.085 (5) | C9B–O3B | 1.425 (6) |
| I1A–C1C | 2.130 (5) | C9B–H9B1 | 0.9600 |
| C1B–C2B | 1.398 (7) | C9B–H9B2 | 0.9600 |
| C1B–C6B | 1.408 (6) | C9B–H9B3 | 0.9600 |
| C2B–O1B | 1.363 (5) | C1C–C2C | 1.372 (7) |
| C2B–C3B | 1.392 (7) | C1C–C6C | 1.372 (7) |
| C3B–C4B | 1.392 (7) | C2C–C3C | 1.396 (7) |
| C3B–H3B | 0.9300 | C2C–H2C | 0.9300 |
| C4B–O2B | 1.353 (6) | C3C–C4C | 1.381 (9) |
| C4B–C5B | 1.395 (7) | C3C–H3C | 0.9300 |
| C5B–C6B | 1.384 (6) | C4C–C5C | 1.394 (9) |
| C5B–H5B | 0.9300 | C4C–H4C | 0.9300 |
| C6B–O3B | 1.359 (5) | C5C–C6C | 1.382 (8) |
| C7B–O1B | 1.431 (6) | C5C–H5C | 0.9300 |
| C7B–H7B1 | 0.9600 | C6C–H6C | 0.9300 |
| C7B–H7B2 | 0.9600 | C1D–O2D | 1.237 (6) |
| C7B–H7B3 | 0.9600 | C1D–O1D | 1.267 (6) |
| C8B–O2B | 1.447 (7) | C1D–C2D | 1.514 (7) |
| C8B–H8B1 | 0.9600 | C2D–H2D1 | 0.9600 |
| C8B–H8B2 | 0.9600 | C2D–H2D2 | 0.9600 |
| C8B–H8B3 | 0.9600 | C2D–H2D3 | 0.9600 |
Selected torsion angles (°) of Ph(TMP)IOAc.

|      | Value         |      | Value         |      | Value         |
|------|---------------|------|---------------|------|---------------|
| C6B—C2B—C1B—O1B | −179.3 (4) | I1A—C1B—C6B—C5B | 178.0 (3) |
| I1A—C1B—C2B—O1B | 3.4 (5) | C3B—C2B—O1B—C7B | −0.8 (7) |
| C6B—C2B—C3B—C6B | −0.3 (6) | C1B—C2B—O1B—C7B | 178.1 (4) |
| I1A—C1B—C2B—C3B | −177.6 (3) | C3B—C4B—O2B—C8B | −0.6 (7) |
| O1B—C2B—C3B—C4B | 179.3 (4) | C5B—C4B—O2B—C8B | 179.1 (4) |
| C1B—C2B—C3B—C4B | 0.5 (7) | C5B—C6B—O3B—C9B | −1.7 (6) |
| C2B—C3B—C4B—O2B | 178.6 (4) | C1B—C6B—O3B—C9B | 179.1 (4) |
| C2B—C3B—C4B—C5B | −1.0 (7) | C6C—C1C—C2C—C3C | 0.3 (8) |
| O2B—C4B—C5B—C6B | −178.3 (4) | I1A—C1C—C2C—C3C | −177.8 (4) |
| C3B—C4B—C5B—C6B | 1.4 (6) | C1C—C2C—C3C—C4C | 0.5 (9) |
| C4B—C5B—C6B—C3B | 179.7 (4) | C2C—C3C—C4C—C5C | 0.1 (9) |
| C4B—C5B—C6B—C1B | −1.2 (6) | C3C—C4C—C5C—C6C | −1.4 (10) |
| C2B—C1B—C6B—O3B | 179.9 (4) | C2C—C1C—C6C—C5C | −1.6 (8) |
| I1A—C1B—C6B—O2B | −2.8 (5) | I1A—C1C—C6C—C5C | 176.5 (5) |
| C2B—C1B—C6B—C5B | 0.7 (6) | C4C—C5C—C6C—C1C | 2.2 (10) |

Table 4

Selected bond angles (°) of Ph(TMP)IOAc.

|      | Value         |      | Value         |      | Value         |
|------|---------------|------|---------------|------|---------------|
| C1B—C1A—C1C | 91.08 (16) | O3B—C9B—H9B3 | 109.5 |
| C2B—C1B—C6B | 119.1 (4) | H9B1—C9B—H9B3 | 109.5 |
| C2B—C1B—I1A | 120.2 (3) | H9B2—C9B—H9B3 | 109.5 |
| C6B—C1B—C1A | 120.6 (3) | C2B—O1B—C7B | 118.5 (4) |
| O1B—C2B—C3B | 123.1 (4) | C4B—O2B—C8B | 117.4 (4) |
| O1B—C2B—C1B | 115.6 (4) | C6B—O3B—C9B | 117.6 (4) |
| C3B—C2B—C1B | 121.3 (4) | C2C—C1C—C6C | 121.9 (5) |
| C4B—C3B—C2B | 118.0 (4) | C2C—C1C—I1A | 119.0 (4) |
| C4B—C3B—H3B | 121.0 | C6C—C1C—I1A | 119.1 (4) |
| C2B—C3B—H3B | 121.0 | C1C—C2C—C3C | 119.0 (5) |
| O2B—C4B—C3B | 123.7 (5) | C1C—C2C—H2C | 120.5 |
| O2B—C4B—C5B | 114.1 (4) | C3C—C2C—H2C | 120.5 |
| C3B—C4B—C5B | 122.2 (4) | C4C—C3C—C2C | 120.3 (5) |
| C6B—C5B—C4B | 118.9 (4) | C4C—C3C—H3C | 119.8 |
| C6B—C5B—H5B | 120.6 | C2C—C3C—H3C | 119.8 |
| C4B—C5B—H5B | 120.6 | C3C—C4C—C5C | 119.1 (5) |
| O3B—C6B—C5B | 124.1 (4) | C3C—C4C—H4C | 120.4 |
| O3B—C6B—C1B | 115.3 (4) | C5C—C4C—H4C | 120.4 |
| C5B—C6B—C1B | 120.5 (4) | C6C—C5C—C4C | 120.8 (5) |
| O1B—C7B—H7B1 | 109.5 | C6C—C5C—H5C | 119.6 |
| O1B—C7B—H7B2 | 109.5 | C4C—C5C—H5C | 119.6 |
| H7B1—C7B—H7B2 | 109.5 | C1C—C6C—C5C | 118.8 (5) |
| O1B—C7B—H7B3 | 109.5 | C1C—C6C—H6C | 120.6 |
| H7B1—C7B—H7B3 | 109.5 | C5C—C6C—H6C | 120.6 |
| H7B2—C7B—H7B3 | 109.5 | O2D—C1D—O1D | 125.4 (4) |
| O2B—C8B—H8B1 | 109.5 | O2D—C1D—C2D | 118.9 (4) |
| O2B—C8B—H8B2 | 109.5 | O1D—C1D—C2D | 115.6 (4) |
| H8B1—C8B—H8B2 | 109.5 | C1D—C2D—H2D1 | 109.5 |
| O2B—C8B—H8B3 | 109.5 | C1D—C2D—H2D2 | 109.5 |
| H8B1—C8B—H8B3 | 109.5 | H2D1—C2D—H2D2 | 109.5 |
| H8B2—C8B—H8B3 | 109.5 | C1D—C2D—H2D3 | 109.5 |
| O3B—C9B—H9B1 | 109.5 | H2D1—C2D—H2D3 | 109.5 |
| O3B—C9B—H9B2 | 109.5 | H2D2—C2D—H2D3 | 109.5 |
| H9B1—C9B—H9B2 | 109.5 |
to afford Ph(TMP)IOAc (350 mg, 0.81 mmol). Yield 81%. White powder. Melting point 121.8°C.

2.3. General information for NMR analyses

The $^1\text{H}$ and $^{13}\text{C}$ NMR spectra were recorded on an ECS 400 NMR spectrometer (JEOL Ltd., Tokyo, Japan) at 400 MHz and 100 MHz, respectively, using CDCl$_3$ as the solvent. The chemical shifts ($\delta$) are expressed in ppm relative to tetramethylsilane (TMS) as an internal standard. Coupling constants ($J$) are expressed in Hz. Signal multiplicities are represented as singlet (s), doublet (d), and triplet (t). Assignments of the proton and carbon positions in the compound were performed by PFG-HMQC and PFG-HMBC analyses.

**Scheme 1.** Direct synthesis of Ph(TMP)IOAc by the reaction of PIDA with TMP.

**Fig. 1.** $^1\text{H}$ NMR spectrum of Ph(TMP)IOAc.
Fig. 2. $^{13}$C NMR spectrum of Ph(TMP)IOAc.

Fig. 3. HMQC spectrum of Ph(TMP)IOAc.
2.4. NMR

JEOL ECS 400 NMR spectrometer, solvent CDCl₃, TMS standard. Concentration: 13 mg in 0.75 mL (Figs. 1–4). ¹H NMR (400 MHz, CDCl₃): δ 1.95 (3H, s, CH₃CO), 3.83 (9H, s, OMe), 6.12 (2H, s, m-TMP), 7.29 (2H, t, J = 7.8 Hz, m-Ph), 7.41 (1H, t, J = 7.8 Hz, p-Ph), 7.92 (2H, d, J = 8.2 Hz, o-Ph). ¹³C NMR (100 MHz, CDCl₃): δ 24.6 (CH₃COO), 55.7 (p-OMe), 56.5 (o-OMe), 90.9 (m-TMP), 91.0 (ipso-TMP), 119.4 (ipso-Ph), 130.3 (p-Ph), 130.8 (m-Ph), 133.8 (o-Ph), 160.6 (o-TMP), 165.7 (p-TMP), 178.8 (CH₃COO).

2.5. Crystallization

The crystals were obtained at room temperature from chloroform/hexane mixture under a shading condition. Ph(TMP)IOAc was dissolved in chloroform and the insoluble material was removed by
filtration. Hexane was added to the filtrate in sample bottle to reach the chloroform/hexane ratio 2/5. After standing for 1 day, the several crystals suitable for the X-ray structural analysis were obtained.

2.6. X-ray

The single-crystal X-ray diffraction experiment was performed on the HPC diffractometer (Rigaku XtaLAB P200)). The two types of geometries for Ph(TMP)IOAc in a crystal state are shown in Fig. 5. In Fig. 5(A), it was found that the distance between the iodine atom in the cation and an oxygen atom in the anion is 2.77 Å. On the other hand, the distances between the iodine atom in the cation and oxygen atoms in the anion were 2.59 Å and 3.37 Å, respectively (Fig. 5(B)). In both geometries, the distances between the iodine atom in the cation and two oxygen atoms in the methoxy group were 3.10 Å (Fig. 5(A) and (B)).

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Transparency document

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